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BY

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PREFACE

This volume represents a continuing effort to cover comprehensively the unclassified information on explosives and related subjects in the same manner and format as in previous volumes. The reader is urged to obtain the previous volumes and to read both the PREFACE and INTRODUCTION in Volume 1 in order to understand the authors' way of presenting the subject matter

In preparation for and during the writing of this Encyclopedia, the authors have consulted freely with and have had the cooperation of many individuals who contributed their expert knowledge and advice. This fact is acknowledged throughout the text at the end of the subject item. A listing of many others who have helped in various ways would be impractical

Drs J. Roth, J. Brown, A.P. Hardt and Mr T.Q. Ciccone of the private sector, Dr C.H. McDonnell of the Naval Ordnance Station, Indian Head, Md, as well as Dr S. Bulusu and Messrs S. Helf, H.L. Herman, J. Hendrickson and D.J. Veal of the Energetics Materials Division, LCWSL, ARRADCOM, Dover, NJ, all contributed significantly in the literature searching and writing of many of the articles in this volume. Others who contributed to the manuscript, by invitation, are indicated at the end of the articles

Dr Raymond F. Walker, Energetics Materials Division Chief, provided financial support and encouragement to continue this work, as did Mr Edward J. Kolb of Headquarters, US Army Materiel Development and Readiness Command (DARCOM). Further financial support was received from the sale of copies to non-government agencies and individuals by the National Technical Information Service, US Department of Commerce, Springfield, Va 22161

Although considerable effort has been made to present this information as accurately as possible, mistakes and errors in transcription and translation do occur. Therefore, the authors encourage the readers to consult original sources, when possible, and to feel free to point out errors and omissions of important works so that corrections and additions can be listed in the next volume. The interpretations of data and opinions expressed are often those of the authors and are not necessarily those nor the responsibility of officials of ARRADCOM or the Department of the Army

This report has been prepared for information purposes only and neither ARRADCOM nor the Department of the Army shall be responsible for any events or decisions arising from the use of any information contained herein

It will be noted that a change in editors has taken place since the publication of Volume 7 in 1975, this change being the first since the inception of the Encyclopedia program in 1958. It was necessitated by the death of Dr Basil T. Fedoroff in December 1976 (see obituary which follows), and the retirement of Mr Oliver E. Sheffield in October 1975 after some 34 years of Federal service, with incumbency at Picatinny Arsenal since January 1943. He authored or co-authored over 40 Picatinny Arsenal Technical Reports and AMC Manuals on explosives, pyrotechnics and propellants. Sheffield is best known as co-editor of this Encyclopedia, with which he was associated since 1958

This change in editorial leadership has resulted, perhaps inevitably, in a change in editorial policy which is reflected in the contents of Volume 8. There has been a marked de-emphasis on the inclusion of organic "parent compounds" followed by an exhaustive and voluminous cataloging of azide, azido, azo, diazido, diazonium, diazo, nitro, dinitro, polynitro, nitramine, nitrate (esters and salts), dinitrate, polynitrate, nitroso, polynitroso, chlorate, perchlorate, peroxide, picrate, etc, derivatives – regardless of whether any of these derivatives exhibit documented explosive or energetic properties. Only those materials having such properties have been included in this volume

There has also been a distinct effort made not to include subject areas which are not specifically pertinent to the subject of energetic materials

In conclusion, I wish to acknowledge with gratitude the continual support and encouragement of Samuel Helf, without whose efforts in behalf of the Encyclopedia of Explosives program, the publication of this volume would not have been possible

Seymour M. Kaye
Dover, New Jersey
March 1978

IN MEMORIAM

BASIL T. FEDOROFF
(1891–1976)

Dr. Basil T. Fedoroff, scientist and engineer, who worked at Picatinny Arsenal from 1946–1961 and served as an Arsenal consultant from 1961–1975, died in Miami, Florida on 29 December 1976 at the age of 85. Dr. Fedoroff, who was best known as the Chief Editor of the "Encyclopedia of Explosives and Related Items", Volumes 1 to 7 (1960–1975), was born in Merv, Russia on 8 January 1891. He graduated from the Imperial Tomsk Institute of Technology as a chemical engineer in 1914, and earned his doctorate in the same field from the University of Paris, Sorbonne in 1940

After graduating from Tomsk, he served in the Imperial Russian Navy and the French Foreign Legion. He came to the United States by way of Canada in the early 1920's and obtained his citizenship in 1927. He enrolled at Sorbonne in 1931 and returned to this country after obtaining his doctorate

From 1941 until he came to Picatinny Arsenal, Dr. Fedoroff worked in private industry in the field of explosives and propellants. He joined the staff of the Picatinny Arsenal Technical Division as a research chemist in 1946, and remained until his retirement in 1961. In addition to the Encyclopedia, his major publications include "A Manual for Explosives Laboratories", 4 volumes (1942–46) in collaboration with G. D. Clift; "Dictionary of Russian Ammunition and Weapons" (1955); and "Dictionary of Explosives, Ammunition and Weapons (German Section)" (1958)

Dr. Fedoroff was a unique repository of historical facts, as well as an internationally recognized expert in energetic materials

Errata in Volume 6

p E264-R, third paragraph	The US Military Specification for Ethylene Glycol Dinitrate (EGDN) is **MIL-E-48225** (1973)
p F135-R, second paragraph	"reducing" instead of "oxidizing" materials
p F221-R, second paragraph	"0.12cal/g/°C" instead of "1.1cal/g/°C"

Errata in Volume 7

Addendum III	Empirical formula should read $C_{10}H_{10}H_8N_8O_{17}$
Addendum IV	Ethanol group on carbon 3 of second structural formula should read C_2H_4OH
p H66-L, first paragraph	Should be placed on lower part of p H67-L following "with substantial cost savings"
p H67-L, first 3 paragraphs ending with "with substantial cost savings"	Should follow "In addition" at bottom of p H65-R
p H67-L from "produced at Rocky Hill"	Should follow last sentence at bottom of p H66-R
p H237-R, second and third paragraphs	"3,5-Dinitro-2-Hydroxybenzoic Acid" instead of "3,5-Dinitro-4-Hydroxybenzoic Acid"
p H226 title	"Peroxides" instead of "Perioxides"
p L20-L, third paragraph	"Because" instead of "Becuase"
p L28-L, last paragraph	"interesting" instead of "itneresting"
p L29-R, last paragraph	"optical" instead of "optional"
p L43-R, fifth paragraph	(Ref 29, p 344) instead of (Ref 30, p 344)

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M

M1 Thickener. A standard thickener for prepg an incendiary known as *Napalm.* It is a mixed Al soap in which about 50% of the org acids are derived from coconut oil, 25% from naphthenic acids and 25% from oleic acid. When stirred into gasoline at a temp range from 16–29°, M1 swells until the entire vol of gasoline becomes a more or less homogeneous gel

M2 Thickener. A standard (for US Air Force) incendiary oil thickener. It is an intimate mixt of 95% M1 Thickener and 5% devolatilized silica aerogel or other approved antiagglomerate. M2 Thickener is an improvement over M1 for use in fire bombs, not only because of free flowing and faster setting characteristics, but also because the thickener itself and gel formed are more stable

M4 Thickener. A standard incendiary oil thickener. It is a diacid Al soap of isooctanoic acids derived from isooctyl alc or isooctyl aldehyde obtd from the oxidn of petroleum. It contains 2% Santocel C or Attaclay SF which serves as an antiagglomerant. About 1/2 the amt of M4 and about 1/10 mixing time is reqd for M4 Thickener as compared to M1 for thickened fuels of comparable consistency. Fuels prepd with M4 are superior in flame throwing performance with respect to range, burning and target effects, as compared with fuels prepd with other thickeners

Ref: Anon, "Military Chemistry and Chemical Agents", **TM 3-215/AFM 355-7** (Dec 1963), 41

Macarites. Expls introduced in 1891 by J. de Macar of Belg, with the primary objective of replacing PA (Lyddite or Melinite) for filling HE shells, torpedoes, etc. The original Macarite contd TNT 28.1 and Pb nitrate 71.9% at d 2.7–2.8g/cc. Its deton reaction showed complete combn to CO_2, H_2O and Pb:

$$4C_7H_5(NO_2)_3 + 7Pb(NO_3)_2 = 28CO_2 + 10H_2O + 13N_2 + 7Pb$$

(Refs 1 & 2). Later Belg compns contd TNT 30–50 and Pb nitrate 50–70% (Refs 1, 2, 3 & 4). Barnett (Ref 4) gives the following data for 30/70 Macarite: deton vel 4600m/sec at d 1.65g/cc, 4700m/sec at d 2.75g/cc and 4860 m/sec at d 2.89g/cc, vs 7100m/sec for PA at d 1.60g/cc; brisance as detd by crushing the Cu cylinder of Kast's brisance meter 2.52mm at d 2.65g/cc and 2.86mm at d 2.75g/cc, vs 3.88mm at d 1.60g/cc for PA. Marshall (Ref 2, p 449) compared some of its expl properties with PA and TNT and concluded that, although its deton vel is considerably less than that of PA and TNT, the brisance and relative energy "f" of Macarite are slightly higher. Macarite was used in Belg for a considerable period of time, primarily because of its insensitivity to shock, non-hygroscopicity, non-corrosive effect on metals, and safety in manuf, storage and transportation

Refs: 1) E. Bravetta, SS **7** (1913), 124 2) Marshall **2** (1917), 449 & 557 3) Colver (1918), 247 4) Barnett (1919), 185 & 193 5) A. Pérez Ara (1945), 505

Macaroni Press. A hydraulic press with a perforated false bottom. A so-called *preliminary block* is placed between the piston of the press and the bottom. This block consists of NC, previously colloided in a *kneading machine* with solvents such as eth-alc, acet, etc, blended with other ingredients such as diphenylamine, dinitrotoluene, etc, and pressed at about 3500 psi in a *preliminary blocking press* into a compact mass. The block is subjected to a press of 3000–3500psi in the macaroni press and squeezed sequentially thru one 12 mesh steel wire screen, two 24 mesh screens, one 36 mesh screen, and then thru the perforations of a heavy brass plate, from which it emerges in wormlike strands resembling macaroni. The strands drop directly into the cylinder of a *final blocking press,* where it is compressed into a compact cylindrical block of the proper size to fit a *graining press.* The purpose of the macaroni press is to achieve more thorough

blending of the ingredients of smokeless powder than could be achieved in the *kneading machine* and to effect more thorough gelatinization of the NC
Ref: Davis (1943), 302

MacEvoy. Proposed to use primers contg metallic Na and w in sep compartments. A hot flame was produced on the contact of the ingredients
Ref: Daniel (1902), 414

MacGavin Explosive. Prepd by saturating sawdust with a soln of K picrate, drying the resulting prod, and mixing it with K or Na nitrate and S
Ref: Daniel (1902), 414

Mach Number. (abbr as M). The ratio of the vel of a body to that of sound in the medium being considered. Thus, at sea level, in air at the US Standard Atm, a body moving at a mach number of one (M=1) would have a vel of 1116.2ft/sec; the speed of sound in air under these conditions. Term frequently shortened to *mach* or *Mach.* Named for Ernst Mach, 1838–1916, Austrian physicist
Ref: OrdTechTerm (1962), 184

Mach Stem. A shock wave or front formed above the surface of the earth by the fusion of direct and reflected shock waves resulting from an airburst. Also called *mach wave* and *mach front*
Ref: OrdTechTerm (1962), 184

Machine Gun. Automatic weapons which fire small arms ammunition. They are heavier than automatic rifles and are usually provided with a fized mount, such as a tripod, or wheels and a trail. These sustain the force of recoil and provide the means by which the gun may be positioned in the direction of fire. Machine guns utilize the discharging gas, or mechanical recoil of the gun to load, eject the cartridge, lock and unlock the breech. They are fed from either a belt, clip or magazine, and are cooled by either a w jacket around the barrel, or by radiation from metal fins. The machine gun provides a sustained-fire weapon that can be used effectively against personnel and lightly armored vehicles, or for area fire to harass an enemy when he cannot be precisely located
Refs: 1) Newmann (1943), 50–59 2) B.R. Lewis, "U.S. Machine Guns", ArmyOrdn **29**, No 151, 118–21 (Jul-Aug 1945); No 152, 294–30 (1945); No 153, 444–48 (Nov-Dec 1945); No 154, 120–26 (1946), No 155, 242–52 (1946) 3) G.M. Chinn, "The Machine Gun. History, Evolution and Development of Manual, Automatic, and Airborne Repeating Weapons", Prepd for The Bureau of Ordn, US Navy, US Govt Printing Office, Washington, DC (1951), 1688 pp 4) Collier's Encycl **15**, 168–76 (1965) 5) Encycl Britannica **14**, 521–26 (1973)

MacKentosh Propellants. Prepd by mixing fine BlkPdr with a rubber soln, spreading the prod on fabric, drying & cutting to desired grain size. K chlorate was added to increase burning rate, bran or other materials to decrease it. Patented in 1857
Ref: Daniel (1902), 415

Magazine. Any building or structure, except an operating building, used for the storage of ammo, expls or loaded ammo components. See under *Magazine Buildings* in Buildings and Other Structures at Ordnance Establishments in Vol **2**, B320-R to B321-R; under Barricades in Explosives and Ammunition Installations in Vol **2**, B22-R to B23-R; and under Dangerous Materials, Shipping and Storage of, in Vol **3**, D16-L & -R
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Safety Manual", **AMCR 385-100** (April 1970), 11-1 to 11-34, 17-1 to 17-35, 18-1 to 18-13 & 19-1 to 19-36 (Storage and handling of chemical agents and munitions; quantity-distance tables; storage of expls & ammo; quantity-distance classification and storage compatibility)

Magnesium. Mg, at wt 24.312, at no 12, valence 2. Isotopes: 24 (77.4%), 25 (11.5%) & 26 (11.1%). Physical properties of 99.9% pure Mg are given in the following table (Ref 19, p 679)

Mg is very abundant in nature, occurring in substantial amounts in many rock-forming minerals such as dolomite, magnesite, olivine, and serpentine. In addition, it is also found in sea water, subterranean brines, and salt beds. It has been estimated that Mg constitutes 2.5% of the earth's crust, being exceeded only by Al and Fe

Mg is insol in cold w; sl sol in hot w, with which it reacts; sol in mineral acids, conc HF and Amm salts; insol in chromates & alkali

In 1808, Sir Humphry Davy reported the production of Mg in the form of an amalgam by electrolytic reduction of its oxide using a Hg cathode. In 1828, the Fr scientist A. Bussy fused Mg chloride with metallic K and became the first to produce free metallic Mg. Michael Faraday, in 1833, was the first to produce free metallic Mg by electrolysis, using Mg chloride. For many years, however, the metal remained a laboratory curiosity. In 1886, manuf of Mg was undertaken on a production scale in Ger, using electrolysis of fused Mg chloride. Until 1915, Ger remained the sole producer of Mg. However, when a scarcity of Mg arose in the USA as a result of the Brit blockade of Ger in 1915, and the price of Mg soared from $1.65 to $5.00 per lb, three producers initiated operations and thus started a Mg industry in the USA. Subsequently, additional companies attempted production of Mg, but by 1920 only two producers remained – The Dow Chemical Co (one of the original three producers) and the American Magnesium Corp. In 1927, the latter ceased production, and Dow continued to be the sole domestic producer until 1941. The source of Mg chloride was brine pumped from deep wells. In 1941, Dow put a plant into operation at Freeport, Texas, obtaining Mg chloride from seawater. Also in 1941, Permanente Metals Corp began to produce Mg at Permanente, Calif, using the carbothermic process invented by Dr F.J. Hansgirg, an Austrian scientist. In addition to these new privately owned plants, Government plants were constructed, and by 1943 there were thirteen more plants in operation under the management of eleven different companies. Six of the plants were electrolytic, of which two utilized seawater and three used dolomite. The remaining plant used calcined magnesite, which was chlorinated to anhydrous Mg chloride in an electric furnace by a method originated in Ger. The other Government plants were thermal reduction operations which utilized the ferrosilicon process

There are currently three producers of Mg in the USA. The Dow Chemical Co is by far the largest producer, all of it by the electrolytic process. Alamet Division of Calumet & Hecla, Inc, produces Mg from dolomite by the ferrosilicon process in their plant at Selma, Alabama. Titanium Metals Corp also produces Mg as a by-product of their Ti production (Ref 19, p 664)

The electrolysis of Mg chloride to yield chlorine and metallic Mg is the basis of the electrolytic process. Sea w is pumped into large settling tanks where it is mixed with lime obtained by roasting oyster shells dredged from the ocean bottom. The lime converts the Mg into insol Mg hydroxide which is filtered out. This hydroxide is then treated with HCl, obtained from chlorine by reaction with natural gas, to produce Mg chloride soln. The w is evapd, and the dry Mg chloride is fed to the electrolytic cells which separate it into metallic Mg and chlorine, the Mg being poured into ingots. The ferrosilicon process, although first originated experimentally in Ger, was developed commercially during WWII in Canada. Ferrosilicon, an alloy of Si and Fe, is mixed with calcined dolomite ore and pressed into small briquets. These are charged into a steel retort, put under vacuum, and heated to about 2200°F. The Si reduces the Mg oxide (formed by calcining of the dolomite) to form a vapor of metallic Mg which condenses in the cool end of the retort. The Mg is removed in the form of crysts, which are subsequently melted and cast into ingots (Refs 3, 18 & 25)

Table 1. Physical Properties of Magnesium, 99.9% Pure

Property	Constant
At vol, cm^3/g-atom	14.0
Crystal structure	close-packed hexagonal
Lattice parameters, Å	$a_0 = 3.203$, $c_0 = 5.199$
Axial ratio, c/a	1.624
Modulus of elasticity, kg/mm^2	4570
of rigidity, kg/mm^2	1700
Poisson's ratio	0.35
Density, g/cm^3, at	
20°	1.74
650° (solid)	1.64
650° (liquid)	1.57
700°	1.54
Volume contraction, 650° (liquid) to 650° (solid)	4.2%
Linear contraction, 650° (solid) to 20° (solid)	1.8%
Electrical resistivity, μΩ-cm, at	
20°	4.46
300°	9.5
600°	17.0
650° (liq)	28.0
900°	28.0
Temp coeff, at 20°, μΩ-cm/°C	0.017
Electrical conductivity, at 20°	
annealed copper (standard)	
mass %	198.0
vol %	38.6
mp, °	650
bp, °	1110 ± 10
Critical temp, calc	1867
Flame temp, theoret °C	4850
Coeff of expansion	
coeff of thermal expansion, in/(in)(C°), at	
20–100°	0.0000261
20–200°	0.0000271
20–300°	0.0000280
20–400°	0.0000290
20–500°	0.0000299
Specific heat, cal/(g)(°C), at	
20°	0.245
300°	0.275
650° (solid)	0.325
650° (liq)	0.316
Thermal conductivity, cal/(sec)(cm^2)(°C/cm), at 20°	0.37
Thermal diffusivity, cm^2/sec, at 20°	0.87
Heat of combustion, cal/g-mole	145,000
Latent heat of fusion, cal/g	88 ± 2
Latent heat of evaporation, cal/g	1260 ± 30
Heat of reaction with oxygen, at 2900°K, 1 atm	
magnesium	
Btu/lb metal	8,180
Btu/lb O_2	12,430
Thermal neutron, absorption cross section	
barn/atom (cm^2/cm^3)	0.059 (0.00254)

Although Mg is generally considered nontoxic, the inhalation of fumes of freshly sublimed Mg oxide may cause metal fume fever. There is no evidence that Mg produces true systemic poisoning. Particles of metallic Mg or Mg alloy which perforate the skin or gain entry thru cuts and scratches may produce a severe local lesion characterized by the evolution of gas and acute inflammatory reaction, frequently with necrosis. The condition has been called a "chemical gas gangrene". Gaseous blebs may develop within 24 hrs of the injury. The lesion is very slow to heal (Ref 23)

Mg is a dangerous fire hazard, in the form of dust or flakes, when exposed to flame, or by violent chemical reaction with oxidizing agents. In solid form, Mg is difficult to ignite because heat is conducted rapidly away from the source of ignition; it must be heated above its mp before it will burn. However, in finely divided form it may be ignited by a spark or the flame of a match. Mg fires do not flare up violently unless there is moisture present. Therefore, it must be kept away from w, moisture, etc. It may be ignited by a spark, match flame, or even spontaneously when the Mg is finely divided and damp, particularly with w-oil emulsion. Also, Mg reacts with moisture, acids, etc to evolve H_2 which is a highly dangerous fire and explosion hazard (Ref 23)

Mg ribbon and fine Mg shavings can be ignited at air temps of about 950°F (Ref 26). Oxides of Be, Cd, Hg, Mo and Zn can react explosively with Mg when heated (Ref 8). Mg reacts with incandescence when heated with the cyanides of Cd, Co, Cu, Pb, Ni or Zn or with Ca carbide (Ref 9). It is spontaneously flammable when exposed to moist chlorine (Ref 10), and on contact with chloroform, methyl chloride (or mixts of both), an expl occurs (Ref 4). Mg also reacts violently with chlorinated hydrocarbons, nitrogen tetroxide and Al chloride (Ref 14). The reduction of heated cupric oxide by admixed Mg is accompanied by incandescence and an expln (Ref 7). Mg exposed to moist fluorine is spontaneously flammable (Ref 11). When a mixt of Mg and Ca carbonate is heated in a current of hydrogen, a violent expln occurs (Ref 12). When Mo trioxide is heated with molten Mg, a violent detonation occurs (Ref 1). Liq oxygen (LOX) gives a detonable mixt when combined with powdered Mg (Ref 15), as do phosphates (Ref 16). An expln occurred during heating of a mixt of K chlorate and Mg (Ref 2), and powdered Mg plus K or Na perchlorates form friction-sensitive expl mixts (Ref 24). Ellern (Ref 22) reports that a mixt of Ag nitrate and Mg will burst into flame on moistening. The w causes electrochemical exchange between the Mg and the Ag ion. The heat of reaction of this exchange provokes the pyrochemical effect. Na peroxide oxidizes Mg powd with incandescence (Ref 5). The mixt explodes when heated to redness. When the mixt is exposed to moist air, spontaneous combustion occurs. When carbon dioxide gas is passed over a mixt of powd Mg and Na peroxide, the mixt explodes (Ref 6). Stannic oxide, heated with Mg, explodes (Ref 13). A mixt of sulfates and Mg may cause an expln (Ref 17.) It has been detd experimentally that a mixt of Mg powd with trichloroethylene or carbon tetrachloride will flash or spark under heavy impact (Ref 21). Mg alloy powders contg more than 50% Mg readily ignite in air (Ref 20)

The industrial uses of Mg are too numerous to be described here, and are detailed in Refs 18, 19 & 25. The uses of Mg powd in pyrotechnics are discussed under Pyrotechnics. Also see Aluminum Containing Alloys in Vol **1**, A145; Aluminum Dust and Its Explosions in Vol **1**, A151-L to A152-R; Aluminum Flares in Vol **1**, A152-R to A153-L; Aluminum, Illuminating Powders in Vol **1**, A153-R to A154-L; and Aluminum (or Magnesium)–Methanol (or Water) Explosives in Vol **1**, A155

Refs: 1) H.N. Warren, The ChemicalNews & JPhysScience **64** (1891), 75 2) Anon, C&EN **14**, 451 (1936) 3) Gmelin, Syst Nr 27, Teil A, 121 (1937) 4) C.C. Clogston, Underwriters Laboratory Bull Research No 34 (1945), 15 & CA **40**, 209–10 (1946) 5) Mellor **2**, 490 & **5**, 217 (1946–47) 6) Mellor **2**, 490 (1946–47) 7) Mellor **3**, 138 (1946–47) 8) Mellor **4**, 272 (1946–47) 9) Ibid, p 271 10) Ibid, p 267 11) Ibid, p 268 12) Ibid, p 273 13) Mellor **7**, 401 (1946–47) 14) Anon, C&EN **32**, 258 (1954) & CA **48**, 4838 (1954) 15) A.O. Kirchenbaum, "Fundamental Studies of New Reactions", Final Rept, Office of Ordnance Research Institute, Temple Univ, Phila, Pa (1956) 16) H.A.J. Pieters & J.W. Creygh-

ton, "Safety in the Chemical Laboratory", 2nd Ed, AcademicPress, NY (1957) 17) Ibid, p 30 18) E.F. Emley, "Principles of Magnesium Technology", PergamonPress, London (1966) 19) Kirk & Othmer, 2nd Ed, **12** (1967), 664 & 679 20) Anon, "Standard for the Storage, Handling & Processing of Magnesium", No 48, p 5, National Fire Protection Association, Boston (1967) 21) Anon, ASESB Potential Incident Report **39**, Armed Services Explosives Safety Board, Washington, DC (1968) 22) Ellern (1968), 46 23) Sax (1968), 881–2 24) V.E. Ready, Safety Eng Reports, California Division of Industrial Safety, Sacramento (1970) 25) McGraw-Hill Encycl **8** (1971), 18–21 26) Anon, "Standard for the Storage, Handling & Processing of Magnesium", No 48, p 4, National Fire Protection Association, Boston (1974)

Magnesium (Analytical Procedures). The Mg ion can be detected qualitatively by the formation of Mg hydroxide, which is not sol in an excess of the Na hydroxide used to ppt it, but is sol in Amm chloride. Mg may be detd gravimetrically as the pyrophosphate (Ref 2). Feigl (Ref 4) also describes many colorimetric spot tests for its identification

In the construction or assembling of certain machinery or equipment, Mg or one of its alloys having similar properties may have been used for only a few of the component parts, and where finished or painted products are being stored or handled, it may be difficult to determine which contains Mg. Investigation has shown that Ag nitrate, vinegar or acetic acid can be used to distinguish between parts composed of Mg and those composed of Al. The portion of metal to be tested is first cleaned of grease, dirt, oxide, etc, by abrading with sandpaper or steel wool. After the test area has been prepd, a drop of the test soln is placed on it. (a) *Ag nitrate test.* The test soln is prepd by dissolving about 5g of Ag nitrate in one liter of distd w. A black coloration is immediately produced on Mg or Mg alloy, the coloration being essentially reduced Ag. No coloration is noted on Al or its alloys, or most other metals. Zn and Cd will show a similar black coloration, but are much heavier
(b) *Vinegar or acetic acid test:* Ordinary vinegar or a weak soln of acet ac will give a bubbling reaction in contact with Mg, while other common metals are not affected (Ref 5)

The requirements for the US Armed Forces are detailed in the Mil Spec listed as Ref 3, which covers powdered Mg suitable for use in ammo. It states that Mg powder shall be furnished in the following types, grades, and granulations:
Type: Type I (flaked and/or chip), Grade A (96% min Mg content), Grade B (86% min Mg content); Type II (oblong chip with rounded edges), 96% min Mg content; & Type III (atomized), 98% min Mg content

Granulation:

Granulation No.	Nominal US Standard Sieve Size
1	40 to 80
2	40 to 80 (alternate)
3	50 to 100
4	50 to 100 (Army)
5	50 to 120
6	80 to 120
7	100
8	120 to 200
9	140
10	200
11	80 to 200
12	120 to 200 (Army)
13	20 to 50
14	50 to 100
15	100 to 200
16	200 to 325
17	50 to 100
18	30 to 50

A detailed breakdown is given in Table II of the Spec for the min & max weight percentages allowable for retention on and passage thru specific sieves

Material requirements are as follows:
Type I (Grade A), types II and III shall be manufd from primary Mg metal contg not less than 99.80% metallic Mg. Mica fillers or other adulterants shall not be used and "bag house dust" shall not be included in the Mg powder offered for acceptance.
Type I (Grade B) shall be manufd from Mg metal of such purity that the product meets the requirements of this Spec. Mica fillers or other adulterants shall not be used and "bag house dust" shall not be included in the Mg powder offered for acceptance

Form requirements are as follows:
Type I Mg powder shall consist of shavings, turnings, flakes, plates or any combination of these which meets the granulation requirement. *Type II* Mg powder shall consist of oblong chip-like particles with rounded edges. *Type III* Mg powder shall consist of granular or spheroidal particles

Chemical Composition: Mg powder shall conform to the requirements shown in the following table:

Table 2 Chemical Composition

	Type I		Type II	Type III
	Grade A	Grade B		
	Percent	Percent	Percent	Percent
Material volatile at 105° (max)	0.1	0.1	0.1	0.1
Oil and grease (max)	0.02	0.02	0.02	0.02
Carbides (max)	0.004	0.004	0.004	0.004
Material insoluble in sulfuric acid (max)	0.15	–	0.15	0.15
Metallic iron (max)	0.05	–	0.05	0.05
Total iron as Fe_2O_3 (max)	0.25	–	0.25	0.25
Aluminum as Al (max)	–	10	–	–
Free metallic magnesium (min)	96	–	96	98
Aluminum plus free metallic magnesium (min)	–	96	–	–

Apparent Density: Determined using a Scott Volumeter, with the following max & min requirements for each granulation:

Table 3

Granulation No.	Density in grams per milliliter	
	Maximum	Minimum
1	0.65	0.55
2	0.65	0.55
3	0.75	0.65
4	0.625	0.45
5[1]	–	–
6[1]	–	–
7[1]	–	–
8[1]	–	–
9[1]	–	–
10[1]	–	–
11	–	0.45
12	–	0.45
13	–	0.70
14	0.75	0.65
15	–	0.90
16	–	0.90
17	–	0.90
18[1]	–	–

[1] No determination required.

When Mg is alloyed with Al, for use in some incendiary, tracer and photoflash compns, the requirements of the US Armed Forces are given in the Mil Spec entitled, "Magnesium-Aluminum Alloy, Powdered" (Ref 1). It covers two types of Mg-Al alloy, Type A (50/50), and Type B (65/35)

Material requirements are as follows: Primary Al shall be used in the manuf of Type A alloy powder, while primary or secondary Al may be used for Type B alloy powder. Type A powder shall be granular and shall contain no slivers, chips, or machine turnings

Chemical Composition: Mg-Al alloy powder shall conform to the composition requirements shown in the following table:

Table 4 Composition

	Type A	Type B
	Percent	Percent
Magnesium	50.0 ± 2.0	65.0 ± 2.0
Aluminum	50.0 ± 2.0	35.0 ± 2.0
Total magnesium and aluminum (min)	98.0	98.0
Oxides as Al_2O_3 (max)	2.0	2.0
Iron as Fe (max)	0.75	0.75
Silicon as Si (max)	0.5	0.5
Other metals (max)	0.5	0.5
Zinc as Zn (max)	0.1	0.1
Grease and fats (max)	0.01	0.01
Moisture (max)	0.05	0.05
Grit (max)	0.1	0.1

Granulation: Mg-Al alloy powder shall conform to the requirements in the following table using US Standard sieves:

Table 5 Granulation

Through Sieve No	Type A		Type B	
	minimum	maximum	minimum	maximum
	Percent	Percent	Percent	Percent
100	99.5	–	90	–
120	98	–	80	–
230	45	65	40	60

Apparent Density (Type A powder only): The apparent density of Type A powder shall not be less than 0.80g/cc when detd using a Scott Volumeter

Written by: **S.M. KAYE**

Refs: 1) US Joint Army-Navy Specification **JAN-M-454** (21 Feb 1947) with Amendment 1 (15 Feb 1952), "Magnesium-Aluminum Alloy, Powdered" 2) N.H. Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed, Vol 1, Van Nostrand, Princeton, NJ (1961), 539–53 3) US Military Specification **MIL-M-382B(MU)**, "Magnesium Powder (for use in ammunition)", 22 July 1970 4) F. Feigl & V. Anger, "Spot Tests in Inorganic Analysis", 6th Engl Ed, Elsevier Publ Co, NY (1972), 290–97 5) Anon, "Storage, Handling and Processing of Magnesium", No 48, p 48–5, National Fire Protection Association, Boston (1974)

Magnesium Azide. See under Azides

Magnesium Carbonate (Magnesia Alba), $MgCO_3$, mw 84.32, white pdr, mp 350° dec, d 2.958 g/cc, RI 1.515 at 20°; v sl sol in w (0.0106g/100g w), insol in acet & NH_3 ; sol in acids & aq CO_2. Can be prepd by boiling aq solns of Mg sulfate and Na carbonate in equimol quants, then filtering and drying the ppt. Used in 0.5 to 1.0% concn as an antacid in such coml expls as Fr *Forcites* (Ref 3, p 328), Belg gelatin dynamites (Ref 2, p 329) and *Oaklite* No 1 (Ref 3, p 402). In older Hercules expls (Poudres Hercule) it was used in 10–20% concn as an absorbent for NG. Following are some examples: a) NG 75, Mg carbonate 20.85, K nitrate 2.10, K chlorate 1.05 & sugar 1.00%; b) NG 40, Mg carbonate 10, K nitrate 31, K chlorate 3.34, sugar 15.66%

Refs: 1) Daniel (1902), 374 2) Marshall **1** (1917), 391 3) Naoûm (1927), 328, 329 & 402 4) CondChemDict (1942), 410 5) Davis (1943), 339 & 346 6) Anon, "Magnesium Carbonate", **MIL-M-1136B** (May 1962) 7) Anon, EngrDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 191

Magnesium Chlorate. See under Chlorates

Magnesium Cresylate. See under Cresylates

Magnesium Nitrate. See under Nitrates

Magnesium Oxide. (Magnesia), MgO, mw 40.32, colorl cubic crysts, mp 2800°, bp 3600°, d 3.58g/cc, nearly insol in w (0.00062g/100g w, 0.0086g at 30°), insol in alc, sol in acids & NH_4 salts. May be prepd either as a light, fluffy amor pdr by calcining Mg carbonate or as a heavy pdr by calcining basic Mg carbonate. Used in the prepn of Mg styphnate, a starting material for the manuf of Pb styphnate. Has been used as an antacid ingredient in some Dynamites, and in Ger smokeless pdrs during WWII as an extrusion facilitator. Following are some examples of Ger pdrs: a) *flake pdr for howitzers:* NC (13% N) 38.03, DEGDN 31.12, NG 30.00, akardite 0.50, graphite 0.10 & MgO 0.25% (Ref 3, p 85); b) *tubular pdr for cannon:* NC (12% N) 67.65, DEGDN 29.00, centralite 3.00, graphite 0.10 & MgO 0.25% (Ref 3, p 86); c) *rocket pdr:* NC (12.60% N) 59.03, DEGDN 34.82, hydrocellulose 3.00, ethylphenylurethane 1.90, vaseline 0.50, akardite 0.50 & MgO 0.25% (Ref 3, p 89); d) *pdr for naval guns:* NC (12.2% N) 69.38, DEGDN 25.27, centralite 5.00, graphite 0.10 & MgO 0.25% (Ref 3, p 90)
Refs: 1) CondChemDict (1942), 412
2) Davis (1943), 440 3) O.W. Stickland, "General Summary of Explosive Plants", US Office of Tech Services, **PB 925** (1945)
4) Anon, "Magnesium Oxide, Calcined (For Use in Ammunition)", **MIL-M-14779** (April 1972)
5) Anon, EngrDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 173

Magnesium Peroxide. See under Peroxides

Magnesium Picrate. See under Picrates

Magnesium Stearate. See under Stearates

Magnesium Styphnate or Magnesium Trinitroresorcinate. See under Styphnic Acid and Styphnates

Magnesium Sulfate (Epsom Salt, Epsomite), $MgSO_4.7H_2O$, mw 246.49, colorl rhomb or monocl cryst, d 1.68g/cc; loses $6H_2O$ at 150°, $7H_2O$ at 200°; v sol in w (72.4g/100g at 0°, 178g at 100°), sl sol in 95% alc & in glycerin. Can be prepd by action of sulfuric acid on Mg oxide, hydroxide or carbonate. Has been used in expls as a temp reducing agent, for example, in *Dynamite Grisoutite* (Refs 1, 2 & 3) contg NG 42–44, Mg sulfate 46–44 and woodmeal 12%
Refs: 1) Marshall **1** (1917), 397 2) Barnett (1919), 140 3) Naoûm (1927), 399 4) Mellor **4** (1929), 321 5) Davis (1943), 353
6) CondChemDict (1971), 537

Magnesium Trinitrocresylate. See under Cresylates

Magnesium Trinitroresorcinate. See under Styphnic Acid and Styphnates

Magnet Fuse (pronounced *Fuzee*). A medium power electric detonator, invented in 1854 by Abel, which was fired electrically. The original fuze contd a priming mixt of Cu_2O, Cu_2S and K chlorate packed around the exposed wire leads, and a main charge of either mealed pdr or MF. It was used primarily in submarine mines. Because of the sensitivity of the fuse, the main charge was replaced with a mixt of powd graphite and MF. At about the same time, an Austrian, Gen von Ebner, independently invented a fuze resembling Abel's, but contg a priming mixt of Sb sulfide 44, K chlorate 44 and graphite 12%. Both of these *fuzees* replaced, in Europe, the *Statham fuze*, which had been in use since 1840
Ref: Van Gelder & Schlatter (1927), 741–2

Magneto Exploder (Blasting Machine, Plunge Battery). A small portable electric generator which produces direct current and is manually

operated with a rack and pinion device. It gives a momentary current of high voltage and is used to remotely detonate blasting and demolition charges
Ref: Colver (1918), 547

Magnus Force (Magnus Effect). A sideways thrust acting on a spinning projectile in flight because of the component of the air current acting perpendicular to the axis of the yawing projectile
Refs: 1) C. Cranz, "Lehrbuch der Ballistik" **1**, J. Springer, Berlin (1925), 340 2) H. Wagner, Ordn **37**, No 194 (1952), 344–45

Mahieu Chronograph. One of the older chronographs, a modification of the Le Boulangé, Bashford and Schultze-Marcel-Dieprez devices
Ref: Barnett (1919), 205

Maintenance. In connection with expls and ammunition, maintenance means keeping or maintaining stocks on hand in serviceable condition and ready for immediate issue and use, or to restore them to serviceability if required. Thus, the term maintenance includes inspection, testing, servicing, classifying as to serviceability, repair, rebuilding and reclamation
Refs: 1) Anon, "Ammunition Inspection Guide", **TM 9-1904** (1944), 898–920
2) Anon, "Maintenance of Supplies and Equipment", **AR 750-S** (1951) 3) Anon, Engrg-DesHdbk, "Maintainability Guide for Design", **AMCP 706-134** (Aug 1967)

Maize Starch (Indian Corn Starch), $(C_6H_{10}O_5)_x$, mw $(162.14)_x$, white amor powd, does not melt, decomposes when heated; insol in cold w, alc or ether, forms a jelly with hot w. Can be prepd from Indian corn by grinding with w and straining the resulting milky liq. On standing, starch settles out and can be sepd by decantation. Has been used as a binder in blasting expls to form NH_4 nitrate agglomerates which when sieved had a bulk d of 0.65g/cc or less (Ref 2)
Refs: 1) Hackh's (1944), 508 2) J. Taylor & V.H. Williams, USP 2218563 (1941) & CA **35**, 1229 (1941)

Maizite. Expl with a yellow color, resembling that of maize, proposed in 1886 for shell loading. Examples are: a) NH_4 picrate 60.59, NH_4 nitrate 39.41%; b) NH_4 picrate 27.76, NH_4 nitrate 72.24%. The latter mixt was very insensitive to shock or flame (Ref 2)
Refs: 1) Daniel (1902), 417 2) A. Pérez Ara (1945), 224 (under Maicitas)

MALTOSE AND DERIVATIVES

Maltose (malt Sugar), $C_{12}H_{22}O_{11}.H_2O$, mw 360.31 when crystd from w, $C_{12}H_{22}O_{11}$, mw 342.29 when cryst from alc; the monohydrate exists as colorl needles, dec at about 102°, d 1.540g/cc; v sol in w, sl sol in methanol, less sol in et alc, insol in eth. Prepd by action of diastase (usually malt extract) on starch paste, or by heating equimol mixts of α- and β-glucose in vac at 160° (Ref 1)
Refs: 1) A. Pictet & H. Vogel, OR **184**, 1512–14 (1927) & CA **21**, 3046 (1927) 2) Cond-ChemDict (1971), 539

Maltose Octanitrate (Nitromaltose), $C_{12}H_{14}O_3(ONO_2)_8$, mw 702.30, N 15.96%, OB to CO_2 – 9.1%, white amor mass, mp 135°, dec at 163–64° when heated quickly, explds at 171–80°; d 1.62g/cc (cast); insol in w, sol in methanol, acet, AcOH and 1:2 eth-alc, sl sol in alc. Can be prepd (Ref 5) by mixing 20g of pure maltose (previously dehydrated by heating) with 0.5g of urea nitrate. 60g of 99% nitric acid are added dropwise with stirring and cooling at 0–2°. To the resulting brown liq, 100g of 25% oleum are gradually added with stirring. This addition should be stopped and the nitrator cooled if any brown fumes start to evolve. After all the oleum is added, the nitrator is warmed to 80° and the mixt poured into a large vol of ice w. The yellow solid ppt is sepd by filtration and washed sequentially with 1% soda soln and w. To remove any remaining urea nitrate, the ppt is recrystd twice from 1:2 eth-alc and dried. The yield is 159% (31.8g)

Nitromaltose is a powerful expl, being comparable to Tetryl in brisance and Mannitol Hexanitrate in sensitivity to impact. It has been used as a blasting cap charge (Ref 6). Its thermal stability at 50° is comparable to Nitrolactose, with a weight loss of 1.3% after 11 days and

23% after 43 days. Abel's test at 65.5° results in only a 16 minute duration. An expl containing Nitromaltose, Maltobenzit, is described below

Refs: 1) Beil, not found 2) W. Will & F. Lenze, Ber **31**, 84 (1898) 3) Daniel (1902), 560 4) A. Pictet & H. Vogel, HelvChimActa **10**, 588 (1927) 5) S. von Monasterski, SS **28**, 349–50 (1933) 6) W. deC. Crater, USP 1887290 (1933) & CA **27**, 1513 (1933) 7) Davis (1943), 241 8) W.R. Ashford et al, CanJRes **25B**, 155–8 (1947) & CA **41**, 4312 (1947)

Maltobenzit. White amor mass, setting point 95°, deflgr at about 200°. Prepd by thoroughly blending 10g of Maltose Octanitrate with 5g of m-DNB at 70° in a kneading machine with 20g of benz. The resulting plastic mass is heated to 95° while the kneading is continued, and then cooled. Maltobenzit has the following props: Q_e, 936cal/g; Trauzl block test, 260cc; impact sensitivity with 2kg wt, 60–70cm

Ref: S. von Monasterski, SS **28**, 349–50 (1933)

Mammoth Powder. Gunpowder intended for use in larger cal guns, invented in 1861 by Gen T.J. Rodman. It consisted of conventional BlkPdr, compressed to high density in the form of large grains, in order to render them impermeable to gases under press. These powds were much slower burning than the types previously used (see Black Powder in Vol **2**)

Refs: 1) Daniel (1902), 418 2) Van Gelder & Schlatter (1927), 23

Manganese Mn, at wt 54.94, brittle, silvery metal, mp 1245°, bp 2097°, d 7.44g/cc, Mohs hardness 5; decomps in w, readily dissolved in dil mineral acids. Usually associated with Fe ores in sub-marginal concns. Important ores of Mn are pyrolusite, manganite, psilomelane & rhodochrosite. Prepd by reduction of the oxide with Al or C. Pure Mn is obtained electrolytically from sulfate or chloride soln. It is used, in powd form, in the manuf of delay powds and in some pyrotechnic mixts. The requirements of the USA Armed Forces are covered by "Manganese, Powdered (For Use in Ammunition)", **JAN-M-476A** (Aug 1948) which specifies the following three grades:

Table 1

	Grades		
	I (% min)	II (% min)	III (% min)
Total Mn	99.5	98.0	95.0
Free metallic Mn	99.0	–	–
Granulation:			
Thru No 200 Sieve	–	98.0	99.0
Thru No 230 Sieve	100	–	–
Thru No 325 Sieve	98	–	–
Particles smaller than 10μ diam	50	–	–

Grade **I** is used for delay powds while Grades **II** and **III** are for use in pyrotechnic compns

Ref: Mellor **12**, 139–200 (1940)

Manganese Azide. See under Azides

Manganese Bioxide. See Manganese Dioxide

Manganese Delay Compositions. See Vol **3**, D50–D52 under **Delay Charges.** The D-16 series of delay compns, contg Ba chromate–Pb chromate–Mn, exhibit burning rates in the range of 3–13sec/inch. As long as mixts of these ingredients do not come in contact with moisture, their storage stability is good. The sensitivity of finely powd Mn to oxidn in the presence of moisture is the underlying cause of erratic stability. Coating Mn with K dichromate or stearic acid, or utilizing treatments such as H_2 reduction or chromic acid are not always satisfactory (Ref 1, 274–5)

Demand for a delay powd capable of withstanding the effects of repeated impacts on a hard surface, typical of skip bombing, lead to the development of Ba chromate–Mn–S compositions. They proved satisfactory in the M16-A1 delay element, with burning times of 8–11 secs obtained with compns contg Ba chromate 70–74, Mn 20–22 and S 3–4%. Storage at 65° resulted in increased burning time,

although chem analysis showed no appreciable compn change (Ref 1, 268–70)

A review article by Whiting (Ref 2) on the storage stability of Mn delay compns contains 8 refs

Refs: 1) F.B. Pollard & J.H. Arnold, Jr, eds, "Aerospace Ordnance Handbook", Prentice-Hall, Inc (1966) 2) R.A. Whiting, "A Review of the Storage Stability of Manganese Delay Compositions", Expls & Pyrots **5** (1) & (2) (1972)

Manganese Dioxide (Manganese Bioxide, Manganese Black, Battery Manganese, Manganese Peroxide), MnO_2, mw 86.93, black or dark brown rhombic cryst or amor powd; mp, decomps to Mn_2O_3 & O_2 at 535°, d 5.026g/cc; insol in w, alc and HNO_3, sol in HCl. Found in nature as mineral pyrolucite and as a special African ore of different atomic structure used exclusively for the battery grade. Prepd by electrolysis, by heating Mn dioxide in the presence of O_2 and by decompn of Mn nitrate. Used as depolarizer in dry cell batteries and in pyrotechnic compns (Ref 2). Is a strong oxid agent and has been used as such in the expl Prométhée, authorized in France as *Explosif O no 3* (Ref 1). In the USA a Mil Spec covering Manganese Dioxide (For Use In Pyrotechnics), **MIL-M-3281**(25 Aug 1950), details min Mn content (55.0%), available oxygen (15.6%), moisture (2.5%) and granulation requirements

Refs: 1) Davis (1943), 355 2) Ellern (1968), 112, 226, 237, 242 3) CondChemDict (1971), 540

Manganese Heptoxide. Mn_2O_7, mw 221.87, brown liq, mp 5.9°, bp defl 55°, explds 95°, d 2.396g/cc; v sol in cold w, decomposes in hot w, sol in sulfuric acid. Prepd by adding powd K permanganate in small quant to cooled concd sulfuric acid. A dark green soln is formed *which is liable to expld violently* in contact with traces of organic matter, and *should never be prepd in quantity*. When ice-cold w is added cautiously, dark brown drops of Mn_2O_7 separate. It forms a violet vap at 40–50°, but explds violently on warming. Therefore, a potentially hazardous condition exists when K permanganate is placed in a desiccator where sulfuric acid is the drying agent

Refs: 1) Partington (1950), 908 2) A.M. Patterson, C&EN **26** (1948), 711 & CA **42** (1948), 2773 3) R.E. Oesper, JChemEduc **30** (1953), 550 4) Ellern (1968), 50

Manganese Nitrate (Manganous Nitrate), $Mn(NO_3)_2.6H_2O$, mw 287.04, rose-red monoclinic crysts, mp 26°, bp 129°, d 1.82g/cc; v sol in w, deliq, sol in alc. Can be prepd by dissolving Mn carbonate in nitric acid. Combines the props of an oxidizer and a flame reducing agent, but has the disadvantage of low mp

Refs: 1) Mellor **12** (1940), 441 2) CondChemDict (1971), 542

Manganese Oxide. See under Manganese Dioxide

Manganese Peroxide. See under Peroxides

Manganese Picrate. See under Picrates

Manganous Azide. See under Azides

Manlianite. A mixt of NH_4 perchlorate 72, sulfur 13.25 & charcoal 14.75%

Refs: 1) CondChemDict (1942), 290 2) A. Pérez Ara (1945), 219

Mannans (Tagut Nut, Corajo, Vegetable Ivory, Carobean), $(C_6H_{10}O_5)_x$, mw 162.14. Polymeric polysaccharides which yield mannose on hydrolysis. They can be acetylated and nitrated

Ref: H. Pringsheim, "Die Polysaccharide", J. Springer, Berlin (1931), 298

Trinitromannan. Mannan in pure form was obtained from the ivory nut and nitrated, giving nitromannan A & B which gave trinitromannan suitable for artillery use. The products contained both sol & insol fractions

Ref: M.M. Kostevich, Separate, Buenos Aires, Argentina, 14pp (1951) & CA **46** (1952), 9845

MANNITANE AND DERIVATIVE

Mannitane (Anhydride of Mannitol), $C_6H_8O(OH)_4$, mw 164.16; white amor or cryst powd, mp about 137°; v sol in w, insol in alc. Can be prepd by heating 1p mannitol with 1.5ps w at 295° in an autoclave for 1.5 hrs. It can be nitrated

Refs: 1) Beil **1**, 538, (284) & [611] 2) Daniel (1902), 561

Mannitane Tetranitrate. $C_6H_8O(ONO_2)_4$, mw 344.16, N 16.28%, OB to CO_2 −13.9%; yellowish-brown syrupy liq; insol in w, sol in alc & eth. Can be prepd by gradual dissolution of 1p of mannitane in a cooled mixt of 5ps concd nitric acid and 10ps concd sulfuric acid. The slurry is then poured into a large quant of ice w, and the prod sepd by filtn, washed & dried. It is a powerful expl with the same impact sensitivity as NG

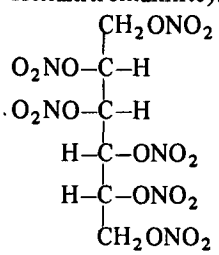
Refs: 1) Beil **1**, 540 2) Daniel (1902), 561 3) Gody (1907), 394

MANNITOL AND DERIVATIVES

Mannitol (d-Mannitol, Mannite, Manna Sugar), $CH_2OH(CHOH)_4CH_2OH$, mw 182.17, colorl rhombic crysts, mp 166–68°, bp 290–95° at 3.5mm, d 1.52g/cc, sol in w (13g/100g at 14°), sl sol in alc (0.01g/100g at 14°), insol in eth. Widely distributed in nature, particularly in fungi. Obtained from manna by boiling in alc or by electrolytic redn of glucose. On nitration yields the expl hexanitrate together with a small amt of pentanitrate (see below)

Refs: 1) Beil **1**, 534, (282) & [607] 2) Davis, **2** (1943), 462–65 3) CondChemDict (1971), 543

MANNITOL HEXANITRATE (Nitromannite, or Hexanitromannite).



Nitromannitane (Fr), Nitromannite (Ger & Ital), Mannitazotnokislyy (Russ); $C_6H_8N_6O_{18}$; mw 452.17; N 18.59%; OB to CO_2 +7.1% to CO +28.3%; fluffy felted needles from et alc, stout grains by pouring a soln in a w-sol organic solv rapidly into w (Ref 33, pp 236–37); mp 112–13° (Refs 28, 34 & 53), after repeated recrystns from different solvs, mp 109° (Ref 44); cryst d 1.230–1.604g/cc (Refs 2 & 22); CA Registry No 130-39-2 (optical isomer unspecified), 15825-70-4 (prepd from D-mannitol)

Historical. The action of nitric acid on mannitol was first examined by A. Sobrero who isolated the hexanitrate in 1847 (Ref 3). The prepn on a lab scale was repeated by other workers in the mid-19th century (Refs 2, 4, 10 & 12). It was mfd on a small scale in the Royal Arsenal at Turin, Italy until 1853, when 400g expld with great damage (Ref 33, p 198); later work has been described in Refs 13 & 15

Preparation. Nitric acid (d 1.51) in a 300ml Erlenmeyer flask is cooled with ice-salt to 0°, 10g of mannitol is added in small pieces with swirling at a rate so as to keep the temp at 0°. After all the mannitol is dissolved, 100g of sulfuric acid (d 1.84) is added from a dropping funnel at a rate so that the temp is held below 0°. The porridge-like mass is filtered on a sintered-glass funnel, washed with w, dil Na bicarbonate, and again with w. The crude prod is dissolved in warm et alc, filtered, and cooled to deposit crysts of pure Nitromannitol. A second crop is obtained by heating the filtrate and washings to boiling, adding w to turbidity, and cooling; total yield ca 23g (92.4%) (Ref 3, p 236). The nitration of mannitol with nitric acid in trifluoroacetic anhydr has been described in Ref 52, yield 45%. A study of the effect of reaction time, temp, and acid compn on the yield of Nitromannitol is described in Ref 57. The highest yield (96.6%) was obtd with a mixt of 40% nitric acid, 55% sulfuric acid, and 5% w for 1.2 min at 1.67°

The value of the optical rotation was found to decrease with increasing wavelength of light: in ethylene dibromide, wavelength 4359Å, rotation was +95.2°; 6716Å, rotation +36.8°. Similarly, in et alc at the same wavelengths the rotations were +87.2° and 32.7° (Ref 22)

Chemical Reactions. Mannitol is regenerated by treatment of the hexanitrate with Amm sulfide (Ref 6), iron in acet ac (Ref 7), ferric chloride (Ref 14), or with hydrogen iodide

(Ref 17). It reduces Fehling's soln (Refs 14 & 15); is decompd with iron turnings in basic soln with loss of nitro groups (Ref 5); is hydrolyzed with K hydroxide in et alc to give K nitrite (Ref 15). The action of ammonia in eth gives a mixt of a pentanitrate, a tetranitrate, and a mannitan tetramine, $C_6H_8O(NH_2)_4$ (Ref 8); action of pyridine in boiling et alc forms a pentanitrate (Ref 15). The rate of hydrolysis in 5% K hydroxide or 1% Na carbonate is less than that of Inositol Hexanitrate, NG, or Erythritol Tetranitrate (Ref 38). Treatment with zinc dust and Ac anhydr in pyridine or HCl soln gives mannitol hexaacetate (Ref 39); in a similar reaction the same hexaacetate is formed when the nitrate is allowed to stand in the cold with Ac anhydr: 100% sulfuric acid 10:1 (Ref 49). The action of pyridine on the hexanitrate gives a pentanitrate whose free hydroxyl group was shown by methylation with Me iodide to be at the 3-position (Refs 50 & 55). Similar results were obtd with an aq acet soln of Amm carbonate (Ref 54). When mixed with N,N,N′,N′-tetramethyl-p-phenylenediamine in an organic solv, a violet color develops which indicates that a charge-transfer complex is formed; however. all attempts to isolate this complex failed (Ref 64). Similarly in Ref 1, {2404} is a tabulation of complexes formed with a number of org compds including aromatic nitro compds and nitrate esters. Charge-transfer complexes with pyrimidine and purine bases as well as with solvents like hexamethylphosphoramide and dimethyl sulfoxide are reported in Ref 66. The action of aromatic amines (primary, secondary, or tertiary) resulted in fume-offs or unidentifiable tars, in all cases purple or red colors developed prior to more violent reactions (Ref 66)

Analytical. Mannitol Hexanitrate can be hydrolyzed in basic soln and the soln acidified in the presence of NITRON to quanty ppt NITRON nitrate (Ref 16). A procedure is described for the quant detn of nitrate esters, including Mannitol Hexanitrate, in the presence of aromatic nitro compds in Ref 17. It gives a yellow color when treated in et alc or acet with 5% aq K hydroxide, then 5% aq ammonia (Ref 24). It can be quanty detd by reduction with Devarda's alloy (Encycl **5**, D-1110) or Al wire in aq et alc and titration of the evolved ammonia (Ref 25). In a similar procedure the ester is hydrolytically reduced and the mannitol quanty oxidized with periodate (Ref 37). It is detd by reaction with 4-hydroxy-m-xylene in 72% sulfuric acid followed by spectrophotometric analysis of the 5-nitro-4-hydroxy-m-xylene formed (Ref 43). A rapid thin-layer chromatog sepn and quant detn of mixts of Mannitol Hexanitrate with other expls is described in Ref 62. The polarographic analysis of Mannitol Hexanitrate is described in Refs 59 & 67, the compd was found to give a peak potential at −0.35 v, limit of deton 5μg/ml

Brisance – Sand Test. 121.5–143% of TNT (Refs 18 & 30); 225% of MF (Ref 23) (See also Encycl **2**, B280 & B298)

Lead Plate Cutting Test. 116–19% of TNT (Ref 30) (See also Encycl **2**, B280)

Detonation Rate. 7000m/sec at d of 1.5g/cc in an iron pipe 25mm in diameter and a wall thickness of 5mm (Ref 20, p 249) (See also Encycl **2**, B280)

Explosion Temperature. It expl spontaneously at 160–70° (Ref 18); in 1 sec at 232° (Ref 19); in 5 secs at 175° (Ref 26); deflagration temp 185° (Ref 51)

Flammability Order. It is not ignited by the spit of a BkPdr fuse, contact with a lighted match causes deton (Ref 20, p 249)

Friction Pendulum Test. Unaffected by fiber shoe, steel shoe causes deton (Ref 18); 3cm for 50% expl with 4kg wt (PETN 12cm) (details of test in Ref 35, pp 12 & 13)

Gas Evolved on Heating. At 100° after 1 hour gas evolution was 2.62, after 2 hours 3.69, and after 5 hours 6.75 ℓ/kg (Ref 45)

Heat of Combustion. −674.9kcal/mole (Ref 32); −1521cal/g (Ref 45); −1484.2 ± 5.8cal/g (purity by nitrometer 99.46%) (Ref 47, p 22); −1565 cal/g (Ref 46); −1525cal/g, Q_c^v −689.5kcal/mole, Q_c^p −683.7kcal/mole (Ref 31); −1515 cal/g (Ref 29)

Heat of Explosion. Calcd −1459, found −1454 cal/g (Ref 60)

Heat of Formation. −165.2kcal/mole (Ref 32); −169.42 ± 0.68kcal/mole (Ref 47)

Heat Test at 100°. Frothed in 48 hours, expld in 100 (Ref 46)

Hygroscopicity. 0.17% wt gain at 30° and 90% RH (Ref 46)

Ignition Temperature. 165° (Ref 45)

Impact Sensitivity. BM app 8–11cm (Refs 42, 45 & 46); PA app 4inches (11mg sample) (Ref 46)

International Heat Test at 75°. 0.4% wt loss in 48 hours (Ref 46)

KI Test. 6min for color at 65.5° (Ref 46)

Power by Trauzl Test. 102% of NG (Ref 20, p 156); 172% of TNT (Ref 26); 150% of PA (Ref 34); 131% of Tetryl (Ref 30)

Sensitivity to Ignition by Shock Wave. When initiated with Melinite (70% PA, 30% NC), it was found to have a shock wave sensy similar to PETN (Ref 51)

Sliding Rod Impact Test. In Ref 36 is a table of heights of fall for 50% expls listed against sample size and angle of fall; extreme values are 0.2cm for 3mg sample at 75°, and 25.5cm for 62mg at 30° angle

Specific Volume of Gases Formed on Explosion. 723ml/g (NG 712ml) (Ref 46)

Stabilization. Chromatographically pure Mannitol Hexanitrate was mixed with varying percentages of 22 stabilizers and the mixts tested for stability in the 100° heat test; best results were obtained with a mixt of 96% MHN, 2% Amm oxalate, and 2% dicyandiamide (4.07% wt loss after 48 hours, 5.74% after 96 hours) (Ref 56). The use of ethylene oxide as a stabilizer is reported in Ref 27

Thermal Decomposition. Slow heating causes decompn at 150° with evolution of red fumes (Ref 20, p 249)

Vacuum Stability. When heated to 100° for 1 hour, 2.62; 2 hours, 3.69; and 5 hours, 6.75 ml/g of gas are evolved (Ref 45)

Solubility. Insol in w (Ref 8); sol in warm et alc, eth, and acet ac (Ref 11). It is very sol in acet, hot et alc, and hot me alc (Ref 44); solys are: 0.012g/100ml in w at 25°, 2.356g/100ml of et alc at 25°, and 3.394g/100ml of acet at 25° (Ref 45). Solns in acet exhibit a large negative deviation of the vapor pressure from ideality. It is presumably caused by H-bonding betw the acet molecules and the H-atoms on carbon bearing nitroxy group (Ref 40)

Stability in Storage. It can be stabilized in storage by the addn of 5–10% Na, K, or Li salicylates (Ref 63)

Uses: It can be used as a secondary charge in detonators replacing Tetryl. Mixts with Diazonitrophenol (Encycl **2**, B59) or Tetrazene are detonators (Ref 41). Use is claimed as a safety blastcap, as it will only transmit combstn after being confined by crimping a fuse on the cap (Ref 41). It is claimed to be an oxidizer in a solid proplnt formulation (Ref 58). An 80:20 mixt with Tetrazene coated with 2% PVA can be hot molded to form propelling charges or primers (Ref 65). It has been incorporated at a level of 10% in an exptl rocket grain formulation whose strand burning rate was 0.33inches/sec at 1000psi (Ref 48). There is an extensive literature on the drug use of Hexanitromannitol whose action is similar to NG (See article in Ref 61 and references therein)

Written by **C.H. McDONNELL**

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Mannitol Pentanitrate (Pentanitromannit), $C_6H_8(OH)(ONO_2)_5$, mw 407.16, N 17.20%, OB to CO_2 −1.96%, colorl needles from alc, mp 77–79°; v sl sol in w (0.00033g/100g at 15°, 0.002g at 60°), sl sol in alc (1.67g/100g at 12.8°) and eth (1.31g/100g at 9°). First prepd in 1864 (Ref 1), together with mannitol tetranitrate, by passing NH_3 gas thru an eth soln of mannitol hexanitrate. It was later obtained (Ref 2) from the mother liquor remaining after crystn of crude mannitol hexanitrate (obtd by nitration of mannitol with mixed nitric-sulfuric acid) from alc. About 2.5g of mannitol pentanitrate were obtd from 25g of crude hexanitrate. Defgr mildly on heating, more strongly on impact

Refs: 1) Beil **1**, 542 2) J.H. Wigner, Ber **36**, 796 (1903) 3) L.D. Hayward, JACS **73**, 1974–75 (1951)

D-MANNOSE AND DERIVATIVE

D-Mannose (Seminose), $CH_2OH(CHOH)_4CHO$, mw 180.16, mp 132° (dec), d 1.53g/cc; v sol in w (248g/100g at 17°), v sl sol in abs alc, insol in eth. A carbohydrate occurring in some plant polysaccharides. Can be prepd by hydrolysis of mannanes by dil acids or by certain enzymes or microorganisms. It is an isomer of glucose. On nitration, it yields an expl compd (see below)

Ref: Beil **1**, 905, (456) & [902]

D-Mannose Pentanitrate (Nitromannose), $C_6H_7O(ONO_2)_5$, mw 405.16, N 17.29%, mp 81–82°, bp dec at about 124°, insol in w, sol in alc, and reduces Fehling's soln slowly on warming. Can be prepd by dissolving d-mannose in cold concd nitric acid and then adding concd sulfuric acid. It is an expl which is unstable at even slightly elevated temps, decompg rapidly when stored at 50°, losing 46% by weight in 24 hours
Refs: 1) Beil **1**, 907 2) W. Will & F. Lenze, Ber **31**, 76 (1898) 3) Davis (1943), 241

Manometric Stability Tests. Based on press measurements developed by gases formed on decompn of expls. Amon this group of tests are: (1) Brame's Method, (2) Chiaraviglio and Corbino Method, (3) Desmaroux Method, (4) Dupre's Vacuum Test, (5) Farmer's Vacuum Stability Test, (6) Haid, Becker & Dittmar Test, (7) Meerscheidt-Hüllassem's Test, (8) Mittasch's Method, (9) Obermüller's Method, and (10) Talliani Test

Manonitrometer. An apparatus for detg N content of NC, mixed acids, etc
Ref: M.F. Planchon, SS **11**, 22–24 (1916)

Manuelites. Expls patented in France in 1891 by Magnier, de Lom de Berg and Vieillard. Consisted of mixts of Amm or Na picrate with Amm or K nitrate in various proportions. They could be blended with resinous hydrocarbons for plastic consistency
Ref: Daniel (1902), 416–17

Maquenne Block. See under Melting Point Determinations

Marble. A variety of limestone ($CaCO_3$). It is a hard, very sl porous stone, which occurs in nature in many forms and colors. It may be prepd artificially by the recrystn of limestone under great press and at high temp. In powd form it has been used as an antacid ingredient of some Dynamites (see under). Silberrad (Refs 1 & 2) proposed its use for purification of nitrated hydrocarbons by refluxing the material to be purified with marble or dolomite
Refs: 1) O. Silberrad, SwedP 42080 (1917) 2) Colver (1918), 741 3) CondChemDict (1971), 544

Marin's Explosives. Expls contg typically Amm perchlorate 32.2–34, Gu nitrate 24–26, Na nitrate 24.6–25, TNT 4–5.6 and liq di- or trinitrotoluenes 11–13.6%
Refs: 1) Daniel (1902), 418 2) BritP 121294 (1918) & CA **13**, 753 (1919)

Marine Fiber (Posidonia). Fibrous material obtained from the marine plant *Posidonia Australis*, found in Spencer's Gulf, south Australia. It consists of short, harsh fibers, resembling jute in appearance, and contains about 56% cellulose and 16% ash. When the crude fiber is purified by boiling with caustics and acids, the resulting prod contains less than 1% ash and is suitable for the prepn of an expl nitrate (see below). The idea of utilizing marine fiber for this purpose was raised during WWI since the cultivation of cotton was not successful in Australia because of the high cost and shortage of labor

Nitrated Marine Fiber (Nitroposidonia). Prepd by gradually adding the previously purified and dried fiber to sufficient mixed acid, consisting of 1 part by wt nitric acid (d 1.5g/cc) and 3 parts sulfuric acid (d 1.84g/cc). After 72 hrs of nitration, the prod was sepd by filtn, washed and boiled with w for a much shorter time period than required for the stabilization of cotton NC. The yield of purified prod was 72% and contd 12.3% N. Stability by Abel's test at 76.6° was 10.5 mins compared with 15 mins for regular guncotton. When mixed with regular ingredients of smokeless powd, it gave a prod resembling in all its properties smokeless powds produced with cotton NC
Refs: 1) B.J. Smart, ChemEngMinReview (Australia) **10**, 380 (1918) & CA **13**, 262 (1919) 2) B.J. Smart & P. Pecover, JSCI **37**, 300–01 (1918)

Marking of Ammunition and Containers for Ammunition and Explosives. Ammo is identified completely by painting and marking, which includes the ammo lot number, on original packing containers. Once removed from its packing, ammo may be identified by painting and marking on ammo items. To identify a particular design, a model designation is assigned at the time the model is classified as an adopted type. This model designation becomes an essential part of the nomenclature and is included in the marking of the item. Prior to WWI, the year in which the design was adopted (preceded by an M) was used as the model designation; for example, M1914. From WWI to 1 July 1925, it was the practice to assign mark numbers; that is, the word "mark", abbreviated "Mk", followed by a Roman numeral. The modification was indicated by the addition of MI to the mark number, the second by MII, etc. However, the use of Roman numerals has been discontinued and all future reference and records will be in Arabic numerals. The present system of model designation consists of the letter "M" followed by an Arabic numeral, for example, "M1". Modifications are indicated by adding the letter "A" and the appropriate Arabic numeral. Thus, "M1A1" indicates the first modification of an item for which the original model designation was "M1". Wherever a "B" suffix appears in a model designation, it indicates an item of alternative or substitute design, material or manufacture

When ammo is manufactured, an ammunition lot number is assigned in accordance with pertinent specifications. As an essential part of the marking, this lot number is stamped or marked on the item, size permitting, as well as on all packing containers. It is required for all purposes of record, including reports on condition, functioning, and accidents, in which the ammo is involved. To provide for the most uniform functioning, all of the components in any one lot are manufactured under as nearly identical conditions as practicable

Ammo is packed and packing containers are marked in accordance with applicable drawings and specifications. Containers are designed to withstand conditions normally encountered in handling, storage and transportation, and to comply with ICC regulation. Marking of containers includes all information required for complete identification of their contents and for compliance with ICC regulations

Ref: Anon, "Ammunition, General", **TM 9-1300-200** (Oct 1969), 1-2 to 1-12

Marksman Powder. An American variety of EC rifle powd, developed about 1900, for mid-range shooting in .22 Cal rifles

Ref: Van Gelder & Schlatter (1927), 800

Marqueyrol's Stability Test. 200g samples of double-base powds were heated at 50° under vac in a round bottom Pyrex flask. Every 3–4 days, the vapors were pumped out, collected in a gasometer over Hg and measured. The test was contd until the powd started to decomp very rapidly, usually after 1800–2000 days. A curve was then plotted of cc of gas evolved vs days of heating, and the gas was analyzed for CO_2 and NO. If any liq formed, it was collected, measured and analyzed

A stable powd, such as one contg NC (11.97% N) 71.98, NG 22.20, vaseline 4.87 and DPhA 0.97%, evolved 35.5cc of gas and 4.75ml liq after 1834 days with a wt loss of 2.55g. The gas contd CO_2 39.7, NO 19.0%, plus other ingredients, and the liq consisted mostly of acet

Some French powds which were stabilized with amyl phthalate, eg, NC (11.89% N) 72.1, NG 22.8 and amyl phthalate 5.1%, evolved 298cc of gas plus 6.9ml liq after 1834 days with a wt loss of 3.55g. Compn of the gas was CO_2 31.3, NO 30.0%, plus other ingredients, and the liq consisted mostly of acet

Refs: 1) M. Marqueyrol, MP **23**, 178–182 (1928) 2) Reilly (1938), 90

Mass, Specific, of Constituents of Smokeless Propellant. Literature data on the specific mass of over 100 compds are given in Ref. Kopp's additive rule applies with an error generally less than 1%, eg, $1/d - \Sigma (n_i/p_i)$, where n_i is % of constituent, p_i is specific mass of constituent, and d is specific mass of propellant

Ref: P. Tavernier, MP **30**, 253–96 (1957) & CA **53**, 1715–16 (1959)

MASS SPECTROMETRY

Definition and Terminology: A mass Spectrometer is an instrument which produces a beam of ions from a given sample and separates the ions according to their mass-to-charge (m/e) ratios. A record of the relative abundance of the ionic species arranged according to their masses constitutes a mass spectrum. Historically, the instrumentation to achieve this has developed along two principal lines, one concerned chiefly with the measurement of relative abundances of ionic species and the other with the determination of their accurate masses. These two kinds of instruments became known as mass spectrometers and mass spectrographs, respectively. Until recently, the mass spectrographs, as the name implies, used a photographic recording technique to register the ion beam, while mass spectrometers relied on measurement of ion current and electronic amplification. However, modern instruments with dual electrical-photographic detection make the distinction less meaningful and current practice is to use the generic terms such as "mass spectrometer" and "mass spectrometry"

Every mass spectrometer consists of four principal components (Fig 1): (1) the source, where a beam of gaseous ions are produced from the sample; (2) the analyzer, where the ion beam is resolved into its characteristic mass species; (3) the detector, where the ions are detected and their intensities measured; (4) the sample introduction system to vaporize and admit the sample into the ion source. There is a wide variety in each of these components and only those types which are relevant to analytical and organic mass spectrometry will be emphasized in this survey. The instrumentation aspects will be discussed after the ionization process and the basic ideas of mass spectrometry are considered first (Refs 7 & 30)

The Ionization Process: Electron "bombardment" or "impact" of the gaseous sample at low pressures (10^{-4} to 10^{-6} torr) is the most common means to generate ions. While it is possible to study both positive and negative ions in mass spectrometry, most of the investigations are designed to study the positive ions since these are produced in much larger numbers than the negative ions under electronic impact. For a sample atom or molecule to be ionized a certain minimum energy characterized by its "ionization potential" has to be supplied. The minimum amount to remove the least strongly bound electron from a gaseous atom or molecule is called the ionization potential. The loss of a single electron by most atoms and organic molecules takes energy in the range 5 to 15 ev and the ions so obtained are referred to as "molecular ions"or "parent ions" in mass spectrometric usage. Occasionally, doubly charged ions are formed in the ionization which exhibit an apparent "mass" one-half of the corresponding singly charged ion because the mass analyzer is responsive only to mass-to-charge (m/e) ratio. However, the vast majority of the ions are singly charged, justifying the imprecise use of the term "mass" in place of m/e in everday mass spectrometry. With energy available in excess of ionization, the molecular ions dissociate to ions of smaller mass. The minimum energy for the appearance of a given "fragment ion" is called the "appearance potential". Since most ionization sources use 70 ev electrons, considerable fragmentation of molecular ions takes place resulting in a series of product ions. The mass spectrum (m/e vs relative abundance) of a

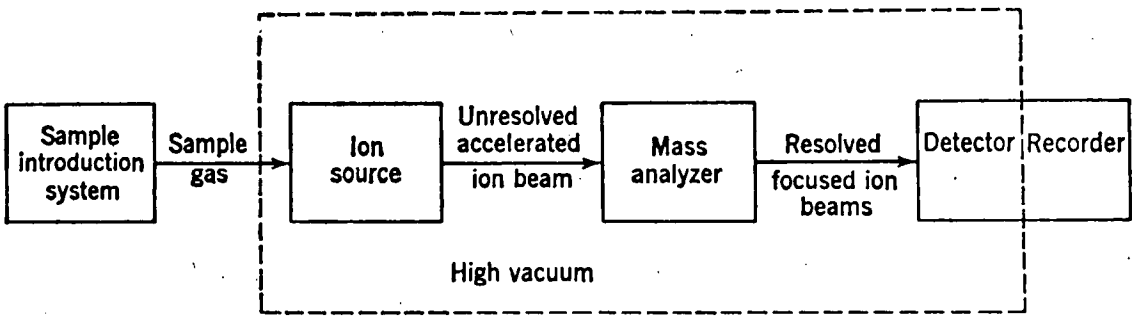


Figure 1 Diagram of mass spectrometer system.

sample can therefore serve as a "fingerprint" of the substance under study and help its characterization in terms of molecular weight, elemental composition and the manner in which atoms are grouped together within its structure. For illustration, the mass spectrum (Ref 30) of carbon dioxide is shown in Figure 2. In this the abscissa is an m/e scale (atomic mass units, amu) and the ordinate shows relative ion abundances. For example, the relative abundance of the ion, m/e = 28 is four times that of the ion, m/e = 22 from a comparison of the peak heights and the corresponding scale factors

Uses of the Mass Spectrum: There are three uses in general for mass spectral information: (a) *Determination of masses of ions:* An example is the carbon dioxide spectrum (Fig 2) where it is adequate to obtain masses in nearest integral numbers. In other cases, the precise mass of ions with an accuracy of a few parts per million may be required to investigate molecular weight, elemental composition and structural details. (b) *Determination of isotopic abundance:* This information can be applied in such diverse areas as isotopic constitution of elements, geochronometry, isotopic dilution analysis and the study of reaction mechanisms by isotopic tracers. (c) *Mass spectral patterns:* The array of peaks in the complete spectrum of a pure substance is referred to as a cracking pattern. Fig 3 shows a line diagram (bar graph) of the mass spectral pattern of methane (Ref 29). If this were an unknown substance it would be obvious from the spectrum that this represents a structure with molecular weight 16. Peaks at masses 15, 14, 13 and 12 show successive loss of fragments of mass 1, 2, 3 and 4 from the molecule and must correspond to the loss of four hydrogens. The remaining fragment of mass 12 can only be a carbon atom, and the unknown is identified as methane. For larger molecules the spectra and their identification becomes more complicated. Mass spectral patterns may also be presented as tables of m/e and relative abundance as illustrated by that of dimethylnitramine (Table 1, Ref 44). These cracking patterns can be utilized for a variety of purposes in qualitative and quantitative analysis and structural determinations. Cracking patterns for thousands of compounds have been obtained, and there are a number of compilations available (Refs 12, 19 & 32)

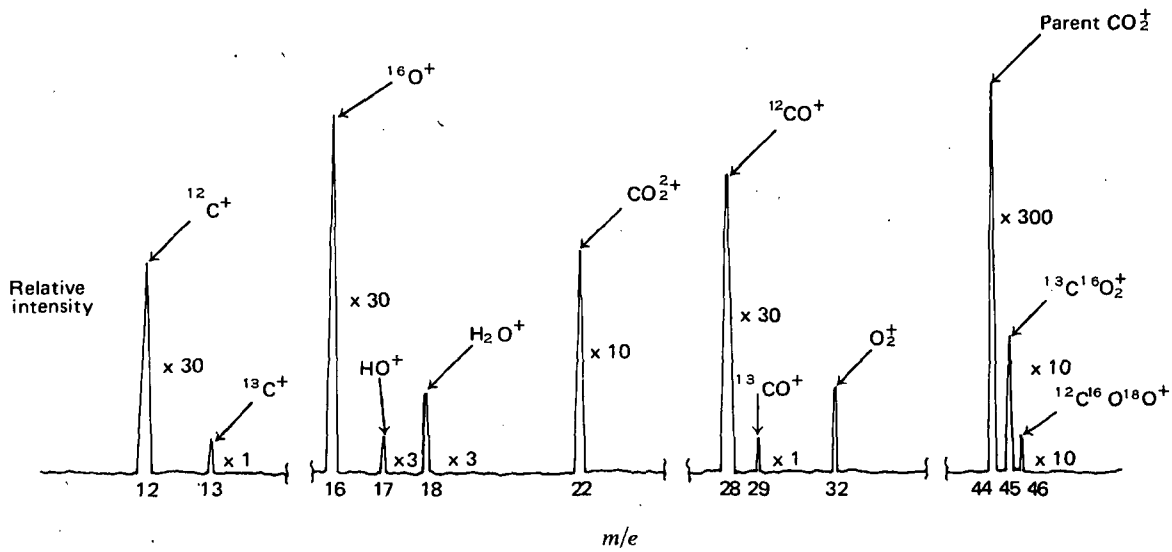


Fig 2 Mass spectrum of carbon dioxide. Relative peak intensities are plotted against *m/e*.

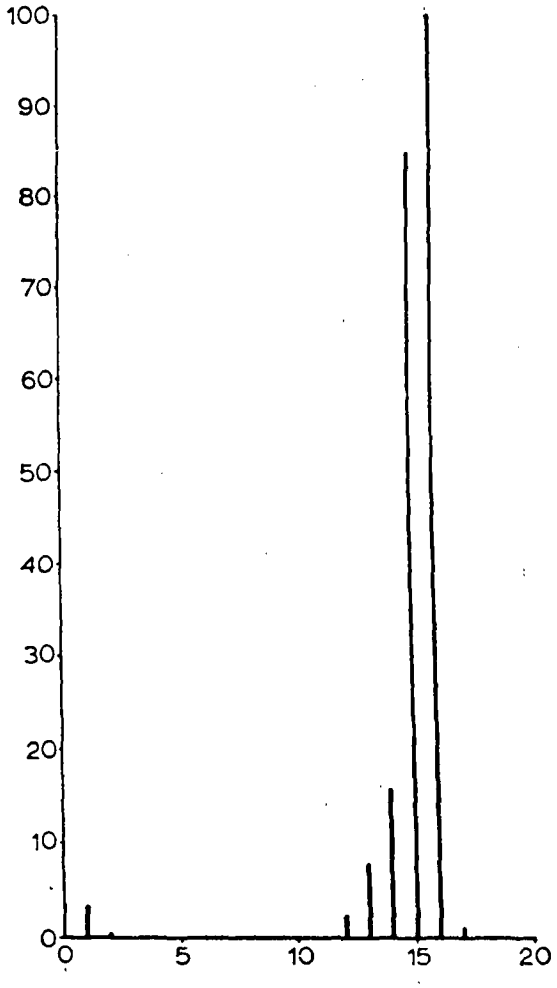


Fig 3 The mass spectrum of methane.

Table 1

Mass spectral fragmentation pattern of dimethylnitramine, $CH_3N(NO_2)CH_3$, mw 90; Instrument, CEC 21-104; Ionization Voltage 70 eV

Mass/Charge Ratio	Relative Abundance
12	0.5
13	1.0
14	4.3
15	30.6
16	0.6
17	0.6
18	14.6
26	0.4
27	4.6
28	3.7
29	3.0
30	19.8
31	0.1
32	2.6
38	1.2
39	1.9
40	6.5
41	7.3
42	100
43	77.6
44	31.2
45	1.6
46	1.8
59	0.6
60	11.0
61	0.3
73	0.6
74	9.9
75	0.4
89	0.2
90	56
91	0.2

Historical: That positive rays could be deflected in electric and magnetic fields was shown as early as 1898 by Wien, but it was not until 1912 that what was to become the forerunner of the modern mass spectrometers was built by J.J. Thompson, who became known as the "father" of mass spectrometry. The existence of two isotopes of neon (m/e 20 and 22) was demonstrated by Thompson with this instrument. The discovery of stable isotopes of elements has been generally considered the greatest achievement of mass spectrometry because of its profound effect on our understanding of the structure of the atom and the properties of elements. The next few years saw the construction of more sophisticated instruments by Dempster (1918) and Aston (1919). Aston's instrument, in particular, suited the determination of exact mass of nucleids, and enabled him to measure the whole number divergence of nucleidic masses of many elements, that led to the important concept of "packing fractions".

During the next 20 years major advances in the field of electronics made it possible to construct reliable, accurate and easy to handle mass spectrometers. The remarkable reproducibility of light hydrocarbon mass spectra soon led to the acceptance of mass spectrometry as a tool for quantitative analysis (Ref 1); especially of hydrocarbon mixtures, valuable to the petroleum industry. Nier's isotope-ratio analyzer in the early 40's, which paved the way for the separation of uranium isotopes 235 and 238 and the development of nuclear energy, was the next milestone in mass spectrometry. In recent years great strides were made in the sensitivity, resolving power and precision in mass measurement, with the result that application of high resolution techniques to organic structure elucidation has become the most active area in mass spectrometry. The advent of computer based data acquisition and processing has further led to automation techniques for the generation and analysis of massive amounts of data

Instrumentation: Several fundamentally different types of ion sources and mass analyzers are currently available and employed in mass spectrometers depending on their application. There appears to be much less of a diversity in detectors and sample handling systems. A detailed account of all the types may be found in a number of monographs (Refs 7, 16, 29, 30 & 64), while Refs 49 & 55 give most recent reviews of ionization sources. Ionization sources which use electron bombardment and analyzers which use magnetic and electrostatic focusing are the common types used in organic analytical mass spectrometry, and these were also the earliest types. This survey will describe only the common types in some detail. However, a brief description of several new ion sources is included for two reasons: first, the mode of ion production generally determines the application of the instrument, and second, a variety of new sources are being applied to expls and proplnts

Ionization Sources

(a) *Electron Bombardment:* In the vast majority of organic analytical instruments today, ions are produced by the collision of electrons with sample molecules in the gas phase. This results in a Franck-Condon transition producing a molecular ion, an odd electron ion, usually in a high state of electronic and vibrational excitation. This excitation and its distribution over various modes of decomposition of the molecule determine the resultant fragmentation pattern

Fig 4 is a diagram of an electron "impact" source. The sample vapor is admitted into the ion source thru the slit in the back of the chamber and it passes thru a collimated electron beam 'b'. On impact of electrons with the neutral molecules, positive ions (to a small extent negative ions) are produced. A small positive potential ("repeller potential") between the back wall 'c' of the ion source and first accelerator plate 'd', expels the positive ions toward the accelerating region and at the same time attracts the negative ions which are then discharged at repeller plate 'c'. The positive ions are accelerated by the potential difference applied to plates 'd' and 'e', pass thru the exit slit 'f' and continue toward the collector

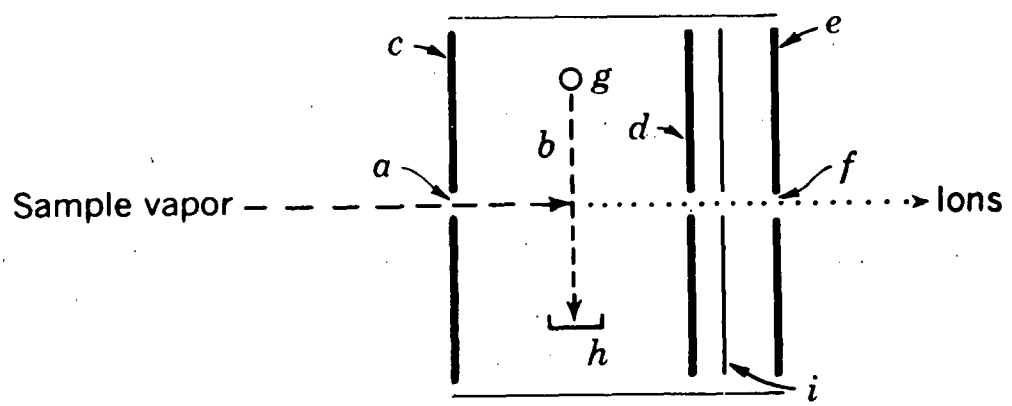


Fig 4 Ion Source

The energy of the electron beam (the potential difference between filament 'g' and the area of impact) is adjusted to 70 ev for maximum ionization efficiency, but it can be varied by appropriate choice of potential difference between the heated filament 'g' and anode 'h'. In the region 50 to 80 ev the peak heights are insensitive to fluctuations in the ionization voltage by a few volts, and reproducible cracking patterns are thus obtained. Ionization and appearance potentials may be determined by scanning the mass spectrum at increasing ionizing voltages in the 5–20 ev range. At a constant sample pressure the number of ions formed and, therefore, the peak heights, are directly proportional to the electron current passing thru the vapor. By adjusting the ionizing current the intensity of the spectrum can be varied. Electron impact sources are the most reliable and highly developed ionization methods. A high yield of ions, good energy homogeneity and stable ion beam are some of its advantages. Samples as little as 0.1 ml of gas or about 1 microgram of solids can be routinely analyzed. However, a serious limitation of the electron impact source is that a 70 ev electron beam is an extremely drastic method of ionizing a sample. As a result of the extensive fragmentation that follows, often including the loss of the molecular ion, vital information about the structure of the intact molecule is destroyed. Some of the newer ionization methods described below obviate this problem and have therefore become attractive to chemists

(b) *Chemical Ionization:* Chemical ionization (CI) is perhaps the most popular among the newer techniques in mass spectrometry (Refs 49 & 55). In contrast to the electron impact (EI) source, a CI source offers the advantage of simple cracking patterns, intense quasi-molecular ions and easy to interpret spectra. In the CI technique a reactant gas such as methane is introduced into the source at a relatively high pressure (1 torr) along with a very much smaller amount of sample. The primary ionization occurs in the normal way by electron impact in the reactant gas. The primary ions then give rise to ion molecule reactions with neutral molecules of the reactant leading to secondary ions. The secondary ions, predominantly CH_5^+, $C_2H_5^+$ and $C_3H_5^+$ in the case of methane react by proton or hydride ion transfer with the sample molecules and convert them to positively charged ionic species which are then mass analyzed

Primary ions: $CH_4 + e \rightarrow CH_4^+ + CH_3^+, CH_2^+$ . . . etc

Secondary ions: $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$

$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

Ionization of Sample, MH:

$CH_5^+ + MH \rightarrow CH_4 + MH_2^+ (QM)^+$

$C_2H_5^+ + MH \rightarrow C_2H_6 + M^+$ or

$\rightarrow C_2H_4 + M^+ + H_2$ . . . etc

A source design of this type is shown in Fig 5

A significant difference between the CI and EI processes is that the energy available in these ion-molecule collisions tends to be somewhat lower, having a profound effect on the fragmentation patterns which provide much of the structural information about the sample molecule. Compounds which do not normally show a molecular ion in EI mass spectrometry are observed to yield a quasimolecular ion (QM) at one mass unit higher than the molecular weight due to addition of a proton. The CI spectrum is therefore quite useful in situations where rapid identification of compounds within a specific class needs to be made, especially if these compounds do not give molecular ions under EI conditions. Examples of other reagent gases used in CI are hydrogen, isobutane and water vapor

An important additional feature of CI spectroscopy is its ability to handle gas chromatographic (GC) effluents directly if a proper reagent gas is used as the carrier gas in the GC. (This arrangement is also shown in Fig 5). Under these conditions the GC-CI system is quite simple and does not require an interfacing device to eliminate the carrier gas

Chemical ionization mass spectrometry has rapidly found extensive application to many substances (Refs 15, 23 & 28). Of particular importance is identification of complex and

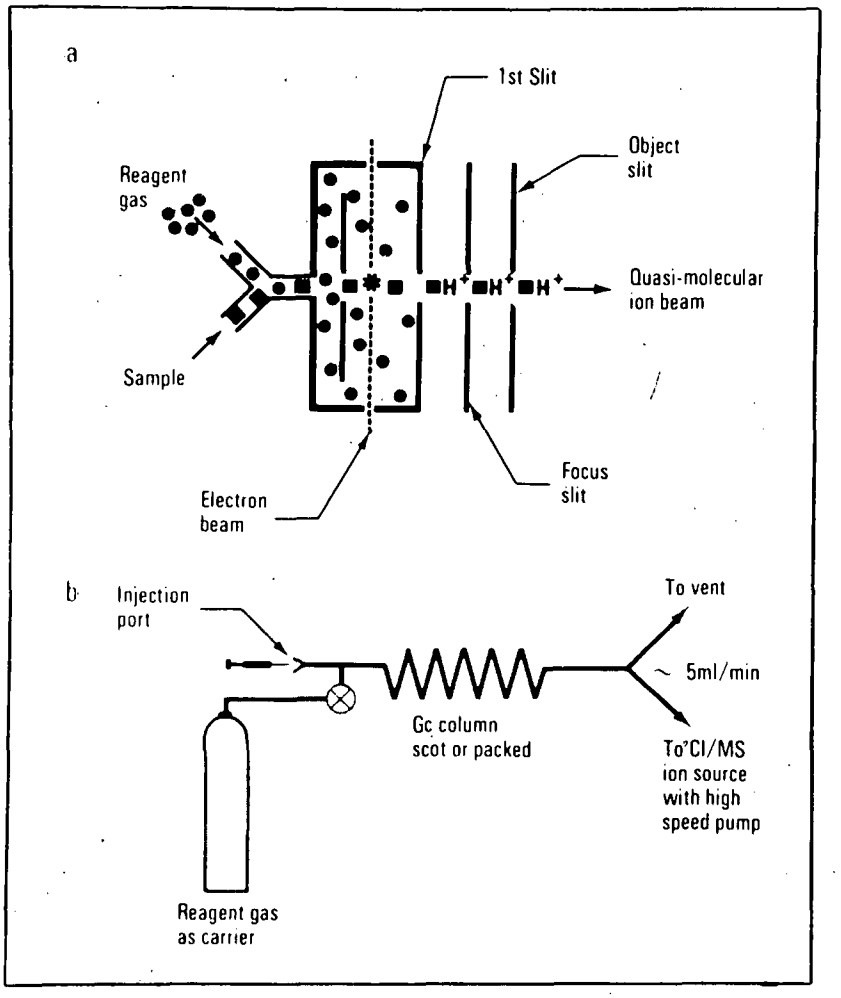


Fig 5 a) Chemical ionization source;
b) Combination gas chromatography/ chemical ionization mass spectrometry

dangerous drugs (Refs 36, 40, 41, 46, 51, 60 & 72), as well as forensic identification of expls (Refs 69, 70 & 71). The EI mass spectra of expls contain a large number of fragment ions and almost no molecular ion, thus making the identification difficult. The CI spectra of these expls resolve the identification in several instances due to the observed quasimolecular ions (Refs 69, 70 & 71). The EI and CI (isobutane) spectra of RDX shown in Figs 6 and 6a illustrate the point about molecular ions. Some explosives however, do not yield a quasimolecular ion but the spectra still contain characteristic fragment ions giving supplementary information to EI spectra. In addition, chemical ionization offers a unique advantage to exploit a variety of reactions possible with different reagent gases to establish structure-reactivity relationships

(c) *Atmospheric Pressure Ionization:* Atmospheric pressure ionization (API) mass spectrometry (Refs 8 & 66) and ion cluster mass spectrometry (ICMS) to be described later (see below) are akin to chemical ionization (CI) mass spectrometry in that all three rely upon mass analysis of ions which are products of ion-molecule reactions occurring in a reactant

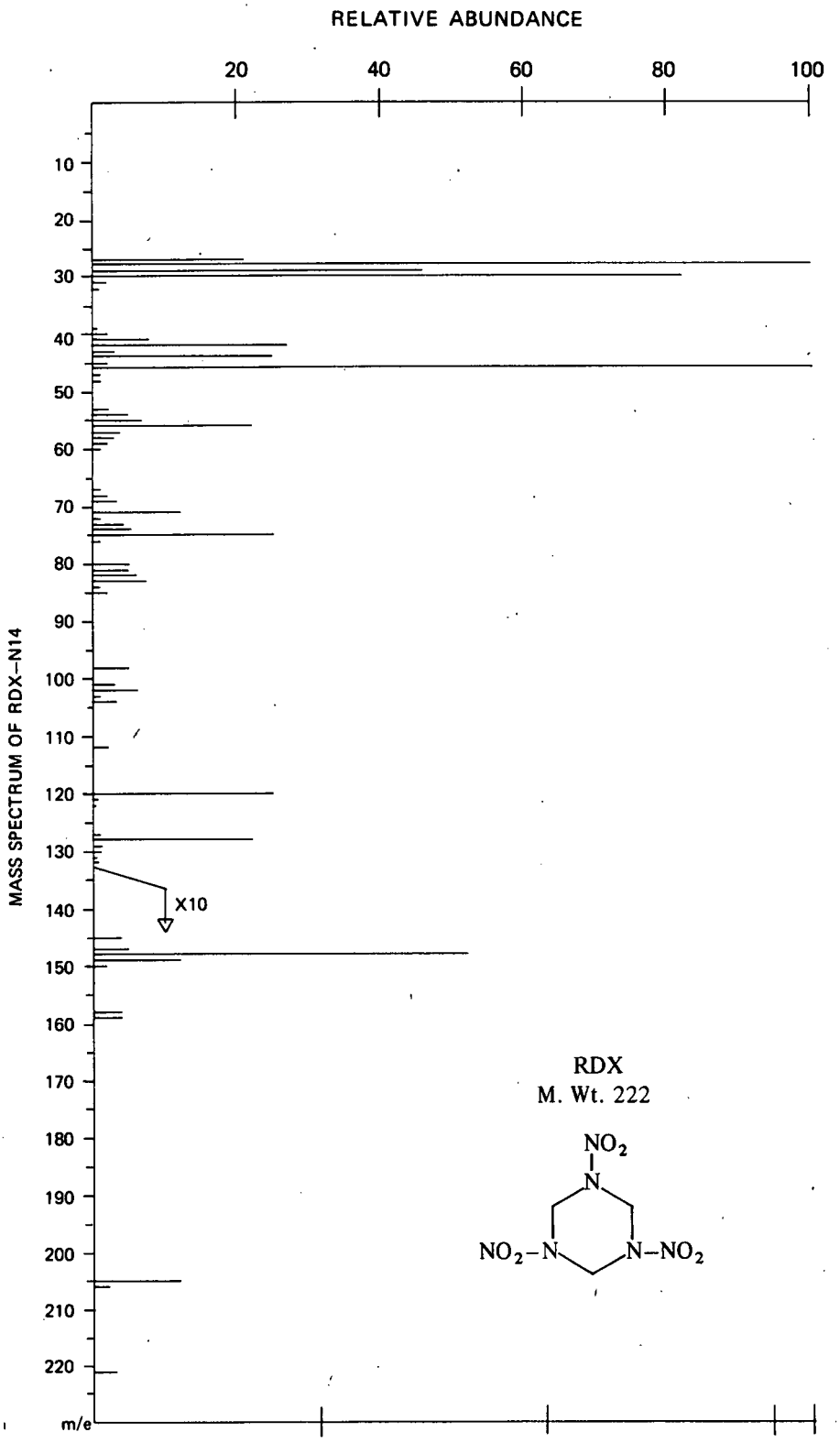

RELATIVE ABUNDANCE
20
40
60
80
100
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
m/e
MASS SPECTRUM OF RDX-N14
X10
RDX
M. Wt. 222
NO2
N
NO2–N
N–NO2

Fig 6

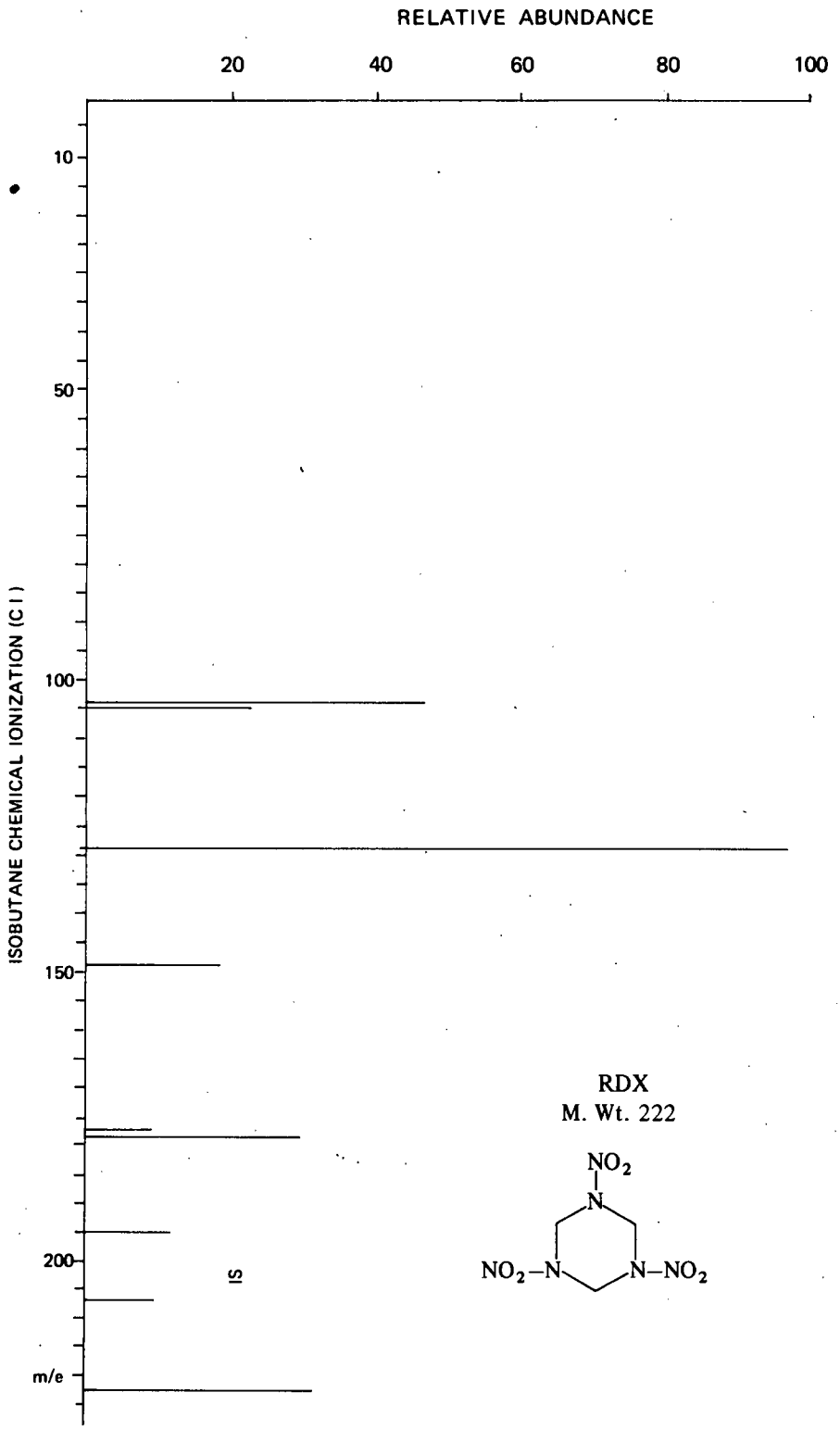

RELATIVE ABUNDANCE
20
40
60
80
100
10
50
100
150
200
m/e
ISOBUTANE CHEMICAL IONIZATION (C I)
IS
RDX
M. Wt. 222
NO2
N
NO2–N
N–NO2

Fig 6a

gas in the ion source. As the name implies, API mass spectrometry depends upon ion-molecule reactions occurring in the reactant gas at atmospheric pressure. The ionization reactions are initiated in a flowing gas stream by electrons from a radioactive ^{63}Ni source. The sample, dissolved in a suitable organic solvent, is injected directly into the source. Both positive ions, eg, M^+ and MH^+, and negative ions, eg, $(M-H)^-$, are formed by a series of complex ion-molecule reactions. The ions are made to exit thru an aperture and subjected to mass analysis. The source, being very small in volume ($0.025cm^3$), is compatible with gas chromatography capillary columns to which it can be interfaced. It is claimed that as little as 150 femtograms of sample can be readily detected. This method has been applied with success to the analysis of drug metabolites and other compounds of biological interest. A substantially similar technique employing a 100 millicurie polonium α-particle source for ionization was reported earlier

(d) *Ion Cluster Mass Spectrometry (ICM):* This relatively new technique (Ref 65) is an outgrowth of studies of ion-dipole clusters in the gas phase and uses hydrated proton species, $^+H(H_2O)_n$ to serve as precursors for ion clusters of a sample molecule, $H^+(H_2O)_n(A)_m$, where A represents the sample molecule. The hydrated protons are formed via ion-molecule reactions with primary ions such as $^+N_2$ and $^+O_2$, which in turn may be generated by several methods including corona discharges. In the presently reported method air or nitrogen containing trace quantities of water vapor and the substance to be analyzed flow into the ion source which is a corona discharge cylinder. The discharge between a coaxial wire (0.08mm, 90% Pt + 10% Rh) and a 12mm I.D. stainless steel cylinder is maintained at 10μa with a 6kv power supply. The ions are extracted from the source chamber by diffusion thru a 35 micron orifice and subsequently mass analyzed. The virtues of this technique are stated to be absence of a spectrum complicated with fragment ions, high mass peaks directly related to the molecular weight, and sensitivity well below the ppm concentration range. An obvious area of application appears to be pollutant analysis

(e) *Fission Fragment Ionization Source (FFI):* Mass spectroscopy is powerless to deal with compounds that are inherently nonvolatile such as polypeptides and polysaccharides. In a very novel adaptation of the familiar means of ionization with a radioactive source, McFarlane and Torgerson used fission fragments from Californium-252. The sample was deposited on a micron thick sheet of nickel foil placed close to a Cf-252 source. The fission fragments passing thru the Ni-foil create localized temperature in the range 20,000–30,000° for about 10^{-11} second. The high temperatures vaporize impurities such as H^+, Na^+ and H^- in both the sample and the nickel. These secondary ions react with heated sample molecules to produce quasimolecular ions. A notable achievement of this technique was to obtain a spectrum showing the quasimolecular ion of vitamin B_{12}. This unique method has a potential for application to unstable expl materials analysis (Ref 76)

(f) *Photoionization:* Ionization of molecules may also be accomplished with ultraviolet radiation of sufficiently short wavelength (Refs 30 & 49). Since ionization potentials of most elements and compounds are in the 10–25 ev range, the wavelengths required are 1200 Å or less. Photoionization sources are similar in principle to electron impact sources in that the neutral gas molecules are "bombarded" with UV light in the ionization chamber at 10^{-4} to 10^{-6} torr. A discharge thru krypton or hydrogen at a few mm pressure provides continuous ultraviolet radiation. The photoionization cross-sections are one or two orders of magnitude less than those for 70 ev electron impact. Electron multiplier detection (see below) is therefore essential. Generally, photoionization yields mass spectra which are similar to those from electron impact at the same energy. Monochromatic UV sources enable very accurate determination of ionization and appearance potentials

(g) *Spark Source:* The vacuum spark ion source is best suited for elemental impurity analysis of solids at very low levels, (Refs 6b, 30 & 64) with the result that it derived a natural stimulus from the growth in semiconductor and reactor materials technology. The technique is known for its high sensitivity (limit of detection, 0.001 ppb) and a complete coverage of elements, and it is the method of choice today for impurity analysis of solids. There are three variations in

the sparking technique, namely, the radio-frequency (rf) spark, vacuum vibrator and pulsed dc arc. The basic principle in all of them is a potential build-up between the electrodes of the material to be analyzed until discharge takes place. The rf spark is the most common one among the three types, and an instrument with this source has recently been employed to analyze impurities in expls (Refs 68 & 75). The technique, however, suffers from the disadvantage of requiring complex and expensive instrumentation including a photoplate recording device

(h) *Field Ionization Source:* Electrical fields of the order of 10^8 volts/an can be caused to produce positive ions from atoms and molecules (Ref 5). The ionization occurs by a strong interaction between the field and the outer electron shell of neutral molecules. These very large electric fields can be obtained by holding very fine metal points at high potentials. In early instruments (Ref 5), for example, the field was set up near a 5 x 10^{-5} cm radius metal tip with a potential of 10kv between the anode and the cathode. An aperture in the cathode was used to extract the ions. When the metal tip is positive, the strong electrostatic field results in the removal of ions of impurities adsorbed on the surface of the metal, or ions may be produced from impinging gas molecules. When the field ionization occurs in the gas phase near the emitter, continuous ion current results. Recently Beckey (Ref 9) replaced the metal tip with a platinum wire of 2.5 microns diameter and 5mm long placed parallel to the cathode diaphragm. An arrangement of this type is shown in Fig 7 which represents both field and electron impact sources within the same source system

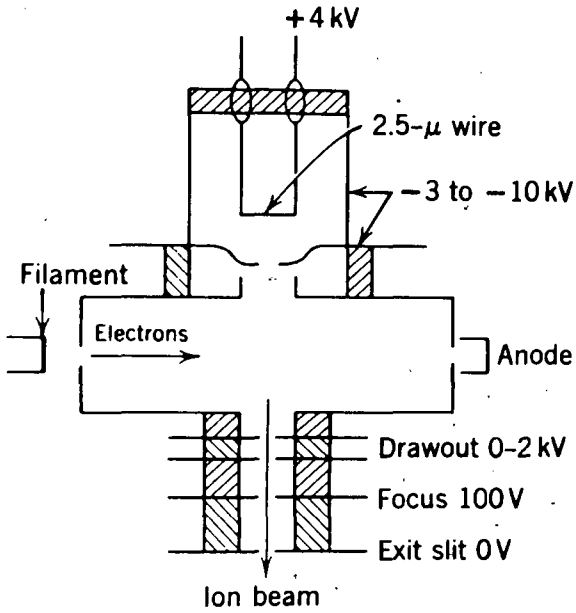


Fig 7 Combined electron impact and field emission source.

Inghram and Gomer showed that the mass spectra of molecules were much simpler using a field ionization source than with an electron bombardment ion source. Mainly parent ions are formed, unlike under electron impact which gives rise to considerable fragmentation. The simplicity of the mass spectra offers obvious applications in analysis of complex organic mixtures and their use is likely to become widespread

(i) *Surface Ionization:* Similar to field ionization in principle is surface ionization (Refs 30 & 55) which employs an an ionization element consisting of a hot ribbon of a metal with a high work function (tungsten) coated with the sample. At sufficiently high temp, emission of a neutral vapor accompanied by positive ions takes place. Some of the atoms and molecules of the sample will have lost an electron to the surface particularly if the compound has a low ionization potential. This approach is suitable only to nonvolatile inorganic salts and it tends to be less destructive to the sample than the spark source. Because it is selective only to the coated material, it produces extremely clean spectra

For the analysis of surfaces there are a group of ion bombardment techniques based on "sputtering" processes described in Ref 30. Since the spectra obtained consists mainly of adsorbed gases and radicals, these techniques are omitted from this discussion

(j) *Negative Ion Mass Spectrometry:* As mentioned earlier, electron impact ionization yields some negative ions along with the positive ions even though their number is smaller by about a factor of 1000. Because of this low yield their use in chemical analysis has been very limited. The low yield of negative ions arises from the fact that with 70 ev electrons the negative ions are formed by the capture of secondary electrons, and that a number of reactions such as

electron capture giving negative ions occur below 20 ev. Also, the negative ion spectra exhibit a strong dependence on source pressures

Despite the above limitations, negative ion analysis offers a possible advantage in electronegative compound analysis and several attempts have been reported (Refs 37, 47 & 48) recently to use high resolution mass spectrometers for negative ion studies using 70 ev electrons and source pressures below 10^{-6} torr. Since many expls are nitro compounds which are strongly electro-negative compounds, negative ion mass spectrometry seems to be an attractive method. A successful technique has been published by Yinon and Boettger (Refs 56a & 57) who modified an Associated Electrical Industries Model MS9 instrument to perform negative ion analysis over a wide range of electron energies and source pressures. They obtained negative ion spectra of nitrobenzene and TNT. Because of its selectivity and sensitivity, this method is well suited to detect TNT in concealed areas such as airline baggage (Ref 56a)

Mass Analyzers

The heart of the mass spectrometer is the mass analyzer, the function of which is to measure the mass-to-charge ratios of ions and provide a means of their identification. This is achieved by a combination of a dispersive action to separate the ions according to their m/e ratios and a focusing action to maximize the resolved ion intensities

All analyzers use one or more of three basic principles: (a) magnetic analysis, (b) electrostatic analysis, and (c) time-of-flight analysis. Magnetic analyzers of single and double focusing types are by far the most common ones currently in use, and will serve to illustrate the methods of analysis. Two other types of analyzers which have gained popularity for analytical applications but are omitted in the following discussion, are the time-of-flight mass

deflected, by means of a magnetic field, thru an angle of 60°, 90°, 120° or 180°. Ions of mass m and charge e when falling thru a potential difference V acquire a kinetic energy, T_{kin}, given by

$$T_{kin} = \tfrac{1}{2}mv^2 = eV \qquad \text{(Eq 1)}$$

In single focusing instruments the beam of accelerated ions enters a magnetic field of constant intensity H, and experiences a force perpendicular to the field. Under the influence of this force the ions assume a radial path in accordance with the relation

$$HeV = \frac{mv^2}{r} \qquad \text{(Eq 2)}$$

where r is radius of curvature of the ion path. Elimination of the velocity terms from Eqs 1 and 2 gives

$$m/e = \frac{H^2r^2}{2V} \qquad \text{(Eq 3)}$$

Only those ions following a path which coincides with the arc of the analyzer tube in the magnetic field will be brought to a focus on the detector slit. To obtain a mass spectrum, either the magnetic field or the accelerating voltage is varied continuously so as to bring ions of varying m/e into focus successively. For proper functioning, the ion source and the path thru which the ions travel to the collector have to be kept under very low pressure of the order of 10^{-7} torr

The effectiveness of mass separation achieved by the analyzer is expressed as resolution R, defined by the equation

$$R = M/\Delta M \qquad \text{(Eq 4)}$$

where M is the mass of the first recorder peak in a doublet of equal size peaks, and ΔM is their difference with the valley between them being equal to 10% of the peak height. The single focusing magnetic analyzer just described permits resolutions in the range 300 to 1000

Double Focusing: For a much higher resolving power usually needed in organic struc-

therefore, be refocused over a wide area, which limits the resolution of the systems employing direction focusing. Considerable increase in resolving power is achieved by elimination of this energy spread in the ion beam before entering the magnetic field. For double focusing the beam is first made to traverse a radial electrostatic field in which it experiences a force given by

$$Ee = \frac{mv^2}{r} \qquad \text{(Eq 5)}$$

For a given electrostatic field, the radius of curvature of the ion depends only on the energy, and ions of the same mass but different velocity will be separated. The ions are then subjected to magnetic analysis to achieve mass separation. With proper design of components a mass spectrometer containing both an electrostatic sector and a magnetic sector can focus with respect to both velocity divergence and energy divergence. The improved double focus enables entrance and exit slits to be narrowed with a corresponding increase in resolving power to as high as ∿50,000. Figs 8 and 9 show two common arrangements used in Nier-Johnson and Mattauch-Herzog double focusing commercial mass spectrometers, respectively. The significance of the high resolution lies, not so much in distinguishing large ions differing by unit mass, but in the ability to distinguish small masses differing by a fraction of a mass unit (see below)

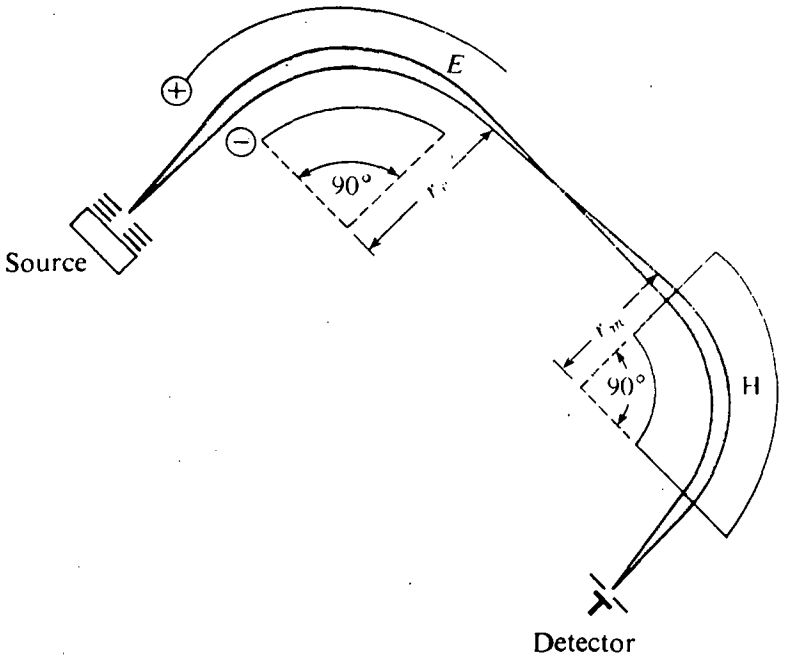
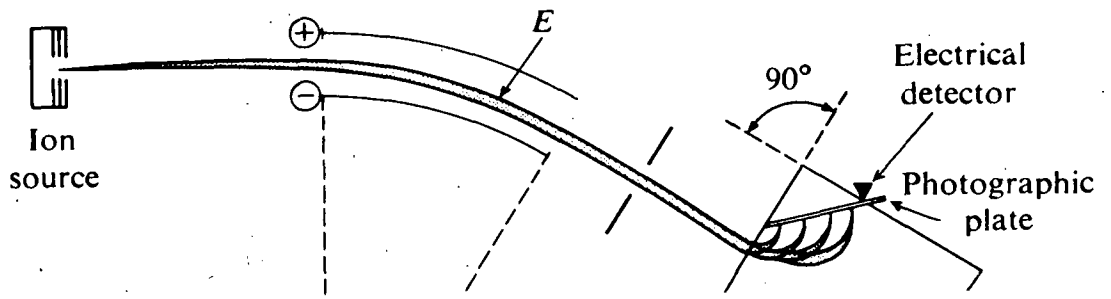


Fig 8 Nier-Johnson double-focusing mass analyzer.

Ion Detection and Recording: The positive ions separated by the analyzer can be detected and measured by either an electrical detector



or by photographic means. The ion currents are usually in the range of 10^{-8} to 10^{-16} amp but occasionally currents as low as 1.6×10^{-19} amp (1 ion/sec) may have to be measured

In the conventional electrical detector, the potential drop produced by the ion current across a resistor is measured after amplification by a direct current amplifier or a vibrating reed electrometer. However, most modern instruments for qualitative organic mass spectrometry use an electron multiplier. This remarkable device gives a current amplification of 10^3 to 10^8 with very low noise and a high speed response. For quant analysis on the other hand, a current amplifier is still preferred because of its superior stability and invariant gain. The output of either of these detectors is recorded on an oscillograph equipped with three to five galvanometers to provide a wide dynamic range

Photographic plates have been used since the early days of mass spectrometry for precision mass measurements. Due to its inherently low sensitivity and requirement of auxiliary equipment for data handling, photographic detection has mostly been replaced by electrical methods. Nevertheless, photographic detection is essential in spark source instruments for the analysis of trace impurities in solids because it is an integrating detector, and furthermore, it is insensitive to the high noise associated with the spark source. Details of various detection methods and equipment are available in a number of books (Refs 30 & 64)

Sample Introduction System: The general method of electron impact ionization of molecules requires a sample to be in the vapor state at a pressure not exceeding 10^{-4} torr. Unless the sample exhibits a slight vapor pressure below its decompn point it cannot be ionized except by special methods like spark source. The function of the sample handling system is, therefore, to vaporize the sample in a heated vacuum system and release it into the ionization source at a controlled rate so as to maintain a low pressure. Gaseous and liq samples are held in a glass or stainless steel reservoir (about 2000ml at 100 microns) served by a vacuum pump and heating oven, and separated from the source by a "gold leak" or a sintered glass leak. While gas samples may easily be expanded into the heated reservoir, liquids are injected thru a silicone rubber diaphragm. Solids, being low in vapor pressure are, however, introduced directly into the source by means of a solid probe. The probe consists of a rod at the end of which is placed a small sample, typically in a glass capillary, and inserted into the ion source thru a vacuum lock

Commercial Instruments: Because of the proliferation of applications of mass spectrometry in organic and analytical chemistry, there are instruments marketed by numerous companies today. Some of the popular ones are the low resolution, single focusing model 21-490 and the high resolution, double focusing models, 21-492 and 21-110 of Du Pont de Nemours Co, and the double focusing model MS-9 of Associated Electrical Industries

Mass Spectra and Chemical Structure: While there are a number of books (Refs 16, 30, 49 & 64) already referred to, which deal with details of the instrumentation and techniques of mass spectrometry, there are several concise introductory texts (Refs 10, 21 & 52) on the interpretation of mass spectra. Still other recent books deal comprehensively with organic structural investigation by mass spectrometry. One of these (Ref 63) discusses fundamentals of ion fragmentation mechanisms, while the others (Refs 7, 15, 20, 28 & 29) describe mass spectra of various classes of organic compounds. In the alloted space for this article methods of interpretation of mass spectra and structural identification can not be described in depth. An attempt is, therefore, made only to briefly outline the procedures used in this interpretation

The first step in the application of mass spectra is obviously to obtain a list of fragment ions formed by electron bombardment of the molecule under study and their relative amounts by appropriate techniques. The goal from this point will necessarily be to relate the positive ions to the molecular structure whether it be an unknown structure to be identified, or a known structure of which a knowledge of fragmentation is desired. The fragment ions observed indicate the pieces of which the molecule is composed

Elemental Composition of Ions: After recognition of the major ions in the spectrum the next step will be to determine their elemental com-

position, partly by "informed" guessing, and partly with the help of isotopic satellite peaks and a calculation of "ring + double bonds". The natural abundance of heavy isotopes of elements, eg, ^{13}C, ^{15}N and ^{37}Cl give associated peaks 1 and 2 amu higher than the normal masses. As an example, in the mass spectrum of naphthalene ($C_{10}H_8$) the 1.1% natural abundance of ^{13}C gives rise to a peak at m/e 129 approximately 11% (1.1 x 10) in intensity compared to m/e 128. The "ring + double bonds" calculation is based on the fact that the total number of rings and double bonds in a molecule of the formula $C_xH_yN_zO_n$ will be equal to $x-\frac{1}{2}y+\frac{1}{2}z+1$ because of the valences of the elements involved. In the example of naphthalene this value will be 7 which is equal to 2(rings)+5(double bonds). Presence of several elements can complicate these basic rules, but logical extension of these rules and consideration of several ions in the spectrum will resolve the difficulties (see Ref 63 for details).

The Molecular Ion: The first important piece of information to be derived from the mass spectrum about the compound under study is the molecular weight, and to obtain this the peak corresponding to the molecular ion (M^+) must be recognized. For a number of compounds however, the M^+ is not sufficiently stable to be present in appreciable abundance. The peak at highest m/e is therefore, not necessarily the M^+. Secondly, the molecular ion usually gives several isotopic peaks (P+1, P+2, etc), and the ion of literally the highest mass in the spectrum is not the most abundant species. Thirdly, the peak of highest mass may be an artifact caused by an impurity, spectrometer background or an ion-molecule reaction. Further purification, background scans and operation of the instrument at lower sample pressure, respectively, can eliminate this uncertainty. After these initial checks, other criteria (Ref 63) which are "necessary but not sufficient"must be met: a) it must be the ion of highest mass, b) it must be an odd-electron ion (see below), and c) it must be capable of yielding the important ions in the high mass region of the spectrum thru the loss of logical neutral species (see below). If the ion fails any of these tests, it cannot be the molecular ion; if it passes the tests, it is still possible that it is not the molecular ion. Then, one may resort to obtaining the chemical ionization or field ionization spectrum

Odd Electron Ions: Ionization of a molecule involves loss of an electron and, therefore, the molecular ion is a radical species. Such an ion with an unpaired electron is called *odd electron ion* denoted by the symbol, ‡. The molecule ion must be an odd electron ion appearing at an even mass unless the molecule contains an odd number of nitrogen atoms. When the odd electron ion decomposes by the loss of a neutral radical species, the resulting ion would then be an even-electron ion. This distinction leads to the important concept of electron "counting" in mass spectral interpretation. This electron "bookkeeping" is very helpful, since the majority of fragmentation reactions are understood in terms of electron shifts governed by the familiar rules of charge stabilization by induction and resonance

Neutral Loss: Only a limited number of neutral fragments of low mass which are eliminated in decompositions of molecular ions. Examples are H, H_2, CH_3 and OH. Therefore, the presence of a major ion below the molecular ion at an improbable interval (eg, loss of 4 to 14, 21 to 25 amu) will indicate that the latter is not the molecular ion

Postulation of Molecular Structures: The postulation of the structure of an unknown molecule is based on several major kinds of general structural information available in the mass spectrum. McLafferty (Ref 63) suggests the following systematic approach:

(a) *General appearance of the spectrum:* The mass and relative abundance of the molecular ion indicates the size and general stability of the molecule. The number of abundant ions and their distribution in the mass scale are indicative of the type of molecule and the functional groups present. Examples are spectra of aromatic compounds showing low fragmentation and spectra of alkanes with characteristic pattern of even electron ions at 14 amu intervals

(b) *Low Mass Ion Series:* Low mass ions indicate general structural features: 1) Series separated by CH_2 groups – 15, 29, 43, 57,etc; 2) Homologous series from substituted alkyl group, -amines, 30, 44, 58 . . . ; alcohols, 31, 45, 59, . . . ; ketones, 43, 57, 71, . . . ; chloroalkanes, 49, 63, 77, . . . ; and 3) aromatic ion series, 39, 50, 51, 52, 63, 64, 65, 75, 76, 77

(c) *Small Neutral Loss:* Fragment ions of a highest mass are the result of the loss of small neutral species which allow simple and positive assignments. For example, the ions at $(M-1)^+$, $(M-15)^+$, $(M-18)^+$ and $(M-20)^+$ almost always represent the loss of H, CH_3, H_2O and HF, respectively, from the molecular ion

(d) *Characteristic Ions:* The mass of a large ion represents structural information about the ionic species as well as the complementary neutral portion of the molecule. For many particular mass values there are only a few characteristic structural groupings that commonly give rise to the corresponding peaks in the mass spectra. Examples are m/e 30 from amines, m/e 74 from methyl alkanoates, m/e 91 from benzyl substituted compounds, m/e $(M-27)^+$ from aromatic ethyl esters and m/e 149 from phthalates

(e) *Probable Structure:* All the information and postulations gathered above must now be utilized to deduce the most logical structure. One should then predict the spectrum from the postulated structure and compare with the unknown spectrum. The elimination of all but one possibility for the molecular structure of course does not prove that this one is correct unless a reference spectrum of this compound can be obtained

Comprehensive correlation tables of various ion series, characteristic fragment ion and neutral fragments from different classes of compounds are available in various sources (Refs 10, 11 & 63). A number of general rules in understanding fragmentation mechanisms and for prediction of prominent peaks in a spectrum are summarized in Refs 10 & 63

High Resolution Technique: As indicated earlier, double focusing mass spectrometers are utilized to achieve a high resolving power. The most common application of the high resolving power is the determination of precise empirical formulas of molecular and fragment ions from an exact mass measurement. The basis of this method is that all atoms have non-integral masses on a C = 12.0000 atomic standard, as shown by the examples in Table 2 (Ref 56b). Using these values it can be seen that several combinations of atoms having the same integral mass show a significant difference in their non-integral masses. Beynon (Ref 6a) was one of the first to realize that measurement of the mass of the ion with sufficient accuracy would give an unequivocal identification of its elemental composition. Thus the ion $C_7H_8^+$, m = 92.06260 can be distinguished from $C_7H_6D^+$, m = 92.06105 if a resolving power of 60,000 is used. Fig 10 illustrates a well resolved multiplet at m/e 260 obtained with a resolving power of ~20,000 (Ref 20)

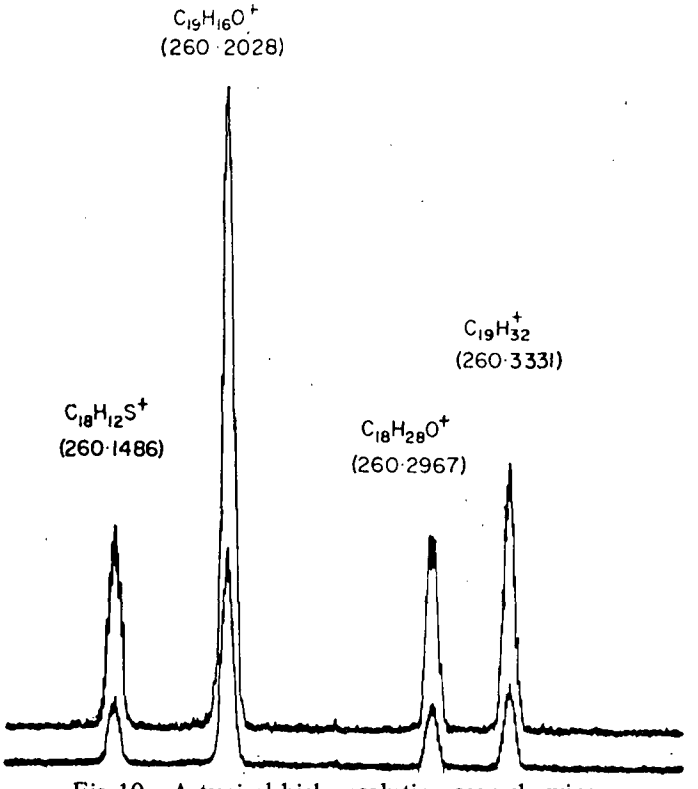


Fig 10 A typical high resolution scan showing the multiplet at mass 260

Another, more reliable and extensively used technique to obtain the exact mass is the "peak matching" method (Refs 7 & 63). Here, instead of slowly varying the magnetic field, a constant magnetic field is used while the accelerating voltage is rapidly changed to bring, alternately, a reference ion and an unknown ion into focus at the collector slit. Eq 3 shows that the ratio of the voltages under these conditions leads to the ratio of the masses. Thus, the ratio required to superimpose the two peaks on the oscilloscope is measured, and the mass accuracy (2 to 5ppm) attained with this method is 10 to 100 times the resolving power of the instrument (Ref 63)

Table 2 Exact Nuclidic Masses

Isotope	Atomic weight	Isotope	Atomic weight
^{1}H	1.00782522	^{19}F	18.9984046
^{2}H	2.01410222	^{28}Si	27.9769286
^{12}C	12.00000000	^{31}P	30.9737633
^{13}C	13.00335508	^{32}S	31.9720728
^{14}N	14.00307440	^{35}Cl	34.96885359
^{16}O	15.99491502	^{79}Br	78.9183320
^{18}O	17.99915996	^{127}I	126.9044755

Computer Techniques: McLafferty (Ref 63) has pointed out that the usefulness of elemental composition information increases exponentially with increasing mass, since the number of elemental combinations with the same integral mass becomes larger. There are compilations of exact masses and elemental compositions available (Refs 12a, 13 & 18a). Spectral interpretation will be simplified in important ways if elemental compositions of all but the smallest peaks are determined. Deriving the elemental compositions of several peaks in a spectrum is extremely laborious and time-consuming. However, with the availability of digital computers such tasks are readily performed. A modern data acquisition and reduction system with a dedicated on-line computer can determine peak centroids and areas for all peaks, locate reference peaks, interpolate between them to determine the exact masses of the unknown peaks, and find within minutes elemental compositions of all ions in a spectrum (Refs 28b & 28c)

In recent years a variety of computer systems and programs have been developed to process and present data in a readily interpretable form (Refs 18b, 28b, 28c, 56c & 77). Detailed accounts of these computer applications are available in the literature (Refs 18b, 28b, 28c, 49, 52, 56c, 63, 64 & 77). Available programs include those which can perform spectral interpretation at various levels (Refs 28a, 39a, 49a, 52a, 52b, 52c, 56d & 65a) and those designed for matching an unknown spectrum against a file of reference spectra and retrieval of closely similar spectra (Ref 78). Even if the unknown spectrum is not on file, valuable structural information can be gained from the located spectra

Combined Gas Chromatography and Mass Spectrometry: Combining a gas chromatograph (GC) with mass spectrometer (MS) has given rise to one of the most powerful tools in instrumental analysis today. Gas chromatography has long been known to be an excellent means to separate the constituents of a mixture, while the mass spectrometer is unique in its specificity, sensitivity and content of structural information. A tandem arrangement of the devices (Ref 28d), therefore, had presented an obvious attraction and a challenge to the chemist. The eluted fractions from a GC may be collected by a cold trap or an adsorbent trap and later introduced into the inlet system of a mass spectrometer for analysis. A logical improvement on this is the direct coupling of the two instruments using an "interface" designed to remove most of the

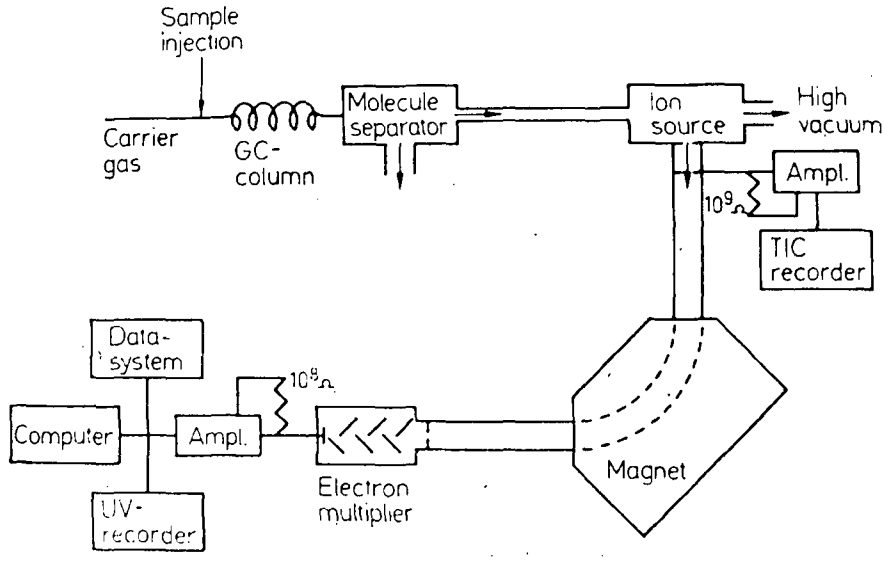


Fig 11 A general block diagram of GC-MS instrument

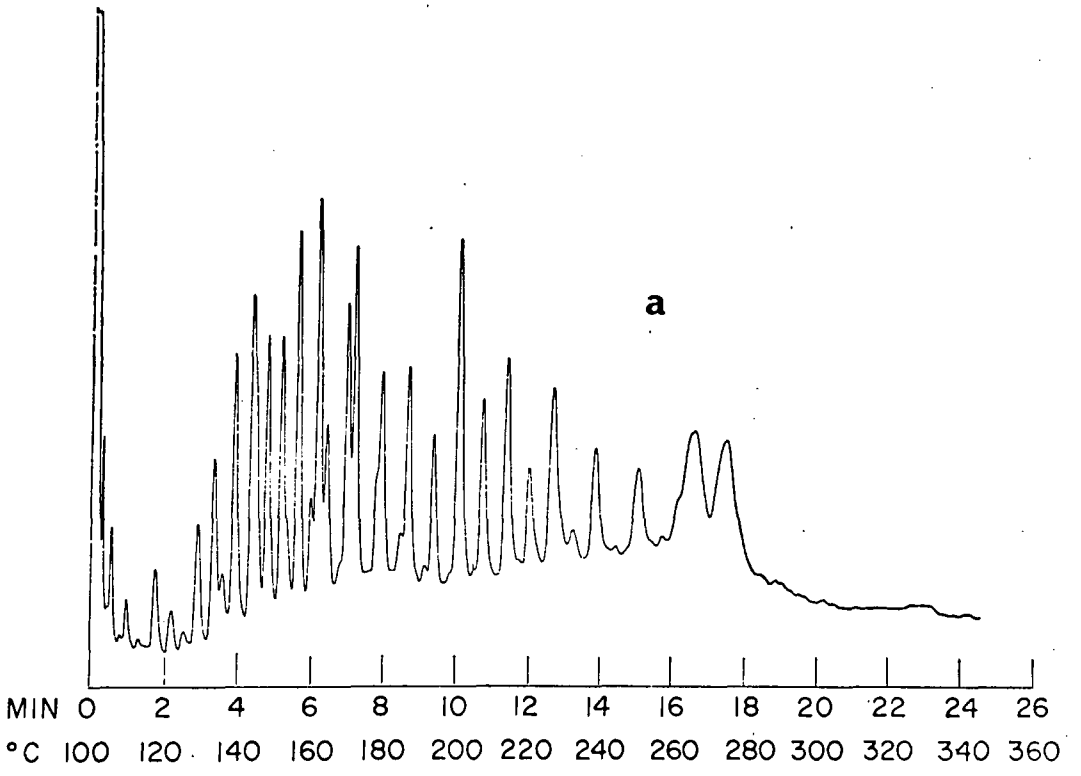


Fig 12 Flame ionization detector chromatogram of methyl esters of a naturally occurring acidic extract

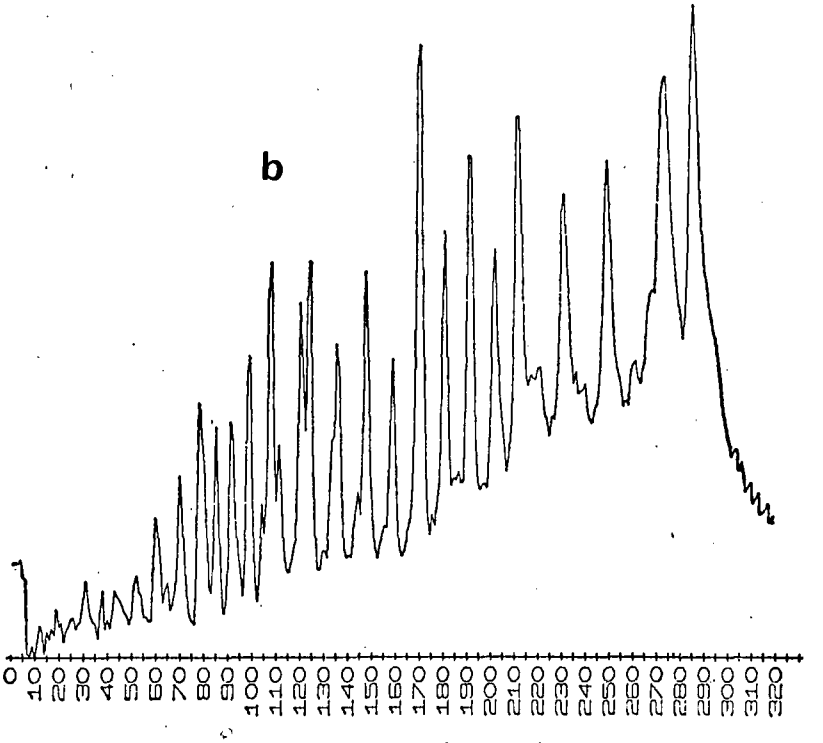


Fig 12a Plot of total ionization (ordinate) vs mass spectrum index number corresponding to chromatogram (a) above

carrier gas and enrich the sample (Refs 30, 49 & 64). A stream splitter at the exit end of the column diverts a portion of effluent to a normal GC detector and the rest passes thru an enrichment device of which there are several types (Refs 30, 49 & 64). As each GC peak emerges a quick mass spectral scan can be taken for its identification. Unresolved or poorly resolved peaks are, however, troublesome to deal with by manual scanning. Digital computers again provide an obvious answer to this problem (Ref 28d). In fact, digital computers have become indispensable in handling complex chromatograms comprising numerous peaks encountered commonly in biochemical, clinical, ecological and forensic samples which contain a formidable wealth of information (Refs 30, 49 & 64). The modern GCMS system, therefore, almost always employs a fast, automatic, repetitive scanning of mass spectrometer in combination with an online computer and data reduction system. Fig 11 shows a block diagram of GCMS system (Ref 49). With this system literally hundreds of peaks that might emerge from a GC in a short time can be efficiently scanned by the mass spectrometer, the scan information stored and presented later in three basic forms: (Refs 49 & 64): a) a plot of total ion current with time which represents the GC profile; b) plot a "mass chromatogram" which traces a few selected ion masses running thru the chromatogram, and c) print partial or complete mass spectrum from a selected scan (Refs 49 & 64). Figs 12 & 12a(Ref 28d) illustrate a typical flame ionization detector chromatogram and the corresponding total ion current trace reconstructed by computer. Detailed descriptions of GCMS data systems and their applications are available in a number of reviews (Refs 45a, 65b & 79) and books (Refs 30, 49 & 64)

Compilations of Reference Spectra: There are several compilations of reference mass spectra available of which the oldest is the American Petroleum Institute (Ref 82) collection of spectra obtained mostly on the older type instruments. Recent collections index spectra variously, eg, under reference number (Ref 19), molecular weight (Refs 12 & 19), molecular formula (Ref 19), fragment ion values (Ref 19), and base peak (Refs 12 & 19). A quarterly journal, "Archives of Mass Spectral Data" (Ref 32) is devoted to publishing new spectra, and in addition there are a few private collections of uncertified spectra (Refs 80, 81 & 83). In structural elucidation work, the eight largest peaks in a mass spectrum need to be used for reference purpose. The "Eight Peak Index Mass Spectra" (Refs 12, 19, 32 & 43) are of this type. The most recent exhaustive collection appears to be "Registry of Mass Spectral Data" (Ref 74) consisting of some 19,000 bar-graph spectra, arranged according to the exact molecular weight and structure of compound

Mass Spectral Studies of Explosives and Related Compounds: The earliest mass spectral investigations of interest to expls and proplnts were by Collin (Refs 2, 3 & 4) who studied the major ions, dissociation processes and appearance potentials of a series of nitrite esters, nitroparaffins and nitrosamines. Mass spectra of many more nitro compounds which include nitro alkanes, nitrate esters, and nitrite esters were next reported by Boschan and Smith (Ref 6). Mechanistic studies of the fragmentation of nitro alkanes (Refs 17 & 18), nitrate esters (Ref 33) and nitro aromatic compounds (Ref 14) were also made and later summarized in Ref 15, ch 16. Contrasting fragmentation pathways of mono and polynitro aliphatic compounds in the series – $C(NO_2)_x(CH_3)_{4-x}$, x = 4 to 0 and $C_2(NO_2)_x(CH_3)_{6-x}$, x = 6, 4, 2 – were investigated as a function of x by Larkin et al (Ref 38). In another series of papers by Meyerson and coworkers (Refs 24, 26, 53 & 54), electron impact fragmentation of isomeric nitrotoluenes, nitro biphenyls and trinitrobenzene were studied using high resolution, metastable scanning and variable ionizing voltage techniques

Mass spectra of the important explosives RDX, HMX, TNT, TNB and Tetryl were first briefly reported by Meyer (Ref 34) and later investigated in greater detail with high resolution and ^{15}N labeling techniques by Bulusu et al (Ref 45). Mass spectrometric studies of the photodecomposition of ^{15}N labeled dimethylnitramine (Ref 56) and the thermal decomposition of HMX and RDX (Refs 27 & 31) illustrate the application of these techniques to studies of reaction mechanism and bond dissociation processes. Nitroguanidines have only recently been investigated by Beynon (Ref 35)

Analytical applications: Mass spectrometry has been applied to a variety of analytical problems related to expls, some of which have already been mentioned. Identification of the principal constituents of expls has been attempted from electron impact cracking patterns (Refs 34, 50 & 58), as well as chemical ionization spectra (Refs 69, 70 & 71). Such methods necessarily include vapor species analysis and are directed to detection of buried mines (Refs 50, 58, 61, 62 & 67) and forensic applications (Refs 69, 70 & 71). The vapor species may include unchanged explosives (Ref 73) themselves or products of thermal decomposition and explosions. Kinetic studies (Refs 25 & 39) of the thermal decomposition of HMX and RDX were aided by quantitative mass spectrometric analysis. Mass spectrometry was also applied to the analysis of the decompn gases from delay powders, M2, M15 and M17 proplnts (Ref 5a). More recently, an application of a gas chromatography/mass spectrometry method to the analysis of exhaust gases from the XM-19 rifle was described (Ref 59). Use of spark source mass spectrometry to trace elemental analysis of expls (Refs 68 & 75) has already been referred to

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Masurites. Coal mining, low freezing expls, manufd from 1903–11 by Masurite Explosives Co of Youngstown, Ohio. They consisted essentially of Amm nitrate (up to 93%) and waste oils from paint factories, together with certain chemicals to sensitize the mixt

Refs: 1) W.H. Blumenstein, CA **5**, 2949 (1911) 2) Van Gelder & Schlatter (1927), 702

Matagnites. Expls fabricated in the village of Matagne-la-Grande, Belg, from which the name was derived: (1) *Blasting Matagnite* or *Detonating Matagnite* contd NC to which was added NG and/or NB in such quantities that no exudation took place; (2) *Gelatin Matagnite* contd the above ingredients plus sawdust and inorganic nitrates

Ref: Daniel (1902), 419

Mataziette. Swiss Dynamite invented about 1877 contg NG 40% plus sand, ochre, powd coal and resinous materials (Ref 1). Ref 2 describes it as a mixt of NG, sand and chalk

Refs: 1) Daniel (1902), 419 2) CondChem-Dict (1942), 290

Match. In lay language a match may be defined as *"an instantaneous fire producer consisting of a short stem, rod, or tube, tipped at one or both ends with a compn or paste, inflammable by friction, or when brought into contact with a chemical reag"*. The term is also applied in military and mining jargon to *"a cord or thread impregnated with combustible material capable of burning along its entire length, in order to convey fire from one point to another, not ignitable by friction"* (Ref 3)

The history and development of commercial and military matches are covered in Refs 1, 2, 3,

4 and 8. Present friction type matches may be divided into "non-safety", or strike anywhere matches, and "safety" matches, which are supposed to ignite only when rubbed on a prepared surface

A safety match head is, essentially, K chlorate in a matrix of animal glue. The striking strip is composed of red P in a similar binder. Use of additives and adjustments in the mfg process results in a safety match which ignites easily when rubbed on the striking surface. The friction and contact of K chlorate crystals with red P results in the ignition of the match head which, in turn, causes the ignition of paraffin impregnated in the match splint

Typical safety match head and striker compns are given in Tables 1 & 2 (Ref 8)

Table 1

Commercial Safety Match Head Composition, %

Animal (Hide) Glue	9–11
Extender (Starch, Dextrin)	2–3
Sulfur (Rosin)	3–5
Potassium Chlorate	45–55
Neutralizer (Zinc Oxide, Calcium Carbonate)	3
Infusorial (Diatomaceous) Earth	5–6
Other Siliceous Filler	15–32
Burning Rate Catalyst (Potassium Dichromate or Lead Thiosulfate)	to suit
Water-Soluble Dye	to suit

Table 2

Safety Match Striker Compositions, %

Animal Glue	–	16	9.3
Dextrin	20	–	7.0
Red Phosphorus	50	50	37.2
Antimony Sulfide	–	–	33.5
Iron Oxide (Fe_3O_4)	–	–	7.0
Manganese Dioxide	–	–	3.4
Calcium Carbonate	–	5	2.0
Powdered Glass	–	25	0.6
Sand	30	–	–
Carbon Black	–	4	–

The large *strike-anywhere* (SAW) or *kitchen* match has a small, easily ignitable tip composed of phosphorus sesquisulfide affixed to a larger bulb composed for a rather insensitive modified, safety match head compn. Typical formulations are given in Table 3 (Ref 8)

Table 3

SAW ("Strike-Anywhere") Match Tip and Base Compositions, %

	Tip	Base
Animal Glue	11	12
Extender (Starch)	4	5
Paraffin	–	2
Potassium Chlorate	32	37
Phosphorus Sesquisulfide (P_4S_3)	10	3
Sulfur	–	6
Rosin	4	6
Dammar Gum	–	3
Infusorial Earth	–	3
Powdered Glass & Other Filler	33	21.5
Potassium Dichromate	–	0.5
Zinc Oxide	6	1

A variation of the regular match is the *pull-match,* a version of which is the *M1 Friction-Type Fuze Lighter* (Ref 5), in which the traditional role of striker and match is reversed. The match mixt is located in a metal cup, and a length of wire, corrugated and covered with striking mixt near the end, is threaded thru a hole in the cup, with a handle for pulling the wire thru it. The match cup is enclosed in a length of stiff paper tubing for insertion of a delay fuse, held in a fixed position in the tube by a metal ferrule with sharp protrusions. On removal of the wire with a fast pull, the device reliably produces a spit of flame within the tube and transfer of the fire to the fuse train

Quickmatch, a type of BlkPdr fuse is used for conveying fire to the combustible portion of pyrotechnic devices. It was formerly used for igniting charges in both military and civilian blasting. A *match* is distinguished from a *fuse* in that it conveys fire nearly instantaneously, whereas a fuze conveys the fire at a comparatively slow, reproducible rate. *Quickmatch* (Ref 7) consists of cotton strands impregnated with BlkPdr mixed with starch paste. *Mealed* (Class A) quickmatch contains additional fine BlkPdr as a coating, which increases the burning rate. Of the three types described in the Military Specification (Ref 7), Type III is intertwined with annealed copper wire. Their burning

rates lie between 8–17sec/ft

Electric matches (Ref 6) are small resin-impregnated paper strips on which conductive brass strips are laminated with a wire loop affixed over one end. Two layers of K chlorate, Pb mononitro resorcinate, and NC priming material are followed by a chlorate, charcoal, lacquer mixt for flame and fire transfer, and protective coatings of clear lacquer form a bulb resembling a book-match tip. Ignition is achieved by a current of 500mA for a minimum of 50msec. This is one example of a series of electric matches which are manufd to various current input requirements with different chemical compns

Written by: **S. M. KAYE**

Refs: 1) Barnett (1919), 162–167 2) Reilly (1938), 94–159 3) Thorpe **7**, 528–39 (1946) 4) Kirk & Othmer **8**, 819–24 (1952) 5) Anon, "Ground Chemical Munitions", **TM 3-300** (1956) 6) Atlas Match M-100 etc, Data Sheets, Wilmington, Del (1957) 7) Anon, "Quick-match", **MIL-Q-378B** (Aug 1963) 8) Ellern (1968), 64–83 & 355–57

Matchlock. A small arm invented toward the end of the 14th century which represented the first attempt at automatic ignition. The device consisted of a long hammer, pivoted in the gun stock, which held a piece of slow match. When the trigger was pulled, it pressed the burning match down until it touched the powd in the pan, and thus fired the weapon. A serious defect in the matchlock design was the vulnerability of the match to moisture, resulting in non-function under rainy conditions. The matchlock was superseded by the flintlock at the end of the 17th century

Ref: Balleison (1945), 3

Materials Handling in Ammunition Plants. Materials handling applications can be made wherever materials are transported, positioned, or stored, the most extensive use being in manufg. Manufg involves elements of motion, time, quantity, and space: motion to transport materials between work stations, time to process and handle materials, quantity to establish work schedules and material flow rates, and space to house materials, machines, and employees. The optimum manufg system is one designed to achieve the best possible integration of these elements relative to the desired goals of the manufacturer (Ref 4)

Materials handling equipment should be selected as part of an integrated manufg-systems design. Factors that enter into equipment selection include (1) what material is to be handled, (2) where the material is to be moved, positioned, or stored, (3) when the material is to be moved in the manufg cycle, (4) how reliable the equipment types to be employed are, (5) whether projected mechanization costs can be justified, and (6) whether the handling system design will permit the types of controls desired by management (Ref 5, p 1054-R)

The productive system may incorporate several different types of materials handling equipment. One basis for classification is by use; eg, transporting equipment, positioning equipment, and storage equipment. Then there are subdivisions, eg, transporting equipment may follow a fixed path or permit movement within an area; positioning equipment may or may not include small storage capacities, and storage equipment may be either fixed or portable. Transporting equipment includes conveyors, monorails, hoists and cranes, industrial trucks, and air-float platforms. Highway trucks, ships, rail cars, and aircraft are excluded. Conveyors, monorails, and certain types of hoists and cranes provide fixed-path movement of materials; other crane types, industrial trucks, and air-float platforms provide for area coverage. Positioning equipment includes parts-handling equipment that is employed at individual work stations. The goals in employing such mechanized loading and unloading equipment are to increase the rate of production, provide greater operator safety, improve product quality, improve cutting-tool life on machine tools, ease the handling of hot, fragile, or clean parts, and reduce operator fatigue. The major types of positioners are levelers, strip and coil feeds, bar transfers, mechanical transfer arms, dial feeds, magazines and parts selectors. Storage equipment includes all types of containers, racks and accessories used to store material (Ref 5, pp 1055–58)

Materials handling in ammo plants, of course, involves unique considerations and constraints relative to personnel safety and the preservation of facilities. These are reflected in limita-

tions on the quantities of material handled in one site or area, scrupulous attention to the elimination of such potential sources of material initiation as impact, friction, electrostatic charge accumulation, etc, extensive use of remotely controlled operations wherever feasible, adequate shielding or barricading of hazardous processing procedures and the structures housing them, and storage areas so spaced that initiation of one will not result in a chain reaction

Modern materials handling techniques in US Army Ammunition Plants are detailed in the Refs given under Modernization Engineering Project for US Army Ammunition Plants in this Vol. A study of materials handling at the Louisiana Army Ammunition Plant, carried out under the above project, is reported in Ref 6. The principal objectives of this study were to develop recommendations to modernize materials handling in a cost effective and safe manner. It was reported that efficient materials handling at **LAP** (load, assembly and pack) plants was constrained by a number of factors that presently exist. These factors include old facilities that do not have adequate access and docks. At many production lines there is not adequate on-line storage, so materials must be double handled by being stored initially in off-line warehouses. The present inventory control system also encourages double handling, as do the warranties that are provided by component vendors. Safety rules also limit the storage of efficient quantities of expls. Recommendations made included a high-rise, automated, random access warehouse for inert materials; a centralized magazine facility for receiving, pre-processing and the temporary storage of bulk expls; barricaded holding yards for the temporary storage of containerized finished ammo; an automated rail transportation system; magazine modernization; new on-line warehouses; new conveyors; and a new manual tow tractor system

Other material handling studies at the Kansas, Lone Star and Longhorn Army Ammunition Plants are detailed in Refs 2, 3, 7 & 8

Written by: **S. M. KAYE**

Refs: 1) M.P. Aleksandrow, "Development of Mechanical Handling Equipment in the USSR", Army Foreign Science and Technology Center Rept No **FSTC-HT-23-453-68** (1969), AD-852173L 2) David C. Malm, "Modernization of Materials Handling in LAP Plants. Kansas Army Ammunition Plant", Contract DAAA21-71-C-0298, Booz-Allen Applied Research Inc, Bethesda, Md (1971), AD-888037L 3) Ibid, "Modernization of Materials Handling in LAP Plants. Lone Star Army Ammunition Plant" (1971), AD-888930L 4) J.M. Apple, "Material Handling Systems Design", The Ronald Press, NY (1972), p 4 5) Encycl Britannica **14** (1973), pp 1054-R & 1055–58 6) Anon, "Modernization of Materials Handling in LAP Plants. Phase II. Total Plant Study of Louisiana AAP", Contract DAAA21-74-C-0210, Industrial Technological Associates, Inc, Bethesda, Md (1974), AD-B001023L 7) Ibid, "Modernization of Materials Handling in LAP Plants. Phase II. Total Plant Study of Lone Star AAP" (1974), AD-B001022L 8) Ibid, "Modernization of Materials Hnadling in LAP Plants. Phase II. Total Plant Study of Longhorn AAP" (1974), AD-B001021L

Materials of Construction in Ammunition Plants. Over the last 60 years criteria and methods based upon results of catastrophic events have been used for the design of expl facilities. The criteria and methods did not include a detailed or reliable quantitative basis for assessing the degree of protection afforded by the protective facility. Recently, extensive research and development programs have been undertaken to establish procedures which permit a more sound and scientifically based approach to current and future design requirements (Refs 1 to 9)

Modern methods for the manuf and storage of expl materials, which include many exotic chemicals, fuels, and propInts, allow less space for a given quantity of expl material than previously permitted. Such concns of expls increase the possibility of the propagation of accidental explosions (one accidental explosion causing the detonation of other expl materials). It was evident that a requirement for more accurate design techniques had become essential. Ref 3 describes a rational design method to provide the required structural protection. It presents methods of design for protective construction used in facilities for the manuf, maintenance, modification, inspection, and storage of expl

materials. Its primary objectives are to establish design procedures and construction techniques whereby propagation of explosions (from one bldg or part of a bldg to another), or mass detonations will be prevented and protection for personnel and valuable equipment provided. Secondary objectives include (1) to establish blast load parameters required for design of protective structures, (2) to provide methods for calculating the dynamic response of reinforced concrete and other materials, (3) to establish construction criteria necessary to afford the required strength to resist the applied blast loads, and (4) to establish guide lines for siting expl facilities to obtain max cost effectiveness in both site planning and structural arrangement, providing closures, and preventing damage to interior portions of structures caused by structural motion and shock

The design method described in Ref 3 accounts for the close-in effects of a detonation, including associated high press and nonuniformity of the blast loading on protective structures or barriers. The dynamic response of structures can be calculated, and qualitative and quantitative values are developed to provide the properties necessary to supply the required strength and resiliance specified by the design. Although this Ref concentrates on the procedures and techniques required for the design of reinforced concrete protective structures, this does not imply that concrete is the only useful material for protective construction

In this connection, mention must be made of suppressive panels as an alternative to the conventional laced concrete wall (Fig 1) to protect against the effects of accidental explosions. Suppressive structures are comparatively new and, hence, represent an infant technology as contrasted with concrete barriers. These structures use steel panels made of several layers of louvered and perforated plates, and of angle irons or zee bars. The venting that results from this construction is designed to allow controlled release of blast effects from an explosion within the structure, thereby reducing the resulting external overpressure. At the same time, complete containment of fragments and fire brands, and significant reduction of the fireball can be achieved. Successful tests, both sub-scale and full scale, have been conducted with suppressive

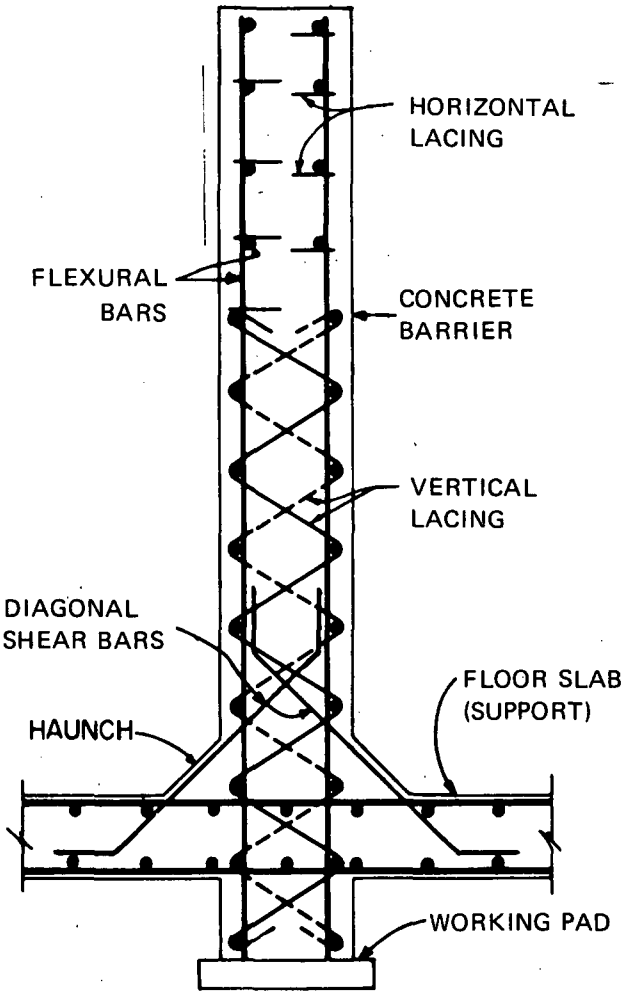


Fig 1 Typical Laced Concrete Wall

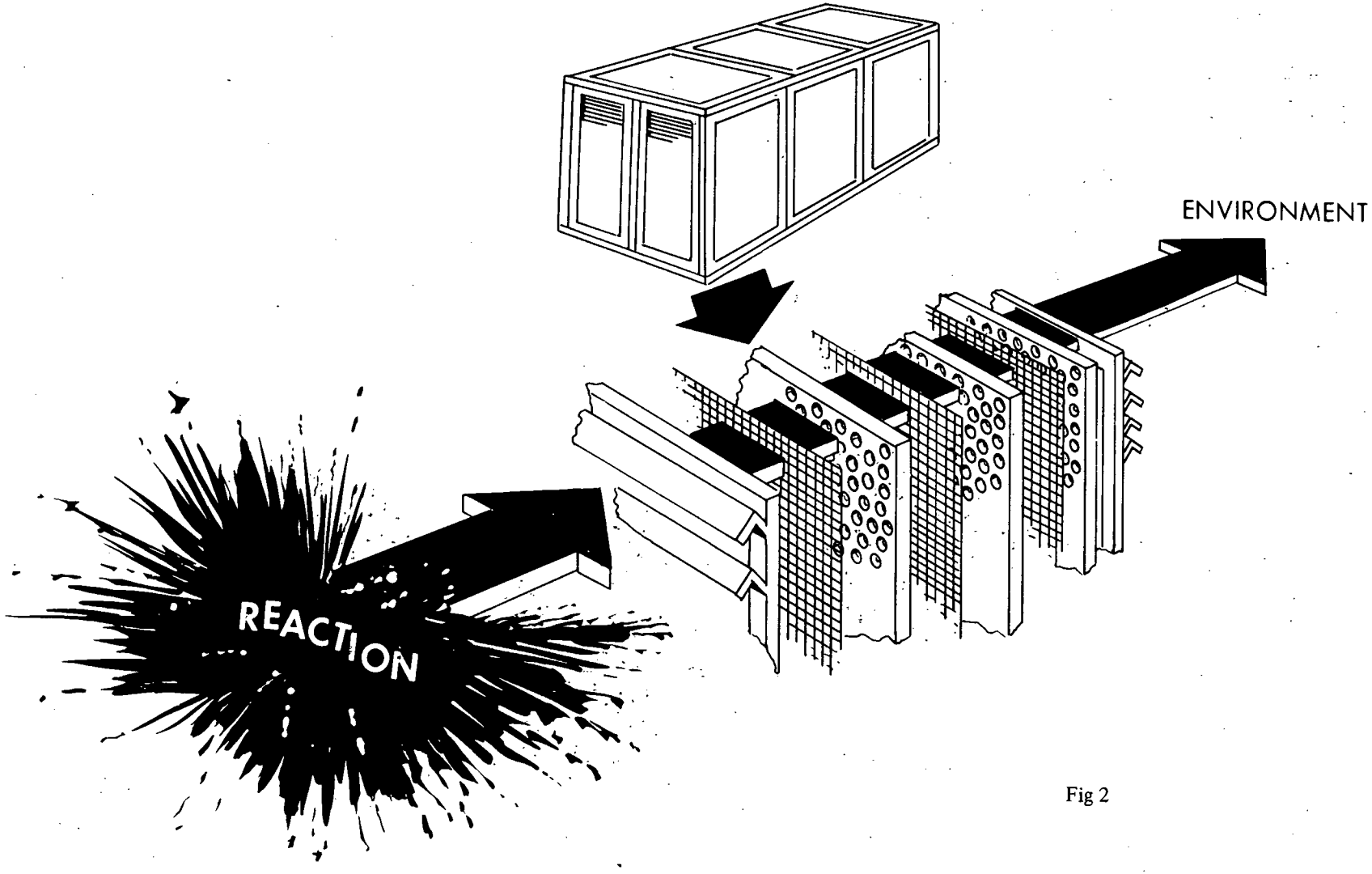
structures. Fig 2 shows some of the detail of a structure's panel construction representing one of many panel configurations that have been used. The inner layer is made of angle irons. The next three layers are perforated plates, and the outermost layer is louvered plate. The layers are held together by steel channels (Refs 5, 6, 7, 8 & 10)

See also under Buildings and Other Structures at Ordnance Establishments in Vol **2**, B320-R to B321-R, and Barricades in Explosives and Ammunition Installations in Vol **2**, B22-R to B23-R

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Refs: 1) E. Cohen et al, "Establishment of Safety Design for Use in Engineering of Explo-

OPERATIONAL SHIELDING APPLICATION



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Fig 2

sive Facilities and Operations; Blast Pressures and Impulse Loads Produced by Explosions in Cubicle-Type Structures", PATR **3604** (1967) 2) R.M. Rindner et al, "Establishment of Safety Design Criteria for Use in Engineering of Explosives Facilities and Operations", PATR's **3484, 3594 & 3712** (1966 to 1968) 3) Anon, "Structures to Resist the Effects of Accidental Explosions", **TM 5-1300** (June 1969) 4) R.M. Rindner et al, "Preliminary Estimate of Concrete Thicknesses and Construction Costs of Laced Reinforced Concrete Structures", PATR **4441** (1972) 5) Anon, "Application of Suppressive Structures Concept to CAMDS", **EA-FR-2B02** (1973) 6) L.A. Izzo, "Suppressive Shielding Symposium", Edgewood Ars Special Publ **EM-SP-74 017** (1974), AD 786-521 7) D. Westerman et al, "An Economic Analysis of Suppressive Structures", US Army Material Systems Analysis Agency (AMSAA) Rept No **108**, APG, Md (1974), AD B000317 8) P.V. King, "An Overview of the Suppressive Shielding Program", Minutes of the 16th Explosives Safety Seminar, Vol **1**, DOD Explosives Safety Board (Sept 1974), 91–139 9) I. Forsten, "Application of Latest Safety Engineering Concepts to Munition Plant Modernization", Ibid, 353–79 10) B. Jezek, D.J. Katnausis, R.G. Thresher, "Applications of Suppressive Shielding in Hazardous Operation Protection", **EM-TM-76-003** (June 1975)

Matter Explosives. The following expls were patented by O. Matter of Switz. A plastic dynamite consisting of tar distillates mixed with inorg oxidizers such as nitrate, chlorate or perchlorate (Ref 1). Mixts of nitrates, chlorates or perchlorates with w sol chlorinated hydrocarbons such as chloronaphthalene, benz or tar-distn residues as thickening agents (Ref 2). A carbonaceous material, free from inorg matter and suitable for use in BkPdr or priming compns, is prepd by extrg coal with high boiling org solv such as coal-tar oils, followed by filtn and removal of the solv from the filtrate by distn (Ref 3)
Refs: 1) SwissP 220755 (1942) & CA **42**, 6538 (1948) 2) SwissP 228653 (1943) 3) SwissP 244352 (1946) & CA **43**, 4468 (1949)

Matweed (Mattgrass, Espartograss, Sparte in Fr). One of several species of seaside grass, among which are the Lygeum Spartum or hooded matweed of the Mediterranean and Anophilia Arenaria of Holland. The name Esparto is used for the fibers covering coconut shells. The dried weed may be nitrated to give an expl compd (see below)

Nitromatweed (Matweed Nitrate, Nitrosparte in Fr). Prepd by nitration of dried matweed with mixed nitric-sulfuric acids in a manner similar to the prepn of NC. Trench, Faure and MacKie (Ref 2), in 1876, patented expls containing as a base "nitrosparte" (or other nitrated cellulosic material such as cotton, hay, agave, hemp, flax, straw, aloe, yucca, etc) together with resin, ozokerite, collodion, glycerin, charcoal and soot. Hengst (Ref 3), in 1898, patented a smokeless powd containing "nitrosparte" prepd by nitration of fibers covering the coconut shell
Refs: 1) Merriam Webster's Dict, 2nd Ed (1963), 1516 2) Daniel (1902), 773 3) Ibid, 373

Maurette Powder. Contd K nitrate 82.4, K chlorate 0.7, sulfur 0.3, charcoal 7.1 & wood ash 6.5%
Ref: Daniel (1902), 420

Maxim Explosive. Patented in 1885 in Engl. Prepd by mixing 1p of compn (K nitrate 74.18, sulfur 14.40 & paraffin 11.42%) with 3ps of regular BlkPdr
Ref: Daniel (1902), 420

Maxim, Hiram Steven, Sir (1840–1916). American expatriate in Engl who specialized in Ord and expls. His major inventions included (1) design and constrn of the modern machine gun (1884–89), (2) gelatinization of NC using acet, either alone or in mixt with eth or alc (BritP of 1888), (3) addition of an oil, such as castor oil, to a mixt of NC and NG to obtain a slow burning smokeless powd for small cal weapons, (4) prepn of smokeless powd in the form of single-perforated rods, plain or with exterior channels running parallel to the long

axis of the rods; such powds burned more uniformly than solid grains, and (5) prepn of smokeless powds containing NC, to which were added resinous materials to reduce firearm barrel erosion (BritP of 1900)
Refs: 1) Daniel (1902), 420–23 2) Van Gelder & Schlatter (1927), 778, 779 & 793

Maxim, Hudson (1853–1927). American inventor, brother of Sir Hiram Maxim. His major inventions included (1) Maximite (see below), (2) Maxim-Schüpphaus powd (see in this Vol), (3) initiating compd prepd by adding 1p of MF to 1p of a paste contg NG 75–85 and NC (previously distd in a small amt of solv such as acet) 25–15%; after evapn of the solv, the resulting mixt was suitable for use in projectiles such as naval torpedoes, where a large amt of initiator was required (BritP of 1894), (4) a proplnt especially designed for use in cannons contg a min amt of volatile solv; 40ps of guncotton and 8–10ps of NC (sol in NG at 38°) were thoroughly blended with 8ps of NG and acet equal to about 25% by wt of the total mixt; the resultant thick gelatinous mass was passed thru heated rollers several times to reduce the quant of acet to a min; the rolled sheets were then cut to the desired grain size (BritP of 1896), (5) single-base proplnt contg mixt of insol and sol NC (BritP of 1897), (6) aerial torpedoes contg a min amt of metal and a max of expl (BritP of 1897), (7) automatic pistol (BritP of 1897), (8) automatic cannons (BritP of 1897), (9) Motorite (see in this Vol), (10) safety delay fuze, magnetic submarine mine, etc
Refs: 1) Daniel (1902), 421–25 2) Van Gelder & Schlatter (1927), 793

Maximite. According to Daniel (Ref 1), it was an expl proposed by Hudson Maxim at the end of the 19th century for charging aerial torpedoes. It was prepd by blending sol NC 20–30 with NG 80–70%, allowed to harden and then pulverized. 75–80ps were mixed with 25–20ps of insol NC, satd with w, and the resulting wet mass charged into torpedoes

Marshall (Ref 4) states it was introduced soon after 1900 as a filling for shells. It consisted of a mixt of 90ps of PA and 10ps of nitronaphthalene, which melted at comparatively low temps, but tended to form cavities and consequently caused premature explns

According to Newman (Ref 5), Maximite was a proplnt consisting of NC, NG and castor oil, patented in 1889 by Hiram S. Maxim, to operate the machine gun he invented

Maximite was used in armor-piercing projectiles (Panzergranaten) until 1903 when it was replaced with Amm picrate, known as Explosive D (Refs 2 & 3)
Refs: 1) Daniel (1902), 425 2) D. Globig & A. Haid, SS **22**, 4 (1927) (Amerikanische Spreng- und Zündladungen) 3) Van Gelder & Schlatter (1927), 941–42 4) Marshall **3**, 174 (1932) 5) J.R. Newman, "The Tools of War", Doubleday, Doran & Co, Inc (1943), 54

Maxim-Nordenfeldt Powder (M.N.). An old American guncotton powd, gelatinized with et acet
Ref: Thorpe **2**, 485 (1917)

Maxim Powder. One of the varieties of smokeless powd invented by Hudson Maxim, contg guncotton 94, NG 5 & castor oil 1%. It was used in the form of either small square flakes or cylinders, 1.64 inches long and 0.5 inch in diam. Other varieties of Maxim powds contd equal parts of NG and guncotton without castor oil
Ref: Van Gelder & Schlatter (1927), 828

Maxim-Schüpphaus Powder. A progressive burning smokeless powd, invented by Hudson Maxim in collaboration with R.D. Schüpphaus. It was the first multiperforated powd grain, earlier powds having been manufd in the form of strips or of solid or single-perforated rods. According to Daniel (Ref 1), there were two varieties of such powds: (1) *double-base powd* prepd by mixing 80ps of insol NC (13.3% N) with 8ps of sol NC (12.0% N) and 12ps of NG at 50° in the presence of 35ps of acet. To this was added 1p of urea (as stabilizer), previously disd in methanol. This powd was less corrosive to gun barrel interiors than Ballistite or Cordite, both of which contd much more NG (BritP of

1895); (2) *single-base powder* contd 80ps of insol NC, 19.5ps of sol NC and 0.5p of urea, and was manufd in the USA by duPont
Refs: 1) Daniel (1902), 425–26 2) Thorpe **2**, 458 (1917) 3) Van Gelder & Schlatter (1927), 780 & 793

Maximum Charge (Charge limite in Fr) is the max charge of an expl that can be fired in a coal mine without causing ignition of firedamp and/or coal dust in air
Ref: Marshall **2**, 585 (1917)

Mayevskii, N.V. (1823–1892), eminent Russian ballistician and originator of the science of *Exterior Ballistics.* He was equally known for work in the field of *Interior Ballistics.* In 1856 he designed a method of measuring the pressures in various sections of a gun barrel on firing. In 1867 he conducted expts to detn projectile velocity and correlated press with velocity
Refs: 1) Hayes, "Elements of Ordnance", J. Wiley, NY, 437 (1938) 2) A.D. Blinov, Kurs-Artillerii, Voyennoye Izdatel'stvo, Moscow, USSR, **1** (1948) 3) M.E. Serebriakov, "Vnutrenniaiya Ballistika Stvol'nykh Sistem i Porokhovykh Raket" (Interior Ballistics of Gun Barrel Systems and of Solid Rockets), Oboronghiz, Moskva (1962), 19 & 30

Mayrhofer Stability Test. A modification of the Bergmann-Junk Test (see Vol **2**, B102-R) for testing the stability of NC and propellants. Mayrhofer recommended the use of 20ml of a 2% KI soln instead of w for the quant collection of decompn products. He also tested NG contg proplnts in both dry and sl moist states, and found that while a stable sample behaved in a similar manner whether heated dry or moist, an unstable powd decompd rapidly in the presence of traces of w. Tonegutti (Ref 3) considered this test reliable for ballistites and unreliable for cordites
Refs: 1) F.M. Mayrhofer, SS **13**, 425–29 & 448–51 (1918) & CA **13**, 3320 (1919) 2) W. Will, SS **14**, 61–63 (1919) 3) M. Tonegutti, AnnChimAppl **17**, 60–65 (1927) & CA **21**, 2064 (1927)

Mazut or Masutt. Residue of Russian petroleum after distg off benz (1% at 100°, d 0.725 g/cc), gasoline (3% at 120° to 130°, d 0.775 g/cc), and kerosene (27% at 150° to 250°, d 0.83–0.84g/cc). The resulting black, oily residue, resembling crude petroleum in appearance, has a flash pt of about 100° and d 0.878–0.900 g/cc. It was purified by treatment with sulfuric acid. It has been used as a fuel in boilers, locomotives and boats, as well as in some internal comb engines. In the expl industry, its use was confined to some blasting expls, particularly those contg chlorates
Refs: 1) Colver (1918), 61 2) Hackh's (1944), 517 3) Merriam-Webster's (1951), 1518

M.B. Powder (Modified Black Powder). Consisted of BkPdr in which part of the K nitrate was replaced by K perchlorate. The finely pulverized ingredients were preliminarily mixed, as in the prepn of BkPdr, and then incorporated together in a steam jacketed pan. The last operation was dangerous and some fires occurred, which were ascribed to friction in the hot, dry caked material. A similar expl was called **Roslin Giant Powder**
Ref: Marshall **1**, 385 (1917)

MC (Poudre). BkPdr used in Fr as propellant for muzzle loading cannons and as a bursting charge in projectiles
Ref: Daniel (1902), 427

MC No 3 Powder. Austrian safety expl (1898) contg Amm nitrate 91.6 and collodion cotton 8.4%
Ref: Daniel (1902), 427

McRoberts Type Incorporating Machine. Brit device for blending expls contg NG. Unlike earlier equipment, it had no bearings inside the mixer, therefore reducing the danger of NG being initiated by friction. It consisted of a flat-bottomed elliptical vessel placed on a platform which could be raised or lowered. The vessel was provided with two vertical, parallel shafts, supported from above by bearings,

which did not touch the bottom of the bowl. Each shaft had two or more horizontal blades, serving as mixers. The arrangement closely resembled the duPont dipper used to nitrate cellulose, except that the bottom of the mixer was flat and contd no opening. The McRoberts machine allowed gelatinization and incorporation to be carried out in the same vessel, thus avoiding transferring the jelly from a gelatinization vessel to a mixing machine, as was usually done in other systems

In charging the machine, the platform supporting the mixing vessel was lowered so that the mixing arms cleared the top of the vessel. It was loaded with the required ingredients, and then raised. The mixing blades rotated in opposite directions to each other. When incorporation was complete, the vessel was lowered to clear the blades, and the load was discharged by transferring to wooden containers

Ref: Barnett (1919), 100–01

MDN. See Explosif MDN in Vol **6**, E361-R

MDPC. See Explosif MDPC in Vol **6**, E361-R

Meal Powder (Meal Black Powder). The finest granulation of BkPdr procured for military use. It is designated as Class 8 in Ref 4 and has the following formulation requirements: K nitrate 74 plus 1.0 minus 2.0, S 10.4 plus 1.5 minus 1.0, and charcoal 15.6 plus 1.5 minus 1.0%. Granulation requirements are a max of 5% retained on a No 100 US Std sieve, and a max of 50% passing thru a No 270 sieve. Modern methods of prepn are given in Ref 3

Historically, it was prepd in a stamp mill by a procedure developed by the National Fireworks Co (Ref 1). This mill consisted of a solid block of granite in which 3 cup-shaped cavities had been cut. The stamps, which operated in the cavities, were fitted at their lower ends with cylindrical wooden blocks cut from a hornbeam tree. The blocks were replaced when worn

Weingart (Ref 5) gives the details of another older method as follows: Mount a 50 gal wooden barrel on two uprights in such a manner that it can revolve in a horizontal position on centers attached to the heads. To one of the centers, attach a long rod with a pulley, to be operated by remote control either by a water wheel, air or electric motor. Cut a hole in the side of the barrel and provide it with a tightly fitting plug. Place 300 to 500 lead balls, 1 inch in diam, in the barrel, followed by a thoroughly mixed compn of K nitrate (double refined), 15 lbs, willow charcoal, 3 lbs, and sulfur (flour), 2 lbs. Revolve the barrel slowly, by remote control, for at least 500 turns. The longer it is turned, the finer and more uniform will be the powd. *Note:* Care must be taken that no foreign matter, such as nails, sand, etc, is introduced into the barrel as this might lead to an expln

Meal powd has been used historically in pyro for ignition and priming purposes (Ref 1), in colored star compns (Refs 1 & 2), and generally in fireworks, rockets, Roman candles and firecrackers (Refs 5 & 6)

Refs: 1) Davis (1943), 5, 44, 83 & 455 2) J.J. Berliner et al, "Fireworks", Res Rept **3854**, 10–25 (1953) 3) Encycl **2** (1962), B168–69 4) Anon, "Powder, Black", **MIL-P-233B** (July 1963) 5) Weingart, 2nd Ed, 13–14 (1967) 6) Ellern (1968), 368–71

Measurement of Acidity or Alkalinity of Explosives. (Measurement of pH value). These tests consist essentially of extrg the sample of expl with w (either cold in the case of liquids such as NG, or hot for solids such as TNT, Tetryl, PA, etc), and detg the acidity of the resulting extr either by titration, colorimetric methods or by means of a pH meter. These tests are described under the individual compds

Measurement of pH value, Stability Tests by. These tests det the acidity (pH value) of powds which is produced when they are heated for prescribed times and temps (usually 80 to 110°). In the group are the Hansen, Grottanelli and Pavlik tests (qv)

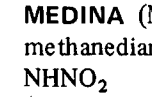
Refs: 1) Hansen, DanskArtilleritidskrift **12**, 129 (1925) 2) L. Metz, SS **24**, 245, 291 & 335 (1929) 3) Grottanelli, MémRAccadd'Ital **11**, No 6, 5 (1931) 4) Marshall **3**, 215 (1932) 5) Pavlik, Chim&Ind **29**, 978 (1933) 6) A. Kufferach, SS **31**, 327 (1936) 7) Reilly (1938), 91

Mechanical Fuze. Any fuze which depends for its arming and functioning on events primarily of a mechanical nature. Fuzes may consist of a combination of mechanical and electronic features. Proximity fuzes may contain a mechanical delayed arming device; mechanical fuzes may be functioned by electrical energy from a piezoelectric element. The classification is dependent upon which features are predominant

Variations of mechanical fuzes are: (a) *Mechanical Time Fuze* (MTF) which is actuated by a clocklike mechanism preset to the desired time, (b) *Mechanical Time and Superquick Fuze* which contains an additional device to cause instantaneous activation as a result of impact, (c) *Mechanical Time Fuze, Dummy* which is an imitation of a mechanical time fuze having the same shape, weight and center of gravity as the fuze, but without expl components, and (d) *Mechanical Time Fuze, Training* which is an item identical in configuration to a mechanical time fuze, but is designed for use in training procedures associated with assembly and/or disassembly of a weapon

Refs: 1) Ohart (1946), 122–70, 248–90, 334–40 & 356–58 2) Anon, EngrgDesHdbk, "Explosive Trains", **AMCP 706-279** (March 1965) 3) Encycl **4** (1969), D879–931 & D968–1010 4) Anon, "Fuzes", EngrDesHdbk, **AMCP 706-210** (Nov 1969) 5) G. Cohn, "Sources for Fuze Information", The Franklin Institute Research Laboratories, Phila, Pa, 24pp (1972)

MEDINA (Methylenedinitramine, N,N-Dinitromethanediamine), $CH_4N_4O_4$, mw 136.17, N 41.18%, OB to CO_2 0.0%; wh orthorhombic needles and rods, also plates and tablets from et dichloride: iso-Pr alc 9:1 (Ref 18); mp 105–06° (Ref 1), 104° (Ref 2), 103.5–4.5 (Ref 11, p 21); CA Registry No 14186-44-6



MEDINA in an acronym for **ME**thylene **DIN**tr**A**mine. In earlier literature it was called MEDNA (Ref 2), the latter name later used for the isomeric compd methylenedi-isonitramine which was obtained by the action of nitric oxide on acet (Beil **1**, 592) (See under MEDNA in this Vol). This name should also not be confused with MeEDNA, which is N-Methylethylenedinitramine (Ref 2a and see under MeEDNA in this Vol)

Historical. MEDINA was first isolated as a degradation prod from the nitrolysis of hexamine (WWII work done at the Univ of Bristol, cited in Ref 5). It was prepd by the hydrolysis of PCX (qv) in boiling et alc and isolated as the Ba salt (Ref 4); and by the hydrolysis of N,N′-DiacetylMEDINA with aq ammonia, yield 25% (Ref 5)

Best Preparation on a Laboratory and Commercial Scale. A. Methylenediformamide. In a 2ℓ round bottom 1 neck flask are placed 540g of formamide and 70g of hexamine. The flask is fitted with a wide bore air condenser topped with a w jacketed reflux condenser, and the flask held at 140° for 5 hours. It is chilled in ice, the solid filtered, and washed on the filter with 90g of formamide. The crude prod may be used in the next step. For a pure sample, the crude solid is dissolved in et alc, decolorized with charcoal, and the soln chilled, mp 142–43°

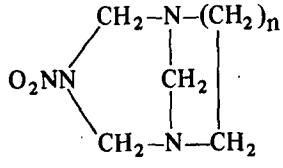
B. Methylenedi(nitroformamide). Abs nitric acid (19ml) is added dropwise with stirring to a suspension of 5g of crude methylenediformamide in 19ml of acet anhyd at 10–15°, the soln held 2 hours at 0°, poured into 150ml of ice and w with stirring, the ppt filtered, washed twice by slurrying with ice w, pressed dry on the filter, and dissolved in 30ml of et acet. The soln is sepd from w, dried over anhyd Na sulfate, concd in vacuum, 10ml of iso-Pr alc added, and the prod collected. The methylene di(nitroformamide) is purified by recrystn from acet/iso-Pr alc/Skellysolve B or from boiling et chloride, mp 87.0–7.5°

C. MEDINA. The crude methylenedi(nitroformamide) is pressed dry on the filter, stirred into 105ml of formic acid, and the paste allowed to stand overnight. The next day the soln is filtered thru an acid-proof filt, the formic acid and w removed by codistn with xylene, and the crude MEDINA, which seps as a sand, filtered and dried over paraffin and NaOH in a vacuum; yield 80–100% based on methylene diformamide, mp 98–103°. The crude MEDINA is recrystd from 2-nitropropane or et chloride:iso-Pr alc 9:1, mp 104–05° (Ref 11, p 54). This prepn is also covered in Ref 20

Other preparations and isolations. If damp methylenedi(nitroformamide) is allowed to stand for several days, the odor of formic acid is noticed, and MEDINA can be isolated from the residue (Ref 11, p 14). The details of scale-up to 150 lb batches, including exp details and flow sheets, and further scale-up with the aim of prodn of 1000 lbs are given. The report describes a fume-off and fire which occurred during the 53rd run. The cause was attributed to a stuck valve which allowed nitric acid to build up in the reactor (Ref 13, p 57). In Ref 16, p 73 there are cost analysis data for pilot plant and large scale prodn, flow sheet for a proposed coml plant, and material balances. The action of acet anhydr on N,N′-bis(hydroxymethyl)MEDINA regenerates MEDINA (Ref 6); the diNa salt of N,N′,N″-trinitrotrimethylenediamine, on warming with me alc, ppts the Na salt of MEDINA

Properties. Two cryst modifications are known: I formed from soln and II formed from the melt and is unstable with respect to I (Ref 11, p 23). Photographs and crystal angles of a single cryst of MEDINA I are given in Refs 11, p 25; & 18. Phase diagrams for mixts of MEDINA with RDX, TNT, EDNA, and PA are given in in Ref 11, p 26. Optical props of single crysts of MEDINA are given as n_α 1.572, n_β 1.584, n_γ 1.598 (Ref 13, p 76). X-ray diffraction patterns of powd MEDINA are given in Ref 13; addnl phase diagrams are given in Ref 13 for mixts of MEDINA with HMX, PETN, BTNEU, Tetryl, Styphnic Acid, and 2,4-Dinitrophenol; ternary diagrams for PA:TNT:MEDINA and PA:PETN:MEDINA are also given. MEDINA behaves in aq soln as a dibasic acid, forming well-defined salts with alkali and alkaline earth ions (for reactions involving the Ba and Na salts, see above). Similarly are formed salts with 2 moles of methylamine (mp 120° decompn), cyclohexylamine (mp 99–100° decompn), and benzylamine (mp 112° decompn) (Ref 7). The addn of 2 moles of hydrazine in iso-Pr alc to 1 of MEDINA in the same solv gives the fairly stable 2:1 hydrazine salt, mp 126° decompn, Q_c 2446 kcal/kg, power 148% TNT (Trauzl), 143% TNT (ballistic mortar) (Ref 13). The Ba salt is pptd by addn of Ba chloride soln to solns of MEDINA (it can be regenerated by the addn of HCl to the Ba salt); this salt is used in isolation procs for obtaining high-purity MEDINA (Ref 5). By heating in w to 70° MEDINA is decompd quanty into formaldehyde and nitrous oxide, the vel of this decompn varies strongly and in a complicated way with pH (Ref 8). It is presumed to occur by hydration to formaldehyde and Nitramide, which decomps into w and nitrous oxide, the kinetics is discussed at length in Ref 16. In the solid phase or concd solns the decompn takes a different course to give a high melting polymer insoluble in most solvs (Ref 11, p 29). The action of 2N aq ammonia gives a small amt of DNPT (Encycl, Vol **5**, E91-R), and the mono-amm salt, when allowed to stand with aq formaldehyde gives the same compd (Ref 8). The action of Amm Nitrate in acet anhyd & acet ac gives a small amt of RDX and a very small amt of 1,5-diacetoxy-2,4-dinitrazapentane (Ref 3). The addn of MEDINA improves the yield of HMX from the reaction of para-formaldehyde with Amm Nitrate in acet anhyd & acet ac (Ref 3). Similarly, the addn of MEDINA to hexamine nitration mixts raises the yield of RDX from 82 to 145% based on 1 mole of RDX from 1 mole of hexamine (Ref 26); a plausible mechanism is given. A soln of MEDINA in w or acet ac is treated with formaldehyde, then concd nitric acid to give 1,5-dinitroxy-2,4-dinitrazapentane, mp 105–06° which is not stable on long storage (Ref 11, p 38). The action of formaldehyde alone gives 2,4-dinitraza-1,5-pentanediol (Ref 11). The action of acet anhyd & Na acetate at 95° gives a small amt of 1,5-dinitroxy-2,4-dinitrazapentane and an amor solid $C_{11}H_{24}N_{15}O_{16}$ which decomps betw 280 and 315° (Ref 3). MEDINA gives with formaldehyde in pyridine a compd $C_6H_{12}N_9O_{10}$ (Ref 3). The action of ammonia in et eth on a soln of MEDINA in et ac which has been satd with formaldehyde gives 1,3-dinitrotrimethylenetriamine, isolated as the N-acetyl deriv (code name TAX), mp 156° (decompn) (Ref 7). The reaction of MEDINA in 40% aq formaldehyde with 40% methylamine in et alc gives 1,3-dinitro-5-methyltrimethylenetriamine, mp 100–04° (decompn). Similarly prepd were the benzyl (mp 127–30° decompn), cyclohexyl (mp 101–02° decompn), and ethyl derivs (mp 88–89° decompn) (Ref 7). A soln of MEDINA in et acet is satd with formaldehyde, the soln cooled to 0°, and the rosettes filtered

to give N,N'-Bis(hydroxymethyl)methylenedinitramine, mp 70–75° (decompn) (Ref 6); the Can workers were unable to isolate a definite prod from this reaction (Ref 3) (See Encycl, Vol **5**, D1356). A compd, mp 122°, was isolated when MEDINA was allowed to stand in the presence of acid, or not completely freed of acid during prepn; from IR and other data it appeared to be N-hydroxymethylmethylenedinitramine, but its structure was not rigorously established (Ref 11, p 29). MEDINA, primary amines, and formaldehyde give hexahydrotriazines contg 2 nitro groups and 1 alkyl group, or 1 nitro group and 2 alkyl groups, depending on reactant ratios (Refs 6, 7, 21 & 24). A similar reaction with aliphatic diamines is reported in Ref 19, the prods isolated are bicyclic compds of the type:



The Na salt of MEDINA was fluorinated in w, the soln extd with methylene chloride, and the solv evapd to give a yellow oil whose IR spectrum showed absence of NH and the presence of NF absorption, and analysis indicated was a mixt (Ref 22). Nitramines in the presence of sulfuric acid are capable of nitrating reactive aromatic compds, but when acetanilide was treated with MEDINA in the presence of this acid, no nitroacetanilide was isolated. Instead compds indicating that the MEDINA had been fragmented and the fragments reacted with the acetanilide were isolated (Ref 12)

Solubility. No quant data is in the literature. In Ref 11, p 19 the order of decreasing soly is given as w, ketones, alcs)) esters) organic acids, aliphatic nitro compds) ethers, chlorinated hydrocarbons, hydrocarbons. Within each class the solubility decreases with increasing chain length

Spectral properties. The UV spectra of MEDINA and the Traube compd (MEDNA) in et alc, acid, and base are compared in Ref 4. The peaks for MEDINA are similar in all three solvs, but the MEDNA peak is shifted from 2600 to ca 2200 Å in N HCl. The IR spectrum in mineral oil is given in Ref 21a; the IR spectra of MEDINA from different sources are compared and appear to be almost identical. The IR spectra of MEDINA and decompn prods are given in Ref 16, p 59. The NMR^H is given as: chem shifts N-proton 13.1, C-proton 5.10 ppm (Ref 27)

Analytical. The thin layer chromatog of MEDINA and the sepn from other expls and nitramines on thin layer plates (MEDINA spots tend to comet) are described in Ref 23

Explosion temperature test. 300–330° in 5 secs (RDX 260°) (Ref 13)

Friction pendulum test. Steel shoe explodes; fibre shoe unaffected (Ref 13)

Heat of combustion. –230.3 kcal/mole (Ref 11, p 1); –216.85 ± 0.32 kcal/mole at 25° (Ref 15)

Heat of formation. –13.84 kcal/mole (Ref 15)

Heat of fusion. The Q_{fusion} of mixts of MEDINA with PETN, HMX, TNT, RDX, BTNEU, EDNA, Styphnic Acid, PA, & Tetryl are given in Ref 13, p 97

Heat test at 80°. 1.13–3.89% wt loss after 72 hours (Ref 11, p 30)

Heat test at 85°. 2.77–6.54% wt loss after 72 hours (Ref 11, p 30)

Hygroscopicity. No wt gain to 90% RH at 30° (Ref 13, p 424)

Impact sensitivity. PA app 10–11 inches (18.3mg sample) vs 8 for RDX, hydrazine salt 15 inches (11mg sample); BM app 14–21cm vs 70–100+ for RDX and 100+ for TNT, hydrazine salt 92cm (Ref 13), also in this Ref are listed the impact sensy of 8 samples of MEDINA coated with wax (15–31cm)

International Heat Test @ 75°. 0.66% wt loss after 4 hours, 1.47–2.24% after 72 hours; the effect of many additives & recrystn solvs on stability are given in Ref 13. PA seems to be the best stabilizer; it is covered in C.W. Sauer, USP 2786078 (1957) & CA **51**, 9163 (1957)

Power. It is reported to have the highest expl power of all pure compds tested to date (Ref 13, p 423); Ballistic Mortar, 198% of TNT (Ref 11, p 1); Trauzl test, 681–727cc (10g sample); spherical lead block test, 568–76cc (10g sample) (Ref 11, p 1). Power by spherical lead block test of 14 formulations contg MEDINA as well as formulations contg varying proportions of TNT, MEDINA, and Al are reported in Ref 16

Sand test. 71.9g of sand are crushed (RDX 58–61g) (Ref 13)

Toxicity. MEDINA is apparently non-toxic to rabbit penile mucosa; its cumulative effect on abraded and intact rabbit skin is slightly greater than Tetryl; no damage was observed to rabbit cornea; and there was no evidence of sensitization by subcutaneous injection in guinea pigs. It was concluded that its toxicity is similar to that of Tetryl (Ref 11, p 138)

Vacuum stability. Gas evolution was 1.92 mg/g/40 hours (material recrystd twice from et chloride:iso-Pr alc 9:1); 0.89–0.98ml/g/40 hours (sample dried at 40° in vacuum) (Ref 11, p 30). Another stability test, developed by W.C. McCrone of ARF, consists of following the behavior of crysts of the compd on a hot stage microscope at temps close to the mp. The most stable samples of MEDINA were found to be those recrystd from et chloride/iso-Pr alc; the least were prepd by vacuum evapn (Ref 11, p 30)

Velocity of detonation. 8700m/sec (Ref 14), deton vel of 7 formulations contg MEDINA are measured and plotted in Ref 16

Uses. Screening tests showed MEDINA to be 5–10% more powerful than RDX (Ref 16). Several formulations of MEDINA, TNT, & Al were tested as air-blast expls, and some were found to be slightly superior to H-6 (RDX: TNT:Al:wax 47:31:22:5). Three MEDINA-contg formulations were compared with std expls in plate dent, air blast, underwater blast, and fragn tests. MEDINA showed a 4% improvement over RDX in shaped charge penetration (Ref 14). MEDINA was tested as a detonator fill, but was unsatisfactory due to poor stability (Ref 14)

Written by: **C. H. McDONNELL**

Refs: 1) Beil **1**, {2606} 2) H.D. Springall, "Index of Compounds Related to Hexamine & to RDX", Gt Brit Advisory Council on Scientific Research & Tech Development; Explosive Research Comm Advisory Committee **7791** (Nov 1944) 2a) Blatt, OSRD **2014** (1944) 3) E. Aristoff et al, CanJRes **27B**, 521 (1949) 4) R.N. Jones & G.D. Thorn, CanJRes **27B**, 828 (1949) 5) R.C. Brian & A.H. Lamberton, JCS **1949**, 1633 6) D. Woodcock, JCS **1949**, 1635 7) F. Chapman et al, JCS **1949**, 1638 8) A.H. Lamberton et al, JCS **1949**, 1641 9) N.D. Mason, "Impact Sensitivity Determinations of Explosive Compounds Tested During the Period 1 Jan to 1 Nov 1950", NOL NAVORD Rept **1589** (Nov 1950) 10) A.H. Lamberton, QuartRevs **5**, 89–91 (1951) 11) Anon, "Synthesis and Properties of MEDINA", Interim Report to Office, Chief of Ordnance; Contr DA-19-020-ORD-47; ADL **C-58247** (Jan 1952), ATI-140492 12) C. Holstead & A.H. Lamberton JCS **1952**, 1886 13) Anon, "Synthesis & Testing of High Explosives", 3rd Report to Office, Chief of Ordnance; Contr DA-19-020-ORD-47 & -12; ADL **C-58247** (Oct 1953), AD-21289 14) E.M. Fisher, "Air Blast Performance of two Mixtures of MEDINA, TNT, & Al"; NOL NAVORD Rept **2959** (Nov 1953) 15) J. Murrin & S. Goldhaven, "Heats of Combustion of Some Simple Aliphatic Nitramines", NPF Memo Report **88** (Nov 1954), AD-49349 16) Anon, "Evaluation of Methylenedinitramine (MEDINA) as a High Explosive", Summary Report to Office, Chief of Ordnance; ADL **C-58247** (Mar 1954) 17) Anon, "Research in Chemistry", NOTS **1170**, NAVORD Rept **4874** (June 1955) 18) J. Krc, AnalChem **30**, 1301 (1958) 19) R. Reed, Jr, JOC **23**, 496 (1958) 20) C.W. Sauer, "Nitramines", USP 2856429 (1958) & CA **53**, 5130h (1958) 21) A. Weissberger, ed, "Chemistry of Heterocyclic Compounds", **13**, "s-Triazines & Derivatives" (Interscience, 1959), p 524–5 21a) F. Pristera et al, AnalChem **32**, 495 (1960) 22) Anon, "Quarterly Progress Report on Research on Advanced Solid Propellants", Esso Res & Eng Co Rept **61-3** (11 June to 10 Sept 1961) 23) J.A. Bell & I. Dunstan, JChromatog **24**, 253 (1966) 24) N.V. Makarov et al, Izvest-AkadNSerKhim **1967** (8), 1759 (Eng Trans), Russ 1837 25) Urbański **3** (1967), 16–18 26) J.A. Bell & I. Dunstan, JCS **1969C**, 1559 27) T.J. Mayer & J.M. Duswalt, JChemEng-Data **18(3)**, 336 (1973)

MEDNA (METHYLENEDIISONITROSOAMINE, or N,N′ DINITROSOMETHANEDIHYDROXYLAMINE) and Salts.

MEDNA is an acronym for **ME**thylene**D**i-iso-**N**itros**A**mine (erroneously called methylenedinitroamine in Blatt, OSRD **2014** (1944) (see MEDINA

in this Vol); structure $(HON)_2CH_2$, NO

mw 136.07, N 41.18%; the free acid is unstable and is known only in salts (Refs 2 & 3)

Historical. The Na salt was first isolated by the reaction of nitric oxide on acet (Ref 2); later the same worker found that the action of nitric oxide and Na hydroxide on any compd contg the acetyl group would give Na MEDNA [compds treated were mesityl oxide, methylisopropyl ketone, acetophenone, and ethyl dimethyl-acetoacetate (Ref 3)]; still later it was found that MEDNA salts could be obtained by prolonged contact of nitric oxide with Na ethoxide or K ethoxide (Ref 4). The Ba salt was obtained by the action of nitric oxide on Na isopropoxide or Na 1-phenylethoxide followed by the addn of Ba chloride soln (Ref 6). The UV spectra were used to distinguish between salts of MEDNA and MEDINA and to prove the structure of each (Ref 8)

Salts. Monoammonium. UV spectra in N HCl λ_{max} 231 mμ, log E_m 4.10; in w λ_{max} 254 mμ, log E_m 4.16; in N Amm hydroxide λ256 mμ, log E_m 4.24 (Refs 8 & 9)

Barium. Pptd by the addn of Ba chloride to w-sol salts of MEDNA (Refs 2 & 3); it has the least expl effect in lead plate test when primed with MF (Ref 7)

Cadmium. It is ranked between the Cu and Ba salts in expl effect in lead plate test when primed with MF (Ref 7)

Calcium. It is pptd when Ca chloride soln is added to a w soln of the Na salt (Ref 3)

Cesium. Impact sensy on PA app 4 inches (MF 2 inches) (Ref 11)

Copper. Impact sensy on PA app 4 inches (Ref 9); it is ranked between Fe and Cd salts in expl effect when primed with MF (Ref 7)

Monohydroxylamine. The UV spectrum was studied by R.N. Jones of the Univ of Toronto, cited in Ref 8

Iron (valence not stated). It is ranked between the K and Cu salts in expl effect in lead plate test when primed with MF (Ref 7)

Lead. It is pptd when a soln of a lead salt is added to a w soln of the Na salt (Ref 3); ign point 250°; impact sensy on BM app, 65cm (50% explns)(Ref 12); PA app 7 inches (MF 2 inches) (Ref 11). It is useful as a detonator when mixed with Pb Picrate, Pb Styphnate, or similar salts (Ref 5)

Mercury. Ign point 195° (Ref 12)

Potassium. Prepn from the Na salt: to a soln of 30g of the Na salt (see below) in 150ml of w is added a soln of 56.1g of Ag nitrate in 150ml of w, the curdy Ag salt filtered on a Büchner funnel, washed on the filter with 450ml of w, the damp salt suspended in 200ml of w, and the suspension added slowly with stirring to 33.2g of K iodide in 150ml of w. The mixt is stirred for 3 hours, allowed to stand 16 hours, the pptd Ag iodide filtered off, and the w removed in vacuum to give 18.8g (85%) of a gray solid. This is dissolved in 50ml of hot w, clarified with Celite, and cooled to 0°. A small amt of solid is filtered off, and the w evapd as above to give 13.5g (61%) of an almost white solid which analyzed as $CH_2N_4O_4K_2.\frac{1}{2}H_2O$ (Ref 10). It is ranked between Na and Fe salts in expl effect in lead plate test when primed with MF (Ref 7); impact sensy on PA app, 3 inches (MF 2 inches) (Ref 11)

Rubidium. Impact sensy on PA app, 3 inches (Ref 11)

Silver. Prepd by addn of Ag nitrate soln to a soln of the Na salt (see above) (Refs 3 & 10); ign point 181° (Ref 12). When treated with alkyl iodides it gives alkyl esters. From the reaction with Me iodide a colorless and a yellow dimethyl ester were isolated (Ref 3). The UV spectra of the colorless (called α) and the yellow (called β) esters are given in Ref 9; it is concluded that the color of the β ester is due to a nitroso group, hence its structure is probably $(CH_3ON)_2CH_2$ NO

Sodium. Prepn by Traube proc: Na metal (13.8g) is dissolved in 300ml of anhyd et alc, the soln cooled to 6° under N, 34.8g of acet added slowly with vigorous stirring as nitric oxide is passed in at 320ml/min for 140min, and the fine yellow solid collected on a Büchner funnel. This damp solid is dissolved in 130ml of w, made just acid with glac acet ac, and the soln heated on a steam bath until gassing ceases. The mixt is poured into 400ml of ice cold et alc to give 25.3g (39%) of a brown solid which is recrystd twice from et alc:w 2:1 to give a white solid which decomposes without melting at 225–60° and analyzes as a dihydrate

(Ref 10). Its impact sensy on BM app is 75cm (Ref 12), and is ranked between the Sn and K salts in expl effect in lead plate test when primed with MF (Ref 7)

Thallium. Ignition point 208° (Ref 12); has greatest expl effect in lead plate test when primed with MF (Ref 7). It is a useful detonator at d 1.1–1.2g/cc, but usefullness decreases at higher d (Ref 7)

Tin. Is ranked between Tl and Na salts in expl effect in lead plate test when primed with MF (Ref 7)

Written by: **C. H. McDONNELL**

Refs: 1) Beil **1**, 592, [651], {2608} 2) W. Traube, Ber **27B**, 1507 (1894) 3) W. Traube, Ann **300**, 110 (1898) 4) M. Stechow, Ber **57(B)**, 1613 (1924) 5) von Herz, GerP 424380; USP 1625966 & CA **21**, 2065 (1927) 6) H. Wieland & F.N. Kerr, Ber **63(B)**, 570 (1930) 7) T. Urbański, IX CongrInternQuimPuraAplicada **4**, 438–46 & CA **30**, 3649 (1936) 8) M. Carmack & J.J. Leavitt, "The Ultraviolet Absorption Spectra of Nitramines, Nitrosohydroxylamines, and Their Salts", OSRD **3565** (Apr 1944) 9) R.N. Jones & G.D. Thorn, CanJChem **27(B)**, 845 (1949) 10) Anon, "Quarterly Progress Report on Organic Chemistry", Rohm & Haas Co, Redstone Res Div, Huntsville, Ala, **P-53-10** (Dec 1953), US Army Ord Corp Contr W-01-021-ORD-334; AD-53813 11) A.M. Anzalone et al, "Characteristics of Explosive Substances for Application in Ammunition", PATR **2179** (May 1955) 12) M. Piskorz & T. Urbański, BiulWojskowejAkadTechnImJaroslawaDabrowskiego (Warsaw) **8** (84), 112–15 (1959) & CA **54**, 17012f (1960)

MeEDNA (N-METHYLETHYLENEDINITRAMINE or N-MethylEDNA). Structure $O_2NNHCH_2CH_2N(NO_2)CH_3$, $C_3H_8N_4O_4$, mw 164.13, N 34.14%; OB to CO_2 –58.5%; crysts; mp 120.5–22° (Refs 1, 2 & 5). The compd was first prepd in 1888 by the action of Me iodide in alc K hydroxide on EDNA (Ref 2), but no further work was done until WWII when the expl props of MeEDNA were examined at ERL (Ref 3). Other prepns are by the methylation of EDNA with dimethyl sulfate in aq K hydroxide (Ref 7); and by the action of nitric acid in acet anhyd on the compd $O_2NNHC(=NH)NHCH_2CH_2N(NO_2)CH_3$ (Ref 5)

Best Laboratory Preparation. A soln of 82.4g of 3-nitrazabutylamine in 100ml of dry benz was placed in a 500ml 3-necked flask fitted with a stirrer, dropping funnel, and thermometer. The soln was cooled in an ice bath, 75ml of acet anhyd added dropwise, the pptd white solid collected, and dried to give 71g (64% yield) of N-acetyl-N′-methyl-N′-nitroethylenediamine, mp 79–80°. This compd (20g) was added in small portions to a mixt of 100ml of 100% nitric acid and 100ml of acet anhyd cooled to –10 to –5°. The mixt was stirred for 45 mins, poured onto crushed ice, the solid filtered, washed with w, and dried to give 9.5g (37.1% yield) of N-acetyl-N′-methyl-EDNA, mp 55–56°. To 7.6g of this compd was added 25ml of 14% aq ammonia, whereupon it dissolved with evolution of heat. The soln was cooled, acidified with dil HCl, the pptd solid filtered, washed with cold w, and dried to give 5.1g (84.3% yield) of MeEDNA, mp 118–21°, recrystd from ethylene dichloride, mp 121–22° (Ref 6)

Properties. Slightly sol in w, sol in eth & chloroform (Ref 2). UV spectrum in et alc, λ2375Å, E_{max}12950; K salt in 0.2N hydrochloric acid, λ2360Å, E_{max}12200 (Ref 4)

Explosion Temperature. Does not expl to 360° (Ref 3)

Hygroscopicity at 25°. No wt gain at 90% RH, 3.77% at 100% RH (Ref 3)

Impact Sensitivity. BM app, above 90cm (Ref 3)

International Heat Test at 75°. Loses 10.7% by wt (Ref 3)

Power by Ballistic Mortar. 120% of TNT (Ref 3)

Thermal Stability at 135°. Not acid after 300 min (Ref 3)

Vacuum Stability at 120°. Over 12ml evolved in 26–48 hours (Ref 3)

Written by: **C. H. McDONNELL**

Refs: 1) Beil **4**, 573 2) A.P.N. Franchimont & E.A. Klobbie, RecTravChim **7**, 347 (1888) 3) R. McGill in NDRC/OSRD Div 8 Interim Rept **PT-9**, "Preparation and Testing of Explosives", (15 Apr–15 May, 1943), 27 4) R.N. Jones & G.D. Thorn, CanJRes **27B**, 828 (1949)

5) M.W. Kirkwood & G.F. Wright, JOC **18**, 640 (1953) 6) M.B. Frankel & J.P. Kispersky, "Explosives Research", Aerojet Gen Corp Rept **920** (11 Mar 1955) Contr N70NR-46208 7) Y.P. Carignan & D.R. Satriana, JOC **32**, 285 (1967)

Meerscheidt-Hüllessem Stability Tests. J. von Meerscheidt-Hüllessem published a series of papers from 1926 to 1939 describing various stability tests for proplnts and NC. Some of the tests were modifications of existing methods and others were original. Ref 1 describes a weight loss method in which 10g samples were heated in test tubes in a thermostatic bath at 115° with weights taken every 8 hrs. In Ref 2, 2.5g samples were heated at 120° or 135° until litmus paper, suspended inside the app, turned pink. Ref 3 describes a new thermostatic bath for detg stability on heating at 75°. Ref 4 covers the detn of the stability of proplnts from the vol of gases of decompn at const press and temp. Modifications made in the Bergmann-Junk-Mayrhofer test (see Vol **2**, B102-R) are given in Refs 5, 6 & 7, while small changes in the method of Ref 4 are described in Ref 8. Ref 9 contains a method for detg the chemical stability of expls and proplnts at 120° by collecting evolved gases in a burette and then analyzing them by titration or by detg the acidity of a w soln

Refs: 1) J. von Meerscheidt-Hüllessem, SS **21**, 137–41 (1926) 2) Ibid **24**, 10–13 (1929) 3) Ibid **25**, 141–43 (1930) 4) Ibid **28**, 6–8 (1933) 5) Ibid **29**, 192–94 (1934) 6) Ibid, **30**, 73–75 (1935) 7) Ibid **31**, 362–63 (1936) 8) Ibid **32**, 205–06 (1937) 9) Ibid **34**, 167–70 (1939)

Megadina (Megadyne). Belg expl contg Amm perchlorate 78, paraffin wax 16 and Al powd 6%

Refs: 1) CondChemDict (1942), 290 2) A. Pérez Ara (1945), 247

Meganit. A dynamite contg NG 60, nitrated wood pulp 10, nitrated ivory nut meal 10 & Na nitrate 20%

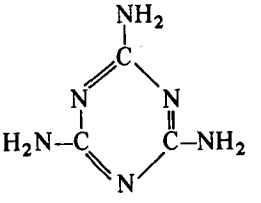
Refs: 1) Naoûm, NG (1928), 284 2) PATR **2510** (1958), Ger 112-L

Meganites. Dynamites manufd in Hungary. One of the compns is as given above under "Meganit". Two other compns are: (1) NG 38.0, Nitrolignine 6.0, Na nitrate 37.5, nitrated ivory nut meal 6.0, sawdust 12.0 and Na carbonate 0.5%, and (2) NG 7.00, Nitrolignine 9.00, Na nitrate 56.25, nitrated ivory nut meal 9.00, rye flour 18.00 and Na carbonate 0.75%

Ref: Daniel (1902), 434

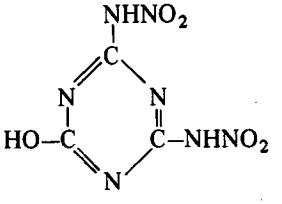
MELAMINE AND DERIVATIVES

Melamine (2,4,6-Triamino-s-triazine, Cyanurotriamide, Cyanuramide). $C_3H_6N_6$, mw 126.13, N 66.64%, OB to CO_2 −114.2%; colorl monocl crysts, mp 354° (decompn), bp subl, RI 1.872



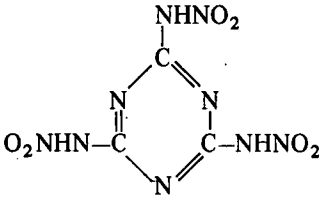
at 20°, d 1.573g/cc. Sl sol in cold w, sol in hot w (0.32g/100g at 20°, 0.60g at 35°, 1.05g at 50°, 2.4g at 75° and 5.14g at 100°), sl sol in alc, insol in eth & acet. Can be prepd by the fusion of dicyandiamide with an acid salt of guanidine, and subsequent purification of the prod (Ref 6), or polymerization of dicyandiamide in an electric arc with N and NH_3 (Ref 9). Melamine has been used as a flash reducing agent in proplnts (Ref 10). It is nonhygr, of low volaty, highly resistant to hydrolysis up to 60°, and is practically neutral in aq solns (pH 7.7). Tests conducted at PicArsn indicated satisfactory impact sensitivity (40 inches with 2kg wt), and no sand crushed in the Sand Test bomb

Melamine Dinitrate (N,N′-dinitroammeline), $C_3H_3N_7O_5$, mw 217.13, N 45.17%, OB to CO_2 −18.4%, mp 228° (decompn). It was prepd and



tested during WWII in Ger & the USA and was found to be an expl less sensitive and less powerful than TNT. Cason (Ref 5) directly nitrated melamine with nitric acid in the presence of Ac_2O at 5° to obtain it as a prod, and Atkinson and Whitmore (Ref 8) elucidated its structure

Trinitromelamine. $C_3H_3N_9O_6$, mw 261.05, N 48.28%, OB to CO_2 −9.2%.



The existence of this compd is uncertain. Ref 7 states that the work by Cason (Ref 5) left the whole problem of synthesizing trinitromelamine in a confusing state. It was therefore important to detn whether this compd could be prepd and whether its performance would show this particular triazine ring to have plosophoric value. Atkinson & Whitmore (Ref 8) showed that the chances of a successful prepn of trinitromelamine was close to being impossible because of extreme hydrolytic susceptibility. They found the closest approach to the desired compd was N-N′-dinitroammeline (Melamine Dinitrate), which has reasonable stability. They further stated that the Q_C value for this compd gave no encouragement to the thought that sym-triazine is a useful plosophoric group

Melamine Picrate. $C_3H_6N_6.C_6H_3O_7N_3$; mw 355.27, N 35.49%, OB to CO_2 −69.8%; light yellow powd; mp 316–17°; nearly insol in w. May deflagrate when heated rapidly (Refs 1, 2, 3 & 4)

Refs: 1) Beil **26**, 245, (74) 2) H. Krall, JCS **103**, 1385 (1910) 3) E. Werner, JCS **107**, 720–21 (1915) 4) A. Ostrogovich, Gazz **65**, 566–88 (1935) & CA **30**, 465 (1935) 5) J. Cason, JACS **69**, 495–98 (1947) 6) Anon, ChemEng **57**, No 4, 134 (1950) 7) ADL, Synthesis HE's, 2nd Report, 21–22 (March 1951) 8) E. Atkinson & E.F. Whitmore, JACS **73**, 4443 (1951) 9) ChemIngTech **26**, 380–83 (1954) & CA **49** (1954), 8311 10) P. Tavernier & M. Lamouroux, MP **38**, 78, 84, 310 & 330 (1956)

Melamina. Ital dynamite invented in 1873 consisting of NG absorbed in a mixt of powd charcoal and siliceous earth

Ref: Davis (1943), 198

Melanite. Fr expl contg NG 83–87, NC 17–13%

Ref: Daniel (1902), 434

Melénite. Gelatinized expl used in Belg

Ref: Daniel (1902), 434

Mélinite. Fr expl used in shells. The original "Melinite" was composed of 70ps PA mixed with 30ps NC, disd in acet or eth-alc (Ref 1). Later Mélinites were either 100% PA or PA to which small quantities of other aromatic nitrocompds were added in order to reduce the mp of PA (120–122°), thus facilitating casting operations (see under Picric Acid)

Refs: 1) Daniel (1902), 434–6 2) CondChemDict (1942), 290 3) Davis (1943), 166

Melland Powder. Prepd in Engl in 1865 by soaking paper sequentially in boiling aq solns of K chlorate, K nitrate and K ferrocyanide. This was followed by rolling the paper thru powd charcoal and then treating it with K chromate and starch. The paper was then rolled to form cartridges, dried at 100°, and waterproofed with a soln of nitrostarch in acet ac

Ref: Daniel (1902), 436

Melling Powder. Brit permissible expl contg Amm nitrate 51–55, Amm oxalate 18–20, Na nitrate 11–13, TNT 5–7, NG 4–6 and wood flour 3–5%

Ref: CondChemDict (1943), 290

Melsens Powder. One of the earlier "progressive smokeless powds". Its grains were ball shaped with outer layers burning more slowly than inner layers

Ref: Daniel (1902), 653

Melting Point (mp). The melting point or freezing point of a pure subs is the temp at which its crysts are in equil with the liq phase at atm press. It is usually called the mp when the equil temp is approached by heating the solid. Ordinarily, mp refers to temps above 0°, the mp of ice (Ref 1). As the mp of a solid subs which does not subl or decomp is one of the best criteria of its purity or identity, the detn of mp is of considerable importance. The presence of even small amts of impurity may alter the mp considerably, usually lowering it. The mp of typical expl and proplnt materials are given below (Ref 2)

Table 1

Material	Formulation or Chemical Name	MP (°C)
Baratol	24/76 TNT/Ba nitrate	79–80
Boracitol	40/60 TNT/Boric Acid	79–80
BTF	Benzotrifuroxan	198–200
Comp B, Grade A	36/63/1 TNT/RDX/Wax	~80
Comp B-3	40/60 TNT/RDX	79–80
Cyclotol 75/25	75/25 RDX/TNT	79–80
DATB	1,3-Diamino-2,4,6-trinitrobenzene	286
DiPAM	Dipicrylamine	304
HMX	Cyclotetramethylene tetranitramine	285–287
HNAB	2,2′,4,4′,6,6′-Hexanitroazobenzene	215–216
NC (12.0% N)	Nitrocellulose, lacquer grade	135 dec
NC (13.35% N, min)	Nitrocellulose, guncotton	135 dec
NG	Nitroglycerin	13.2
NGu	Nitroguanidine	246–247
Octol	25/75 TNT/HMX	79–80
PETN	Pentaerythritol Tetranitrate	139–142
RDX	Cyclotrimethylene trinitramine	204
Tetryl	2,4,6-Trinitrophenylmethylnitramine	130
TNM	Tetranitromethane	14.2
TNT	2,4,6-Trinitrotoluene	80.9

Refs: 1) CondChemDict (1971), 548 2) B.M. Dobratz, "Properties of Chemical Explosives and Explosive Simulants", **UCRL-51319**, Lawrence Livermore Laboratory, Univ of Calif (Dec 1972), 4-6 to 4-7

Melting Point, Determination. Most methods for the detn of mp are microprocedures, and may be conveniently classified on the basis of the type of app used for the detn: (1) the *capillary tube method,* (2) the *heating bar method,* and (3) the *microscope heating stage (micro hot stage) method.*

The *capillary tube method* initially involves packing a powdered sample into a glass capillary tube of uniform diameter and length, carefully sealed at one end so that it forms a rounded tube of uniform thickness. The tube is then attached to a standardized thermometer so that the end of the tube reaches the middle of the thermometer reservoir bulb. This assembly is then inserted into a vessel contg a suitable liq which is uniformly heated so that the temp rises at a rate of about 1° per minute. Ref 1 discusses in detail equipment design and thermometer calibration. It should be noted that this technique is the method most widely used by organic chemists for mp detns, and that most of the mp's of organic compds cited in the literature were obtained in this manner

The *heating bar method,* utilizing heating bars, blocks or benches was developed primarily to overcome some of the shortcomings of the liq bath app (discoloration and fuming at high temps), and to obtain better temp control so as to provide a more accurate measurement of the melting temp. Three general types exist, (1) a simple type heated by a gas flame, in which the temp is recorded by a thermometer, (2) an electrically heated type, with a thermometer to record the temp, and (3) an electrically heated

type, with a thermocouple and potentiometer for temp measurement (Ref 2)

For more precise work, *micro hot stage methods* under a microscope are used. For all compds, except those which are isotropic or become so on heating, the mp can best be observed by means of a polarizing microscope, since the temp at which color disappears and the space lattice is ruptured is the true mp. Among numerous models of micro-hot stages, the Kofler micro-hot stage has attained widespread use and is commercially available (Refs 3 & 4)

Refs: 1) A. Weisberger, "Technique of Organic Chemistry", **VI**, 145–57, Interscience, NY (1954) 2) Ibid, 157–61 3) Ibid, 161–64 4) Kofler & Kofler, "Thermo-Mikromethoden zur Kennzeichnung Organischer Stoffe", Verlag Chemie, Weinheim/Bergstr (1954)

Melville Powders. Expls invented in 1850 consisting of K chlorate, K ferrocyanide and As trisulfide

Ref: Daniel (1902), 436

Mendeleyev, Dmitry I. (1834–1907). Distinguished Rus scientist best known as creator of the Periodic System of the Elements. Inventor of one of the first successful single-base NC proplnts using "pyrocollodion" which was adopted by the Rus Navy in 1895. The same powd, with slightly higher N content, was later introduced in the US Navy

Refs: 1) A. Sapajnikoff, SS **2**, 161–64 (1907) 2) W.A. Tilden, JCS **95**, 2015–77 (1909) 3) A. Pérez Ara (1945), 449

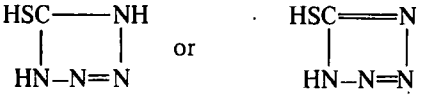
Mendoça-Corteso Powder. Portuguese proplnt similar to Cordite (see Vol **3**, C531-R)

Ref: Daniel (1902), 437

MeNENA. Designation for N-(β-nitroxyethyl) methylnitramine, described under N-(β-hydroxyethyl) methylnitramine in Vol **7**, H241-R

Me_2NENA. Designation for N-(2-nitroxypropyl) methylnitramine, described under N-methyl-n-(2-nitroxypropyl) nitramine in this Vol

5-Mercaptotetrazole (5-Tetrazolethiol). CH_2N_4S, mw 102.13, N 54.93%; needles from alc, mp 205° (dec at about 206–210°);



sol in eth, meth, et acet and w, nearly insol in bz and chlf. Can be prepd in the impure state by heating 5-methyl-mercaptotetrazole with concd hydriodic acid in the presence of AcOH. In a purer state, it may be prepd by acidifying the Na salt of mercaptotetrazole with sulfuric acid (see below). Forms salts, some of which are sl expl (see below)

Sodium Mercaptotetrazole. $NaCHN_4S$, mw 124.11, N 45.15%; colorl needles. Can be prepd by adding to the prod of the reaction between methylmercaptotetrazole and aq hydriodic acid a sufficient amt of soda soln to make the reaction sl alkaline (Ref 2). The resulting cryst compd cont 1.5 mols of w. It is sol in w and alc, less sol in abs alc, insol in eth. May be obtd in a very pure state by dissolving in w and pptg with eth. Such crysts would give pure 5-mercaptotetrazole on acidification with sulfuric acid

Refs: 1) Beil **26**, 409 2) M. Freund & T. Paradies, Ber **34**, 3117–18 (1901)

Mercerized Cellulose (Mercerized Cotton). Mercerization is a process of treating cotton with 25% Na hydroxide which causes it to shrink and become heavier, stronger, denser, and acquire a milky luster; it will not shrink and is more easily dyed. It is more active and easier to nitrate than the original cellulose, but the resulting prod is not very stable

Refs: 1) Hackh's (1944), 523 2) Dorée (1947), 84

Mercuric-Ammonium Salts. Several expl compds of general formula Hg_2NX, where X is either NO_2, ClO_3, ClO_4, IO_4, CrO_4, MnO_4 or BO_3, were prepd by double decompn of Hg_2NiNO_3 with salts of NH_4, Na and K. Trinitrobenzoate, picrate, acetylide and azide compds of Hg_2N are very expl. Compds in which X=I, CNO, SCN or styphnate do not deton but defgr or burn away

Refs: 1) W. Ciusa, BollSciFacoltàChimInd-Bologna **2**, 33–6 (1941) & CA **37**, 3271 (1943) 2) Ibid **3**, 187–9 (1942) & CA **38**, 4133 (1944)

Mercurit. Ger blasting expl contg K chlorate 88 and a high bp neutral tar oil 12%. In *Mercurit II*, up to 20% of the chlorate was replaced by perchlorate
Ref: Marshall, Dict (1920), 60

MERCURY AND ITS SALTS

Mercury (Quicksilver, Hydrargyrum), Hg, at wt 200.61, silvery liq, mp $-38.87°$, bp $356.9°$, d 13.546g/cc at $20°$. Insol in w, HCl, alc and eth; sol in nitric acid. Sometimes found native; *poisonous*. Can be prepd by heating the ore cinnabar (HgS) either in air or with lime. Forms numerous salts, some of which are very expl, eg, Hg fulminate, Hg azide, etc. The presence of Hg in expls, even in minute quants, is undesireable because it affects the result of thermal stability tests. Marshall (Ref 1) describes various tests used in Engl and Ger for its detection in different expls and proplnts
Refs: 1) Marshall **2**, 708–12 (1917) 2) Mellor **4**, 695, 768 (1927) 3) CondChemDict (1950), 429 4) Sax (1968), 902-R

Mercury Azide. See under Azides (Mercuric and Mercurous)

Mercury (Mercurous) Chlorate. See under Chlorates

Mercury (Mercuric) Chlorite. See under Chlorites

Mercury Fulminate. See under Fulminates, Vol **6**, F217-L

Mercury, Fulminating. See Vol **6**, F232-L

Mercury Nitride. See under Fulminating Mercury

Mercury as Masking Agent. Mercuric salts such as $HgCl_2$ were frequently added to wet NC to prevent mold formation. Their presence also allowed defective NC to pass the K iodide-Starch heat (thermal stability-Abel's Test) test (Ref 2). According to F.L. Nathan (Ref 3) the Hg of $HgCl_2$ acted on the iodine liberated in the test paper by nitrous acid fumes, forming a colorless substance and thus masking the color reaction on the paper. Non-vol Hg salts did not affect the test. The usual tests for Hg could not be used because of the difficulty in extrg the salts from org material. A variety of test procedures were proposed to detect Hg salts in micro quantities in NC and expls (Refs 1, 4, 5 & 6)
Refs: 1) W.A. Hargreaves & W.T. Rowe, JSCI **26**, 813 (1907) & CA **1**, 2637 (1907) 2) J. Moir, JSCI **27**, 421 (1908) & CA **2**, 1886 (1908) 3) Anon, Arms&Expls, 7–11 (1909) & CA **3**, 836–37 (1909) 4) J.B. Henderson & P.W. Jones, PrRoySocQueensland **21**, 51 (1909) & CA **3**, 1460 (1909) 5) G.W. Patterson, JSCI **28**, 747 (1909) & CA **3**, 2226 (1909) 6) S.P. Jannopoulos, SS **5**, 47 (1910)

Mercury (Mercuric) Oxycyanide. $HgO.Hg(CN)_2$, mw 469.26, N 5.97%; wh cryst powd, mp (expls on heating), d 4.437g/cc at $19°$, *poisonous;* moderately sol in w, nearly insol in alc, eth and bz. Used as an antiseptic. Can be prepd by heating 10ps Hg cyanide with 10ps Hg oxide in 100ps w, or by other methods (Ref 4). Its expl props were investigated by Kast and Haid (Ref 3), and it was found to be a weak expl. Some of its expl props are as follows, compared with BkPdr as detd by the same investigators, shown in brackets: Trauzl block expansion, 10cc; Sp Energy, 2090kg/l (2810); Q_c, 138cal/g (665); Vol of gases of expl, 190 l/kg (280); Temp of Expl, $2620°$ ($2380°$); Impact Sensitivity with 2kg wt, 60cm; Friction Sensitivity, snaps; behavior in open flame, weak deflagration
Note: An expl took place in Philadelphia in 1916 as mercuric oxycyanide was being transferred from a factory container to storage bottles. The cause was not known (Ref 2)
Refs: 1) Beil – not found 2) Anon, JIEC **8**, 1174 (1916) & CA **11**, 300 (1917) 3) H. Kast & A. Haid, SS **17**, 116–17 (1922) & CA **16**, 4065 (1922) 4) Ullmann **8**, 625 (1931) 5) CondChemDict (1950), 427 6) Sax (1968), 903–04

Mercury Phenyl Nitrate (Hydroxymercuribenzene nitrate). $C_6H_5.HgO.NO_2$, mw 339.72, N 4.12%; plates from alc; mp 188–89° (decompn); very sl sol in hot w, sol in bz and hot alc. Can be prepd by mixing a cold chlf soln of NO_2 with Hg DPhA, or by other methods. It is mildly expl
Refs: 1) Beil **16**, 953 & (563) 2) E. Bamberger, Ber **30**, 511 (1897)

Mercury Perchlorates. Are not expl

Mercury Picrate. See under Picrates

Mercury (Mercuric) Sulfocyanate (Mercuric thiocyanate, Mercuric rhodamide). $Hg(SCN)_2$, mw 316.77, white powd; mp (decompn), *poisonous;* sl sol in w (0.07g/100g at 25°), sol in alc and in NH_3 & NH_4 salts. Can be prepd by pptn of Hg nitrate with Amm sulfocyanate and subsequent soln in a large quant of hot w, followed by crystn. Used in prepn of "Pharaoh's Serpent" and other fireworks (Ref 4)
Refs: 1) Beil **3**, 166, (70) & [115] 2) Ulmann **8**, 626 (1931) 3) CondChemDict (1950), 428 4) Ellern (1968), 143

Mercury Methazonate. See under Methazonic Acid in this Vol

Mérino. Pat in 1882 in Fr, a mixt designed for coating grains of hygroscopic ingredients of expl mixts, such as nitrates or chlorates, to render them waterproof. It contd the following: K chlorate 73, NG 10, sulfur 7, caoutchouc or hard pitch 3, resin or soft pitch 1 & anthracite coal 6%
Ref: Daniel (1902), 437

Mesabi Blasting Agents. A series of metallized expls originated by Dr M.A. Cook at the Univ of Utah, and manufd since 1961 by Mesabi Blasting Agents, Inc. These expls consist of slurries of finely divided Al-AN, Al-AN-TNT and TNT-AN, and present advantages over AN-fuel oil mixts conventionally used in mining operations
Ref: Anon, C&EN **42**, 29 (27 April 1964)

Mesa Type Propellants. An increase in the press at which a proplnt is burned increases the rate of heat transfer from the flame to the proplnt by increasing the density of the gas phase and thereby decreasing the thickness of the region thru which the heat must be transferred, thus increasing the burning rate. The relationship is most commonly expressed by the equation $R=bP^n$, where R is burning rate and P is press, which is known as the *de Saint Robert* or *exponential burning rate equation.* If a log P vs log R plot is made for many proplnts, a family of curves is obtained from which the values of b and n can be evaluated (Fig 1). Some proplnts will not follow this straight-line log relationship and may demonstrate regions of nonconstant, reduced, or negative n. When n is markedly reduced, as shown in Fig 2, the proplnt is known as a *plateau* (from the shape of the curves) proplnt. When n becomes negative for a portion of the press range, as shown in Fig 3, the proplnt is called a *mesa* type proplnt

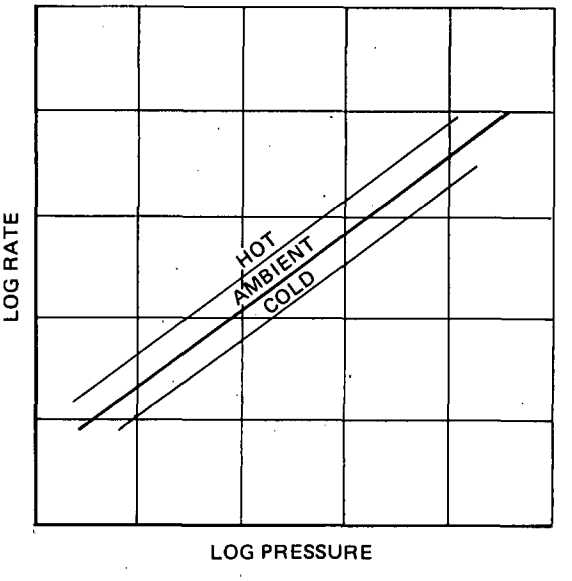


Fig 1 Rate-Pressure Relationship of Propellants for Which $R = bP^n$

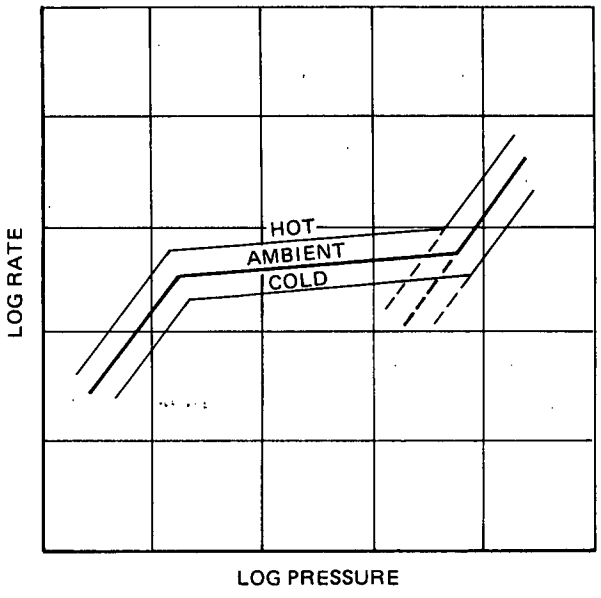


Fig 2 Rate-Pressure Relationship of Plateau Propellants

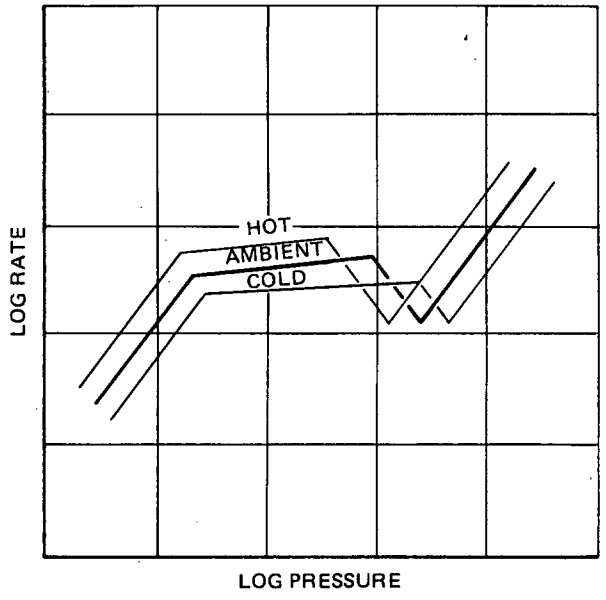


Fig 3 Rate-Pressure Relationship of Mesa Propellants

Refs: 1) Anon, EngrgDesHdbk, "Solid Propellants Part One", **AMCP 706-175** (Sept 1964), 13–14 2) F.B. Pollard & J.H. Arnold, Jr, "Aerospace Ordnance Handbook", Prentice-Hall, Inc (1966), 151–52

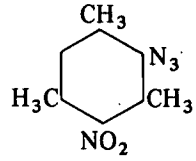
MESITYLENE AND DERIVATIVES

Mesitylene (2,3,5-Trimethylbenzene). $C_6H_3(CH_3)_3$, mp 120.20, colorl liq, fp –44.7°, bp 164.7° at 760mm, 48.7° at 40mm, d 0.8652 g/cc at 20/4°, RI 1.4994 at 20°. Insol in w, misc with alc, eth, acet, benz & CCl_4. Can be prepd by heating benz with 3 moles of formic acid methyl ester & 5 moles of $AlCl_3$ at 80–100° (Ref 2)

During oxidn of mesitylene with nitric acid in an autoclave at 115° to give 3,5-dimethylbenzoic acid, a *violent expln occurred.* The reaction was attributed to local overheating, formation of a trinitro compd, 1,3,5-tri (nitromethyl) benzene, and to *violent decompn* of the latter. Smaller scale prepns with better temp control were uneventful (Ref 3)

Refs: 1) Beil **5**, 406, (199), [313] & {912} 2) S. Landau, Ber **25**, 3011–18 (1892) 3) H. Wilma et al, AngewChemIntern, EdEngl **74**, 465 (1962)

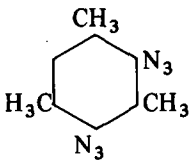
2-Azido-4-nitro-mesitylene (2-Azido-4-nitro-1,3,5-trimethyl benzene). $C_9H_{10}O_2N_4$; mw 206.23, N 27.17%, OB to CO_2 –155.17%,



Needles+H_2O (from aq eth), anhydr crysts (from abs eth), mp 23°. Can be prepd by adding Na azide to a soln of 4-nitro-mesitylene-diazonium chloride-(2) (Ref 2). Expls on fast heating in all org solvs. Loses 2/3 of its N content in concd sulfuric acid

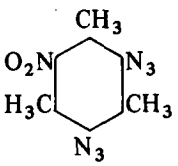
Refs: 1) Beil **5**, [316] 2) G.T. Morgan & G.R. Davis, JCS **123**, 231 (1923) & CA **17**, 1632 (1923)

2,4-Diazido-mesitylene (2,4-Diazido-1,3,5-trimethyl benzene). $C_9H_{10}N_6$, mw 198.21, N 42.41%. Yellow oil, pleasant fruity odor, turns brown in light. Can be prepd by the diazitozation of 2,4-diamino-mesitylene by heating with Na azide in the presence of Na nitrite in alc HCl (Ref 2). Decompn on heating; emits white fumes in sulfuric acid



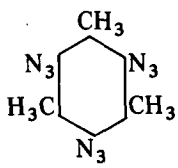
Refs: Beil **5**, [316] 2) G.T. Morgan & G.R. Davies, JCS **123**, 231 (1923) & CA **17**, 1632 (1923)

2,4-Diazido-6-nitro-mesitylene (2,4-Diazido-6-nitro-1,3,5-trimethyl benzene). $C_9H_9O_2N_7$, mw 247.25, N 39.66%, OB to CO_2 −132.66%, clear yellow needles from petr eth; mp 50°. Can be prepd by treating 2,4-diamino-6-nitro-mesitylene with Na nitrite under cold conditions (Ref 2). Decompn on heating; emits N_2 in concd sulfuric acid



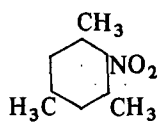
Refs: 1) Beil **5**, [316] 2) G.T. Morgan & G.R. Davies, JCS **123**, 235 (1923) & CA **17**, 1632 (1923)

2,4,6-Triazido-mesitylene (2,4,6-Triazido-1,3,5-trimethyl benzene), $C_9H_9N_9$, mw 243.27, N 51.83%, needles from petr eth; mp 50°. Can be prepd by treating 2,4,6-triamino mesitylene in HCl with 6 moles of Na nitrite in dil HCl in the presence of NaN_3 at −5° (Ref 2). Turns brown in light. Decompn in concd sulfuric acid with N_2 evolution



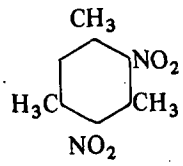
Refs: 1) Beil **5**, [317] 2) G.T. Morgan & G.R. Davies, JCS **123**, 237 (1923) & CA **17**, 1632 (1923)

2-Nitro-mesitylene (2-Nitro-1,3,5-trimethyl benzene). $C_9H_{11}NO_2$, mw 165.21, N 8.48%, OB to CO_2 −208.22%, rhmb cryst (from alc); mp 44°, bp 255° at 760mm, d 1.51g/cc; v sol in hot alc. Can be prepd by nitration of mesitylene with nitric acid (Ref 2).



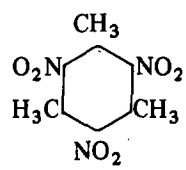
Refs: 1) Beil **5**, 410, (200), [316] & {923} 2) G. Powell & F.R. Johnson, OrgSynth **14** (1934), 68 & CA **28**, 2687 (1934)

2,4-Dinitro-mesitylene (2,4-Dinitro-1,3,5-trimethyl benzene). $C_9H_{10}N_2O_4$, mw 210.21, N 13.33%, OB to CO_2 −144.62%; rhmb cryst (from alc), mp 86°; insol in w, sl sol in hot alc. Can be prepd by dissolving mesitylene in fuming nitric acid, followed by the addition of w which causes dinitro-mesitylene to ppt (Ref 2)



Refs: 1) Beil **5**, 411, (200), [316] & {923} 2) G.M. Dyson & R.F. Hunter, JSCI **45**, 84 (1926)

2,4,6-Trinitro-mesitylene (2,4,6-Trinitro-1,3,5-trimethyl benzene). $C_9H_9N_3O_6$, mw 255.21, N 16.47%, OB to CO_2 −103.4%, triclinic needles (from alc) & prisms (from acet), mp 238.2°, bp expl at 415°, d 1.48g/cc. Insol in w, sl sol in hot alc & eth, misc in hot acet & benz. Can be prepd by treating mesitylene with a mixt of nitric & sulfuric acids in the cold (Refs 2 & 3). Blanksma (Ref 4) prepd it by dissolving mesitylene in sulfuric acid, partial sulfonation taking place, and then adding the soln to nitric acid, with the pptn of trinitro-mesitylene. Kholevo (Ref 6) nitrated mesitylene with nitric acid 27, sulfuric acid 69, water 4% to yield white crysts. The expl power of trinitro-mesitylene is less than PA (Ref 9), and it develops a bomb press 84% that of TNT (Ref 8). Its impact sensitivity is 52% that of TNT (Ref 7), and it expls at 415° (Ref 5)



Refs: 1) Beil **5**, 412, (200), [316] & {923} 2) A. Cahours, AnnChim(Paris) **25**, 40 (1849) & Ann **69**, 245 (1849) 3) A.W. Hoffman, Ann **71**, 129 (1849) 4) J.J. Blanksma, Rec **21**, 256 & 336 (1902); **25**, 165 (1906); **27**, 98 (1909) 5) R.L. Datta & N.R. Chatterjee, JCS **115**, 1006 (1919) & CA **14**, 226 (1919) 6) N.A. Kholevo, ZhPriklKhim **3**, 251 (1930) & CA **24**, 3999 (1930) 7) L. Wöhler & O. Wenzelberg, AngChem **46**, 173 (1933) & CA **27**, 2579 (1933) 8) Davis (1943), 132 9) Blatt, OSRD **2014** (1944)

Mesityl Oxide (4-Methyl-3-penten-2-one). $(CH_3)_2C:CHCOCH_3$, mw 98.15; OB to CO_2 −260.83%, mp −52.85°, oily, colorl liq, with characteristic honey-like odor; bp 129.76° at 760mm, 41° at 20mm, d 0.865g/cc at 20/4°, RI 1.4440 at 20°, vap press 8.7mm at 20°; sl sol in w (3p at 20°); sol in benz, miscible with alc & eth. Prepd by dehydration of acet or diacetone alc. Although it is an excellent solvent for NC and other cellulose esters, its use should be avoided because of its high toxicity and ready flammability. Flash pt 90°F; autoign temp 652°F

Refs: 1) Beil **1**, 736, (382), [793] & {2995} 2) O. Jordan, "Technology of Solvents", Leonard Hill Ltd, London (1937), 179 & 245 3) Sax (1968), 904-R 4) CondChemDict (1971), 557-L

Mesityloxideperoxide (Mesityloxydsuperoxyd in Ger). $C_{12}H_{22}O_6$ (Ref 2), $C_{12}H_{20}O_6$ (Ref 3). Granular crysts from eth-alc. Insol in w, sol in eth, acet, benz & eth-alc. Prepd by allowing mesityl oxide to remain in H_2O_2 for several hours. Deflagrates on impact

Refs: 1) Beil **1**, 738 & (384) 2) R. Wolffenstein, Ber **28**, 2269 (1895) 3) J. Pastureau, BullFr [4], **25**, 595 (1919)

Metaldehyde (Polymerized acetaldehyde), $(CH_3CHO)_4$; mw 176.21, OB to CO_2 −181.60%, colorl cryst, mp 246°, subl 112–15°, flash p 97°F; sol in benz & chlf, sl sol in alc & eth, insol in w. For prepn of acetaldehyde & metaldehyde see Vol **1**, A14. Used as a substitute for gum lacquer in illuminating compns developed after WWI. It burned without leaving any slag and reduced compn sensitivity to impact (Ref 1). Urbański & Wozniak (Ref 2) prepd compns contg metaldehyde 8–11, Ba chlorate 80 & lactose 4–9%, and reported deeply saturated green flames on burning. In a compn contg metaldehyde 8, milk sugar 6, K chlorate 60 & Sr oxalate 26%, poor propagative burning and a weak red color were obtained

Metaldehyde is flammable and a dangerous fire risk. It is highly toxic and a strong irritant to skin and mucous membranes (Refs 3 & 4). Its condensation reaction with acid anhydrides, alcohols, ketones and phenols can be violent. Acetaldehyde oxidizes readily in air to unstable peroxides that may explode spontaneously. Its combination with bromine, chlorine, fluorine or iodine can be violent (Ref 5)

Refs: 1) S. Foulon, SS **28**, 376 (1933) 2) T. Urbański & S. Wozniak, MAF **16**, 797 (1937) 3) Sax (1968), 905-L 4) CondChemDict (1971), 558-L 5) Anon, "Manual of Hazardous Chemical Reactions", Natl Fire Protection Association, Boston, Mass (1971), 491M-6

Metals, Compatibility of Common Explosives With. The following table, compiled from Refs 1, 2, 3 & 6, details the compatibility of dry expls (0.2% moisture max) with metals commonly used in military hardware. For all of the listed metals, except phosphate coated steel, intimate contact was maintained with the various expls at ambient temp for a two year period (Ref 2). Phosphate coated steel was exposed for six months at 71° (Ref 3)

Exposure of moist expls (0.5% moisture) with common metals at 50° for two years (two months at 71° and 100% relative humidity for phosphate coated steel) resulted in from very slight to very heavy corrosion for practically all of the metals shown in the above table. Stainless steel was unaffected by any expl, acid proof black painted steel was not affected by 75/25 Tetrytol and 50/50 Pentolite, and Mg-Al alloy (J1) was unaffected by BkPdr. Phosphate coated steel exhibited considerable corrosion with BkPdr, but was unaffected by TNT, RDX, Comp B, Tetryl or 50/50 Pentolite (Ref 3)

An important class of expl materials contains metallic fuels and inorganic oxidants. Examples are Tritonal (TNT/Al, 80/20), Amatols (TNT/AN, 28/80 & 80/20), and Minol-2 (TNT/AN/Al, 40/40/20). Oxidants other than nitrates, such as chlorates and perchlorates, may be employed. Water solns containing these cations are highly corrosive to metals. Alkaline metal salts, for example, in the presence of moisture, will pit Al quickly (Ref 6)

In delay compns, such corrosion problems have resulted in the widespread use of chromates, which, in addition to being insoluble in w, tend to inhibit corrosion (Ref 6)

Of particular interest is the reaction of ni-

TABLE 1

COMPATIBILITY OF COMMON EXPLOSIVES AND METALS *

	Lead Azide	Black Powder	Lead Styphnate	Composition B	PETN	RDX	Tetryl	TNT	50/50 Amatol	Haleite	75/25 Tetrytol	60/40 Ednatol	50/50 Pentolite
Magnesium	N	A N			B N S	C VS		BNS	C H	C VS	A	C VS	A
Aluminum	A N		A N		A N VS	A N VS	A N			A	A	B VS	A
Zinc	C N					A	B VS						
Iron	N					A	B S						
Steel	C N	C VS			B N VS	A VS S	C H	C VS	C VS	C VS	C VS	C VS	C VS
Tin	A N					A	A N						
Cadmium	C						A						
Copper	D N		A		B N VS	A S S	A N		B D	A	A	B VS	A
Nickel	C					A	A N						
Lead	N					A	A N						
Cadmium plated steel					B N S	VS VS	A N			A	A	A	A
Copper plated steel	N				B N VS	B VS VS	A VS			A	A	B VS	A
Steel, acid-proof black paint					A N	A N				A N	A N	A N	A N
Nickel plated steel	N				B N VS	A N S	A N			A	A	A	A
Zinc plated steel	N				B N VS	A N S	A N			A	A	B VS	B VS
Tin plated steel	N					A	B VS						
Phosphate coated steel		A N		A N		A N	A N	A N					A N
Magnesium aluminum	VS	A N			B N S	B VS		B N S	C H	B VS	B NS	B S	A N
Monel Metal	C N										A	A	A
Brass	D N				B N S	A S S	B VS						
Bronze	N					A	A VS						
18-8 stainless steel	A N		A		A N N	A N N	A N		A N	A N	A N	A N	A N
Titanium	N					N	N						
Silver	N					N	N						

CODE

A no reaction
B slight reaction
C reacts readily
D reacts to form sensitive materials
H heavy corrosion of metals
VS very slight corrosion of metals
S slight corrosion of metals
N no corrosion

* Multiple symbols under an entry denotes more than one investigation.

trates with Cu in the presence of moisture. Phillips, at PicArsn, conducted storage tests of Cu foil in contact with AN, 80/20 and 50/50 Amatols containing various percentages of w in both open and closed containers at 50°. In the closed containers, a sensitive, purple tetramino cupric nitrate formed very readily in the presence of AN, less readily with 80/20 Amatol, and to little or no extent with 50/50 Amatol. In open containers there was no formation of the purple salt. In all cases except those in which the minimum amount of moisture was present, there was corrosion of the Cu strips with the formation of blue and green basic nitrates, and it was found that at ambient temps, these basic nitrates would react with Cu to form the sensitive purple salt. It was concluded that no Cu or Cu alloys could be used in ammo which could contact Amatol fillers (Ref 1)

The reaction of Lead Azide (LA) with Cu (see Table) deserves special comment. Although this reaction is relatively slow, even in the presence of w, some forms of Cu Azide are so sensitive that they create a serious hazard even in minute quantities, particularly when in contact with LA. For this reason, Al and stainless steel containers are now used exclusively. PicArsn requires that all new fuze designs contain no Cu or Cu alloys, with the possible exception of the electrical system. Even here, the Cu must be coated for protection against the formation of hydrazoic acid. Another prohibition involves the use of Pb thiocyante in contact with Al (Refs 4, 5 & 6)

Written by: **H. L. HERMAN**

Refs: 1) A.J. Phillips, "Study of the Properties of Tetramino Cupric Nitrate", PATR **1302** (1943) 2) L.H. Eriksen, "Action of Explosives on Metals Used in Ammunition", PATR **1493** (1945) 3) B.V.Zlotucha & M. Baer, "The Reactivity of Explosives with Metals and Protective Finishes", PATR **2288** (1956) 4) B.T. Fedoroff et al, Encycl **1**, PATR **2700** (1960), A532-L to A 535-R 5) S. Urman & I. Kabik, "Hazards of Copper Azide (U)", USNOL TR **72-113** (1972) (Confidential) 6) Anon, "Engineering Design Handbook, Explosives Series, Explosive Trains", **AMCP 706-179** (1974), 4-11 & 4-12

Metalline Nitroleum (Nitroglycerin-metal). Dynamite in which powdered red lead (Pb_3O_4) is used as an absorbent. Plaster of Paris may be added to the mixt
Ref: Daniel (1902), 437

Metals, Explosive Working of. See under Explosive Fabrication of Metals in Vol **6**, E415-R to E418-R

Meteor Dynamite. A blasting expl manufd in the 19th century by the Oliver Powder Co of Wilkes Barre, Pa, USA. This company also manufd "Oliver's Flameless Dynamite"
Ref: Daniel (1902), 438 & 590

METHANE AND DERIVATIVES

Methane. (Marsh Gas, Fire Damp), Methan, Sumpfgas, or Grubengas (Ger); Méthane or Grisou (Fr); Metan (Russ); CH_4; mw 16.04; a colorl, odorless, and tasteless gas; mp −182.5°, bp −161.5°, crit temp −82.1°, crit p 672 psi (Ref 1); CA Registry No 74-82-8
Occurrence. It is the chief constituent of natural gas, which is from 60–98% methane. It occurs to some extent in all coal mines where mixts with air are called by the miners "fire damp" as it is the cause of almost all coal mine fires and explns (Ref 3). It also occurs in the gases evolved when organic matter decomposes anaerobically as in the bottoms of swamps and marshes, hence the name "marsh gas"
Preparation. It can be recovered from the gases produced by the destructive distn of coal (coal gas) or from the prepn of coke (coke oven gas). It can also be prepd by the catalytic reforming of other low-boiling hydrocarbons (ethane to butane) (Ref 3)
Flammability. It is very flammable and forms expl mixts with air; the expl limits are: lower 5.3%, upper 14.0% by vol (Ref 1)
Heat of Combustion. 1009 BTU/cu ft (Ref 3)
Solubility. In w 5.6cc/100ml at 0°, 9cc/100ml at 20°; in alc 45.1cc/100ml at 20°; in eth 104cc/100ml at 10°; sl sol in oleum (Ref 1)
Specific Heat. 2.48 cal/g betw 10 and 200° & 1 atm p (Ref 2)

Refs: 1) Beil **1**, 56, (1), [1], {1}& ⟨3⟩ 2) H.B. Dixon & J. M. Crofts, JCS **105**, 2036 (1914) 3) Kirk & Othmer **13**, (1964), 364

Azidomethane (Methyl Azide). (called Azidomethan or Methylazid in Ger); CH_3N_3; mw 57.06, N 73.65%; a colorl, mobile, ethereal liq with an unpleasant odor similar to hydrazoic acid (Ref 2); bp 20–1°; d^{8}_{15}, 0.869g/cc (Ref 2); CA Registry No 624-90-8

Preparation. It was first prepd by warming a strongly alk soln of Na azide with Me sulfate (Refs 2 & 20), and this is the only practical prepn. It has also been prepd by the reactn of diazomethane with hydrazoic acid (Ref 6)

Chemical Reactions. Upon treatment with Amm chloride and Me Mg iodide in aq ammonia, it gives dimethyltriazene ($CH_3NHN{:}NCH_3$) (Ref 2). A mixt of Me azide with H reacts in the cold with triphenylphosphine or triethylphosphine to form the phosphine Me imide ($R_3P{:}NMe$) (Ref 3). It can be hydrogenated over Pd/C to Me amine (Ref 5). Me azide, like other azides, will condense with acetylenes to form 1,2,3-triazoles (Ref 10). It was condensed with either argon or carbon dioxide at 4.2° and 50°K respectively, and the solid photolyzed with a Hg vapor lamp. IR analysis showed the formation of methyleneimine ($CH_2{:}NH$) which is further photolyzed to HNC (the unstable parent of isocyanides) (Ref 17). Treatment of Me azide with toluene in the presence of anhyd Al chloride gave a mixt of N-methyltoluidines (Ref 18). Photolysis of Me azide in inert solvs at –80° gave N and hexamethylenetetramine (Ref 19). Me azide was found to detonate in the presence of traces of Hg, but not in its absence; it was proposed that the deton was caused by the formation of traces of Hg azide (Ref 16)

Explosion Temperature. Above 500° (Ref 2)

Molar Refraction. The molar refraction of the azido group in alkyl azides was estd to be ca 9.4 (Ref 14). For a discussion of molar refraction see Ref 9, p 528

Spectral Data. Infra Red. The band at 2143cm^{-1} is assigned to the N-N stretching freqy (Ref 12); other freqys are assigned in Ref 13

Mass. The appearance potentials and rel abundance of the ions from Me azide are given in Ref 15

Nuclear Magnetic Resonance. The N-14 NMR peaks for Me azide are at 129.5 ± 0.5, 167.5 ± 0.5 and 305 ± 1 ppm (NMe is std). The farthest upfield peak is due to the N attached to C (Ref 21)

Ultra-Violet. In the vapor phase the UV peak is at 3900Å. In eth it is broadened and shifted to ca 3950Å (Ref 7)

Sensitivity. Its sensitivity is greater than indicated in the earlier literature. An explosion occurred when a sample was being sealed in a closed bomb resulting in loss of eyesight (Ref 11)

Thermal Decomposition. The therm decompn at 245° is 1st order and a white residue is formed (Ref 4). It was restudied at 200–240° and 0.08 to 46.6cm of Hg. The decompn was found to be homogeneous and 1st order with a const K of $3.02 \times 10^{15} e^{43,500/RT}$ (Ref 8)

Refs: 1) Beil **1**, 80, [48], {117}& ⟨108⟩ 2) O. Dimroth & W. Wislicenus, Ber **38**, 1573 (1905) 3) H. Staudinger & E. Hauser, Helv **4**, 871 (1921) & CA **16**, 1074 (1922) 4) H.C. Ramsperger, JACS **51**, 2142 (1929) 5) H. Weinhaus & H. Ziehl, Ber **65**, 1461 (1932) 6) E. Oliveri-Mandala, Gass **62**, 718 (1932) & CA **27**, 89 (1933) 7) A. Hantzsch, Ber **66**, 1351 (1933) 8) J.A. Leermackers, JACS **55**, 3100 (1933) 9) S. Glasstone, "Textbook of Physical Chemistry", van Nostrand (1946), 528 10) F.R. Benson & W.L. Savell, ChemRevs **46**, 13 (1950) 11) C. Grundmann & H. Haldenwanger, AngChem **62**, 410 (1950) & CA **45**, 355e (1951) 12) J. Fujita et al, JACS **78**, 3297 (1956) 13) L.J. Bellamy & R.L. Williams, JCS **1956**, 2755 14) E. Lieber et al, JSciIndResearch(India) **16B**, 95 (1957) & CA **51**, 13808a (1957) 15) J.L. Franklin et al, JACS **80**, 299 (1958) 16) C.L. Currie & B. deB. Darwent, CanJChem **41**, 1048 (1963) 17) D.E. Mulligan & M.E. Jacox, JChemPhys **39**, 712 (1963) 18) P. Koviac et al, JACS **86**, 1590 (1964) 19) E. Koch. Tetrahedron **23**, 1747 (1964) 20) Houben **10/3** (1965), p 802 21) M. Witowski, JACS **90**, 5683 (1968)

Azomethane. CA Registry No 503-28-6. The following supplements the article in Vol **1**, A655-R under Azomethane

Preparation. It has been prepd by the oxidn of N,N′-dimethylhydrazine with K dichromate (Ref 2). The action of Cu(II) sulfate in aq Na acetate contg HCl, Na chloride, or Cu(II) chloride on the same hydrazine gives the Cu(I) chloride complex of azomethane (Refs 3 & 13)

Chemical Reactions. It burns with a luminous flame and is readily expld (Ref 2). It is reduced with Zn dust and Na hydroxide to dimethyl hydrazine (Ref 2). Action of concd HCl forms methylhydrazine and formaldehyde (Ref 2). Treatment in anhyd eth with Na metal forms a solid adduct which gives dimethylhydrazine on addn of w (Ref 4). For a review of thermal and photochem reactions see Ref 8

Explosive Limits. In mixts with air the crit press at which expl occurs varies inversely with temp betw 350 and 380° (Ref 6)

Spectra. Infra-Red. In the vapor phase the major peaks are at 3, 4, 6.9, 9 & 10μ (Ref 9)

Nuclear Magnetic Resonance. A single proton peak is at 6.32τ (Ref 12)

Ultra-Violet. There is a single absorption peak at 3390Å (Ref 4)

Viscosity. The visc of the gas is $0.754 \times 10^{-4} \pm 1\%$ poise (Ref 7)

Uses. It is a source of free Me radicals (Ref 8). Its addn at a level of 0.1–5.0% was found to improve the octane rating of diesel fuels (Ref 10)

Cuprous Chloride Complex. For prepn see above. It is a red cryst solid, readily decompd into its components at 135–40° (Refs 4 & 13). X-ray diffraction showed that the azomethane mols lie betw the infinite folded sheets of the Cu(I) chloride (Ref 11). The complex is used in the prepn of highly pure samples of azomethane (Ref 7)

Refs: 1) Beil **4**, {1747} 2) J. Thiele, Ber **42**, 2575 (1909) 3) O. Diels & W. Koll, Ann **443**, 268 (1925)& CA **19**, 2499 (1925) 4) W. Shlenk & E. Bergmann, Ann **463**, 315 (1928) & CA **22**, 4499 (1928) 5) H.C. Ramsperger, JACS **50**, 123 (1928) 6) A.O. Allen & O.K. Rice, JACS **57**, 312 (1935) 7) H. Henken & H.A. Taylor, JChemPhys **7**, 829 (1939) 8) E.W.R. Steacie, "Atomic & Free Radical Reactions", ACS Monograph **No 102** (Reinhold 1946) & 2nd ed, ACS Monograph **No 125** (Reinhold 1954) 9) R.H. Pierson et al, AnalChem **28**, 1223 (1956) 10) C.L. Levesque, USP 2877102 & CA **53**, 12656b (1959) 11) I.D. Brown & J.D. Dunitz, Acta-Cryst **13**, 28 (1960) 12) J.P. Freeman, JOC **28**, 2510 (1963) 13) Houben **10/2** (1967), p 764

Azo-Halogen Derivatives of Methane

1,1,1-Trifluoroazomethane, $F_3CH{:}NCH_3$, mw 112.05, N 25.00%; bp 2.6°; CA Registry No 690-21-1. Prepd by the action of CF_3NO on Me amine in a sealed tube or autoclave

Refs: 1) Beil – not found 2) A.H. Dinwoodie & R.N. Hazeldine, JCS **1965**, 2266 3) Houben **10/2** (1967), p 776

Pentafluoroazomethane, $F_3CN{:}NCHF_2$, mw 148.04, N 18.93%; bp –9°. Prepd by fluorination of $F_3CN{:}NCH_3$ with Co trifluoride or Mn trifluoride

Refs: 1) Beil – not found 2) A.S. Filatov et al, ZhObshchKhim **38**, 33 (1968) & CA **69**, 18501y (1968)

Hexafluoroazomethane, $CF_3N{:}NCF_3$, $C_2F_6N_2$, mw 166.04, N 16.88%; a gas whose color has been described as colorl (Ref 6), greenish (Ref 2), and pale greenish yellow (Ref 5); mp –133°; bp –31.6°; d 1.487g/cc (Refs 1 & 2); CA Registry No 372-63-4

Preparation. A compd $C_2F_6N_2$ was reported in 1936 among the prods of the action of F on Ag cyanide (Ref 2), but the structure was not proved until 1940, when it was prepd in good yield by the action of I pentafluoride on I cyanide (Ref 4). Since then it has been prepd as the major prod from the action of Ag difluoride on cyanogen chloride (Refs 6 & 10); by the interaction of Cl, Na fluoride, and cyanogen chloride in a sealed tube at 50° for 1 hour (Refs 9 & 10); and in low yields by the fluorination of ethylene diamine or ethyleneimine (Ref 7)

Chemical Reactions. Its thermal decompn in toluene gives N and hexafluoroethane plus small amts of tetrafluoromethane and tetrafluoroethylene (Ref 8). Photolysis of the gas gives N, hexafluoroethane, and higher boiling prods; higher press favors the formation of the high boiling prods (Ref 5)

Dielectric Coefficient. In the gas phase it is 0.46×10^{-18} (Ref 3)

Explosive Properties. In the gas phase it expl on contact with a flame or an elec spark (Ref 4). This expln gives an extremely high rate of press development, indicating it to be more hazardous than acetylene in press systems (Ref 9)

Heat of Vaporization. At −31.6° it is 5470 cal/mole (Ref 4)
Spectra. Infra-red. In the gas phase the peaks are at 7.16, 7.91, 8.32, 8.80 and 9.10μ (Ref 9)
Ultraviolet. In Me chloride an absorption peak is at ca 360 mμ (Ref 9)
Refs: 1) Beil **4**, {1748} 2) O. Ruff & M. Giese, Ber **69**, 602 (1936) 3) K.L. Ramaswamy, ProcIndianAcadSci **2A**, 364 (1935) & CA **30**, 1622 (1936) 4) O. Ruff & W. Willenberg, Ber **73**, 725 (1940) 5) J.R. Dacey & D.M. Young, JChemPhys **23**, 1302 (1955) 6) O. Glesmer et al, ZAnorgChem **282**, 80 (1955) 7) J.A. Gervasi et al, JACS **78**, 1679 (1956) 8) D. Clark & H.O. Pritchard, JCS **1956**, 2136 9) W.J. Chambers et al, JACS **84**, 2337 (1962) 10) Houben **10/2** (1967), p 775

1-Chloro-1,1-difluoroazomethane, $ClCF_2N{:}NCH_3$, mw 128.51, N 21.80%; bp 44°; d at 20°, 1.871 g/cc. Prepd by reaction betw $ClCF_2NO$ and Me amine
Refs: 1) Beil – not found 2) S.P. Makarov et al, DoklAkadN **141**, 357 (1961) & CA **56**, 11245g (1962)

1′-Chloro-1,1,1-trifluoroazomethane, $F_3CN{:}NCH_2Cl$, mw 146.50, N 19.12%; bp 47–48°; d at 20°, 1.4400g/cc, RI at 20°, 1.3780. Prepd by action of Cl on $F_3CN{:}NCH_3$
Refs: 1) Beil – not found 2) A.S. Filatov et al, ZhObshchKhim **38**, 33 (1968) & CA **69**, 18501y (1968)

Chloropentafluoroazomethane, $ClCF_2N{:}NCF_3$, mw 182.50, N 15.35%; bp 4.5°; prepn not given in Refs
Refs: 1) Beil – not found 2) V.A. Ginsberg et al, DoklAkadN **142**, 88 (1962) & CA **57**, 642e (1962)

1,1-Dichloro-1′,1′,1′-trifluoroazomethane, $Cl_2CHN{:}NCF_3$, mw 180.95, N 15.48%, bp 80°; d at 20°, 1.4518g/cc; RI at 20°, 1.3860. Prepd by the action of Cl on $F_3CN{:}NCH_3$
Refs: 1) Beil – not found 2) A.S. Filatov et al, ZhObshchKhim **38**, 33 (1968) & CA **69**, 18501y (1968)

1,1′-Dichlorotetrafluoroazomethane, $ClCF_2N{:}NCF_2Cl$, mw 198.94, N 14.08%; bp 40.5°; d at 20°, 1.458g/cc; RI at 20°, 1.3275. Prepn not given in Refs
Refs: 1) Beil – not found 2) V.A. Ginsberg et al, DoklAkadN **142**, 88 (1962) & CA **57**, 642e (1962)

1,1,1-Trichlorotrifluoroazomethane, $Cl_3CN{:}NCF_3$, mw 215.48, N 13.01%; bp 55° at 92mm; d at 20°, 1.6147g/cc; RI at 20°, 1.4628. Prepd by action of Cl on $F_3CN{:}NCH_3$
Refs: 1) Beil – not found 2) A.S. Filatov et al, ZhObshchKhim **38**, 33 (1968) & CA **69**, 18501y (1968)

1,1,1′-Trichlorotrifluoroazomethane, $Cl_2CFN{:}NCF_2Cl$, mw 215.48, N 13.01%; bp 78°; d at 20°, 1.513 g/cc; RI at 20°, 1.3275; prepn not given in Refs
Refs: 1) Beil – not found 2) V.A. Ginsberg et al, DoklAkadN **142**, 88 (1962) & CA **57**, 642e (1962)

Bromopentafluoroazomethane, $BrCF_2N{:}NCF_3$, mw 226.95, N 12.35%. Prepd by the reaction of Ag difluoride with $Br_2C{:}NN{:}CBr_2$
Refs: Beil – not found 2) R.A. Mitch & P.H. Ogden, JOC **31**, 3833 (1966)
All the halogenated azomethanes are yellow gases or liquids which expl on heating
Ref: 1) V.A. Ginsberg et al, DoklAkadN **142**, 88 (1962) & CA **57**, 642e (1962)

Azoxy Derivatives of Methane

Azoxymethane. CA Registry No 25843-45-2. The following supplements the article on Azoxymethane in Vol **1**, A670-L. It has been prepd by the electrochem redn of nitromethane in 1N aq K hydroxide, with N-methylhydroxylamine as an intermediate, yield 60% (Ref 4). The proton NMR spectrum shows chem shifts of 6.93 & 5.95τ (Ref 1). Photolysis with a Hg arc lamp gives N, nitrous oxide, methane, and ethane (Ref 2). It was found to produce colon and rectal carcinomas in rats after oral administration at 12mg/kg weekly, induction period 235 days (Ref 3)
Refs: 1) J.P. Freeman, JOC **28**, 2508 (1963) 2) B.G. Gowenlock, CanJChem **42**, 1936 (1964) 3) H. Druckrey, CarcinomaColonAntecedent-Epithelium **1970**, 267 & CA **75**, 17702b (1971) 4) P.E. Iversen, ChemBer **104**, 2195 (1971)
1,1,1-Trifluoroazoxymethane. $F_3CN(O){:}NCH_3$, mw 128.06, N 21.88%, OB to CO_2 −68.72%; bp −15° at 150mm; d at 20°, 1.349g/cc. Prepd by the interaction of CF_3NO and CH_3NHOH
Refs: 1) Beil – not found 2) A.Ya. Yakubovich et al, DoklAkadN **140**, 1352 (1961) & CA **56**, 9937c (1962)
Hexafluoroazoxymethane. $F_3C(N_2O)CF_3$, mw

182.04, N 15.39%; bp 6.9°, Q_{vap} 6410 cal/mole (Ref 2); CA Registry No 371-56-2. It was first prepd by the reaction of F_3CNO with activated C in a sealed tube at 150° for 1 hour, yield 47% (Ref 2). More recent preps are by the reaction of F_3CNO with guanidine, yield 90% (Ref 3); and by the interaction of F_3CNO with the eth complex of F_3CNHOH, yield "good" (Ref 4). It is stable to w, 10% HCl, and 10% aq NaOH (Ref 2). The IR absorption bands are listed in Ref 2

Refs: 1) Beil – not found 2) J. Jander & R.N. Hazeldine, JCS **1954**, 919 3) M.A. Englin & A.S. Filatov, ZhObshchKhim **38**, 1409 (1968) & CA **69**, 66819e (1968) 4) V.A. Ginsberg et al, ZhObshchKhim **38**, 2505 (1968) & CA **70**, 57055w (1969)

Nitromethane (NMe). Nitromethan (Ger), Nitrométhane (Fr), Nitrometano (It & Sp), Nitrometan (Russ & Pol); CH_3NO_2; mw 61.04, N 22.95%, OB to CO_2 –39.3%, to CO –13%; a liq, colorl when pure, coml grades are pale yellow, mp –28.55° (Refs 1 & 32), bp after drying over Ca chloride and distn 100.85–1.05° (Ref 4), 101.20° (Ref 32); d at 20°, 1.13816 g/cc (Ref 32); RI at 20°, 1.38149 (Ref 40); visc at 25°, 0.632 centipoise; the driest samples have the highest visc (Ref 17); CA Registry No 75-52-5

Historical. NMe was first prepd by Victor Meyer who treated Me iodide with Ag nitrite and obtained a 90% yield (Ref 2). This proc came to be known as the Victor Meyer reaction (Ref 50). It has also been prepd by the action of Me sulfate on K nitrite (Ref 3). In the Victor Meyer reaction the ratio of NMe to Me nitrite obtained was found to be dependent upon solv, temp, and the reagents used (Ref 5)

Preparation. Lab scale: To 500g of chloroacetic acid and 500g of cracked ice is added enough cold 40% NaOH (ca 360cc) to make the soln alk to phenolphthalein as the temp is held below 20°. This soln is mixed with 365g of Na nitrite in 500cc of w and the mixt heated in a 3ℓ round bottom flask fitted with a therm dipping into the liq and an efficient condenser set for downward distn. The soln is heated gently until gas is evolved (ca 80°). The heat is removed and the reaction proceeds spontaneously as the temp rises to ca 100° and the NMe/w azeotrope distils over at 90°. After the reaction subsides, heat is applied until the temp reaches 110° and NMe evolution ceases. About 113cc of NMe and 370cc of w are obtained. The w is mixed with ¼ its wt of NaCl and distd to give 10–12cc of NMe. The crude NMe is dried over anhyd Ca chloride and redistd to give 115–25cc of pure NMe, bp 98–100°, yield 35–38% (Ref 11)

NMe is now commercially available and is prepd by the vapor phase nitration of methane at a ratio of 9 moles of methane to 1 mole of nitric acid at 475° and a residence time of 0.18sec (Ref 12); or by the similar nitration of aliphatic hydrocarbons (Ref 8). Other prepns are from Me sulfate and Na nitrite (Ref 26); by the oxidn of Me amine with dinitrogen trioxide in the gas phase or in methylene chloride, yield 27% (Ref 28); and by the passage of Me chloride into hot aq Na nitrite and Na carbonate in an efficient column, yield 60% (Ref 28). Comm NMe was purified for conductivity and other measurements by the following procedure: The NMe was distd, dried over anhyd Ca chloride, and redistd. During the final distn the distillate was passed thru a conductivity cell and the fractions with the lowest conductivity saved. The lowest obtained was 0.15×10^{-7} mho (Ref 6)

Chemical Reactions. For a review of the reactions of NMe see Ref 10. A brief list of its principal reactions follows:

1) It is readily reduced to Me amine, and a number of chem, catalytic, and electrochem procedures have been used (Ref 10). 2) In most cases the redns can be stopped at the hydroxylamine stage to give N-Me hydroxylamine (Ref 10). 3) The action of strong acids on salts of NMe gives derivs of formaldehyde (Ref 10). 4) Na hydroxide first forms the Na salt of NMe, then the Na salt of methazonic acid, and finally the Na salt of nitroacetic acid (Ref 10). 5) With Hg(II) chloride is formed first the Hg salt of NMe which rearranges and dehydrates to MF (Ref 10). 6) NMe is readily halogenated in the presence of base to give halonitromethanes (see below). 7) It undergoes many condensation and addition reactions with carbonyl compds, active methylene compds, and activated olefins (Refs 10, 43, 46 & 51). 8) It reacts with formaldehyde to form $(HOCH_2)_3CNO_2$, trivial name NIB-glycerol. This is a large volume industrial process

(Refs 1 & 7). 9) Treatment with acrylonitrile in the presence of a trace of Na methoxide gives $(NCCH_2CH_2)_3CNO_2$ (Ref 45). For details of the compds prepd from NMe see in the Encycl under the individual compds

Analytical. A diagnostic test to distinguish among RCH_2NO_2, R_2CHNO_2, and R_3CNO_2 is to treat the compd with nitrous acid. The first gives a red color, the second a blue color, and the third remains colorless (white). The test is called the red, white, and blue test (Ref 10). The polaragraphic analysis of NMe was studied in buffered solns. The half wave potential was found to vary with pH; hence the necessity of using a buffered soln (Ref 22). Gas chromatog retention times for NMe at 50–90° and 110–50° are listed in Ref 38, various supports and stationary phases were used. Small amts were quanty detd by coupling with p-diazobenzenesulfonic acid and detg the colored prod spectrophotometrically (Ref 37)

Azeotropes. NMe forms an azeotrope with w contg 76.4% NMe, bp 90° (Ref 40). It forms azeotropes with a large no of org liqs (Refs 1, {109}& 25)

Brisance. Sand Test. 8.1g of sand were crushed/g of NMe (Ref 36)

Card Gap Test. Results are given on NMe and mixts of NMe with TeNMe. A mixt having a slightly neg OB gave the highest value of 75 cards (Ref 35). Another gap test is given in Ref 22; with a donor charge of 50g of PETN/Mn 95/5 the max gap for deton transfer was found to be 3mm

Critical Diameter. The crit diam for deton propagation in iron tubes is 25mm, in brass 7mm (Ref 31)

Detonability. Some conditions under which deton of NMe has been observed are: 1) When subject to shock in heavy walled containers in large vol, as tank cars and trucks. After two disasterous explns of NMe in tank cars, its shipment in bulk was forbidden by the ICC (Ref 34). 2) It can be detond by the sudden impact of high press air, or by high press flow thru contrictions in piping (Ref 15). 3) Intro of NMe at high press into lines contg air can result in deton, probably due to adiabatic comprsn of the entrapped air (Ref 16, p 24). The effect of a number of additives on the sensy of NMe to initiation with a No 8 blasting cap was examined and several were found to be effective at levels of 5–10% (Ref 16, p 31). Additives which can H-bond to the NMe molecule were found to be especially effective as sensitizers. Some are w, nitric acid, and sulfuric acid; however, phosphoric acid gave erratic results (Ref 16, p 11)

Detonation Rate. In glass tubing 1/32inch in diam, 6210m/sec (Ref 36); in iron tubing, 6280m/sec; in brass tubing, 6060m/sec (Ref 31); and in stainless steel tubing ½inch in diam, 20,000feet/sec (Ref 14, p 1)

Dipole Moment. In vapor phase 3.54 debye units (Ref 9)

Explosion Temperature. At 430° it expls in 5sec (Ref 36). The crit temp for expl was found to be 599°F and the crit press 915psi (Ref 52). Pure NMe under air or N was found to deton betw 500 and 720°F. Ten additives in varying concns were tried as desensitizers, but there was no change in the temp range (Ref 14)

Flammability. The flash point is 112°F (Ref 50); in the Abel-Pensky app it is 35–37°; and by Marcusson's method it is 42–43°. The autoignition point by Constam & Schlaepfer's method was found to be 440° (Ref 48)

Friction Pendulum. It is unaffected by the steel or fiber shoe (Ref 36)

Heat Capacity. The eqn $C_p = 0.4209 - 0.0076 + 0.5605t^2$ is valid over the range 15–75° (Ref 36). Other eqns and data for heat capacity calcns are given in Ref 48

Heat of Combustion. At 25° it is 175.25 ± 0.18 kcal/mole (Ref 17)

Heat of Formation. −21.28kcal/mole (Ref 17)

Heat of Vaporization. 149cal/g (Ref 36)

Heat Tests. Effect of heat: at 300° NMe has a half-life of 30 days, at 350° it decomposes slowly, at 350–400° it decomposes slowly and completely, above 400° an autocatalytic decompn sets in resulting in deton; however, it may detonate unexpectedly at any temp above 300° (Ref 16)

Impact Sensitivity. On BM app 100cm (Ref 36)

Power. Ballistic Mortar. 134% of TNT (Ref 36)

Trauzl Test. 110–27% of PA (Refs 36 & 48)

Rifle Bullet Impact Test. Unaffected (Ref 36). In Ref 15, however, it was reported that NMe, when stored in drums, is detond by the impact of fire from a 0.30 cal MG when firing AP ammo, and set on fire when tracers are used

Solubilities. In w, 9.5ml/100ml; sol of w in NMe

is 2.2ml/100ml (Ref 40). It is miscible in alc, eth, and dimethylformamide (Ref 50). An extensive table of miscibilities of NMe in org liqs is given in Ref 40, p 864a

Spectra. Infrared. The IR spectrum is given in Ref 19

Nuclear Magnetic Resonance. There is a single proton peak at 244τ (Ref 42)

Ultraviolet. There is a n→π^* transition at 3636 cm^{-1} (Ref 41)

Thermal Decomposition. The therm decompn was studied betw 380 and 430° and found to be homogeneous and apparently 1st order. The products were complex and included nitric oxide, methane, carbon monoxide, and w plus small amts of ethane, ethylene, and nitrous oxide (Ref 23)

Toxicity. Vapors of NMe are irritating to the lungs. Prolonged contact produces loss of appetite, nausea, diarrhea, and damage to the liver and kidneys. The lethal concn in air for guinea pigs is 1000ppm (Ref 50). The systemic toxicity is high when inhaled or ingested (Ref 47). The LD50 in mice is 950±122mg/kg; in rats 900± 80mg/kg. The MAC in drinking w is 0.005mg/ℓ due to the formation of chloropicrin during chlorination of the w (Ref 49)

Uses. NMe has been used as a solv, a chem intermediate, a propellant, and an expl. For a review see Ref 10. It is used as a solv for the detn of the HMX content of RDX by differential refractometry (Ref 27). It is used as a solv in the prepn of fine particle size NC (plastisol NC) (Ref 53). It was first considered for use as a liq monopropint by L. Crocco (Ref 20), but it never lived up to its expectations because of these disadvantages: 1) It is difficult to ignite. The addn of oxygen eases this problem, but explns occur on ca 25% of ignitions (Ref 15). 2) It tends to explode erratically when pumped at high press, or when used to cool the walls of a rocket chamber (Ref 33). A gel contg 10–15% NC has been patented as a rocket fuel or an expl (Ref 30). Another gel of NMe with 3% Gengel guar gum has been proposed for use as an expl for cratering, excavation, and other blasting work. The gel has a differential thermal analysis endotherm at 120° due to evapn of the NMe; and a gap test of 0.8–3.1mm (0.38mm for pure NMe) (Ref 54). Gelled NMe is compared with AN/fuel oil as a blasting expl in Ref 55. Advantages of AN/fuel oil are that it is cheaper and easier to handle and store; advantages of gelled NMe are that it is denser, has a higher detonation velocity, and has a higher energy output/cc. NMe can be used as a motor fuel, both spark ignition and diesel, either alone or mixed with gasoline. For a review of this use see Ref 39

Salts. HgOH+ salt. It is prepd from the Na salt and Hg(II) chloride. The Pb block expansion test gives 7.5cc/2g, but it has little effect in the Pb plate test (Ref 13)

Li salt. It is claimed as a corrosion inhibitor for lubricants (Ref 24)

Na salt. It is prepd by the action of Na hydride on NMe in anhyd eth (Ref 44). It is sensitive and when dry will burst into flame when thrown onto w (Ref 50)

PhHg+ salt. Prepd by the reaction betw PhHgOH and NMe, yield 73.7%; mp 172–73° (with ignition) (Ref 29)

K salt. Prepd by the action of K hydride on NMe in anhyd eth (Ref 44)

Tl+ salt. Prepd by the addn of TlOH to NMe, yield 85%; decompd without melting and could not be detonated by impact (Ref 18)

Refs: 1) Beil **1**, 74, (19), [40], {106}& ⟨100⟩ 2) V. Meyer, Ann **171**, 1 (1874) 3) P. Walden, Ber **40**, 3214 (1907) & CA **1**, 2689 (1907) 4) J.W. Williams, JACS **47**, 2644 (1925) 5) R.P. Reynolds & H. Adkins, JACS **51**, 279 (1929) 6) C.P. Wright et al, JCS **1931**, 199 7) I.M. Gorski & S.P. Makarow, Ber **67**, 996 (1934) 8) H.B. Hass et al, IEC **28**, 339 (1936) 9) L.G. Groves & S. Sugden, JCS **1937**, 158 10) H.B. Hass & E.F. Riley, ChemRev **32**, 388 (1938) 11) OrgSyn (Coll Vol **1**, 1941), p 401 12) T. Boyd & H.B. Hass, IEC **34**, 300 (1942) 13) Blatt, OSRD **2014** (1944) 14) K. Kaplan et al, "Thermal and Shock Sensitivity of Nitromethane", JPL Progress Report 1-35, Contr No W-535-AC-20260 (26 Dec 1945) 15) F. Bellinger et al, IEC **40**, 1320 (1948) 16) D.M. Griffin, "The Thermal Stability of Nitromethane", JPL Progress Report 9-24, Contr No W-04-200-ORD-1482 (8 Dec 1948) 17) D.E. Holcomb & C.L. Dorsey, IEC **41**, 2788 (1949) 18) H. Gilman & R.K. Abbott, Jr, JACS **71**, 659 (1949) 19) H.M. Randall et al, "Infrared Determination of Organic Structures", Van Nostrand, NY (1949), p 190 20) L. Crocco, ARSJ **20**, 32 (1950) & CA **44**, 11057d (1950)

21) P.E. Stewart & W.A. Bonner, AnalChem **22**, 793 (1950) 22) L. Médard, MP **33**, 132 (1951) & CA **47**, 5683g (1953) 23) T.L. Cottrell et al, TrFaradSoc **47**, 584 (1951) 24) S.C. Johansson, USP 2532407 & CA **45**, 1006a (1951) 25) L.D. Horsley, "Tables of Azeotropes and Nonazeotropes" in "Azeotropic Data", Advances in Chemistry Series No 6, ACS (1952) 26) J. Decompe, BullFr **1953**, 1038 & CA **48**, 2568b (1954) 27) S.M. Kaye & S.N. Chinai, "The Development of a Method of Determination of the HMX Content of RDX by Differential Refractometry", PATR **2016** (March 1954) 28) F. Klages & J. Dasch, Ber **88**, 379 (1955) 29) G.C. Petukhov, SbornikStatei-ObshchKhim **2**, 989 (1953) & CA **49**, 6858g (1955) 30) H. Maisner, USP 2712989 & CA **49**, 2736 (1955) 31) G. Nahmani & Y. Manheimer, JChemPhys **24**, 1074 (1956) 32) E.E. Toops, JPhChem **60**, 304 (1956) 33) A. Makovy & L. Lenji, ChemRev **58**, 638 (1958) 34) ICC Doc 3666, ExParte MC 13 (Sept 10, 1958) 35) J.G. Tschinkel & C.R. Morrison, JChemEngData **3**, 350 (1958) 36) W.R. Tomlinson & O.E. Sheffield, "Properties of Explosives of Military Interest", PATR **1740** Rev 1 (1 April 1958), p 265 37) I.R. Cohen & A.P. Altshuller, AnalChem **31**, 1638 (1959) 38) A. Wehrli & E. Kovàts, Helv **42**, 2709 (1959) & CA **54**, 12722f (1959) 39) E.S. Starkman, IEC **51**, 1477 (1959) 40) Houben **1/2** (1959), p 845 41) A. Balasubramanian & C.N.R. Rao, Chem&Ind **1960**, 1025 & CA **55**, 1413c (1961) 42) J.R. Cavanaugh & B.P. Dailey, JChemPhys **34**, 1099 (1961) 43) H. Feuer & R. Harmetz, JOC **26**, 388 (1961) 44) J. d'Ans & H. Gold, GerP 1099537 & CA **55**, 27005b (1961) 45) C. Caldo, ChimeInd(Milan) **44**, 258 (1962) & CA **60**, 11893b (1964) 46) H. Feuer, ed, "Nitroparaffins", ProcSymposium, 25-6 May 1961; Publ as Tetrahedron **19**, suppl 1 (1963) 47) Sax (1963), p 970 48) Urbański **1** (1964), p 581 49) V.G. Subbotin, GigSanit **32**, 9 (1967) & CA **67**, 120062b (1967) 50) Merck (1968), pp 740 & 1193 51) Houben **10/1** (1971) 52) "Combustible Solids, Dusts, & Explosives", National Fire Codes, Vol **3** (NFPA 1971–2), pp 49–167 53) G.C. Cox & T.N. Liggett, USP 3671515 (1972) & CA **77**, 64228c (1972) 54) F. Helm et al, "The Development and Manufacture of a Gelled Nitromethane Explosive for Project ESSEX", **UCRL-51536**, Contr IACRO EERL-E-85-72-7006 (10 Oct 1974) 55) M. Heusinkveld et al, "Controlled Blasting Calculations with the TENSOR74 Code", **UCRL-51740** (24 Feb 1975)

NITRO HALOGEN DERIVATIVES OF METHANE

Fluoronitromethane. FCH_2NO_2, mw 79.04, N 17.73%; OB to CO_2 −20.24%; a colorl liq, bp at 125–30mm, 57–62°; CA Registry No 21824-09-9. It has been prepd by the hydrolysis of diethyl fluoronitromalonate, followed by decarboxylation, yield 5–32%, yields are erratic. IR peaks are at 6.27, 7.27, 7.37 and 8.8μ. It is stable only at 0–5°

Refs: 1) Beil – not found 2) J.P. Lorand et al, JOC **34**, 4176 (1969)

Difluoronitromethane. F_2CHNO_2, mw 97.03, N 14.44%; OB to CO_2 −8.24%; a volatile liq, bp 43–3.5°; d at 20°, 1.4600g/cc; RI at 20°, 1.3175 (Ref 5); CA Registry No 1493-05-6

It has been prepd by the reaction of Ag nitrite with difluoroiodomethane (Ref 2); by the decarboxylation of difluoronitroacetic acid with anhyd K fluoride (Ref 3), or anhyd K carbonate, yield 46% (Ref 5); or by heating 1,1-difluoro-4-methyl-1-nitro-2-trifluoromethyl-4-penten-2-ol to 100° with a trace of K hydroxide, yield 82% (Ref 4);

Refs: 1) Beil **1**, {112} 2) O. Ruff, Ber **69**, 299 (1936) 3) Yu.L. Kruglyak et al, USSRP 159821 (1964) & CA **60**, 11897b (1964); 4) N.P. Gambaryan et al, IzvestAkadNSerKhim **1965**, 1466 & CA **63**, 6202h (1965) 5) A.V. Fokin et al, ZhObshchKhim **36**, 540 (1966) & CA **65**, 613b (1966)

Trifluoronitromethane. (Fluoropicrin) F_3CNO_2, mw 115.02, N 12.18%; a colorl gas, bp −21° (Ref 3); CA Registry No 335-02-4

It was first prepd in low yield by the action of Cl trifluoride on bromodifluoronitrosomethane and by the oxidn of trifluoronitrosomethane with Pb dioxide (Ref 2). The Pb dioxide oxidn of the nitroso compd was repeated by Hazeldine who obtd a 37% yield (Ref 3). This oxidn has also been carried out using dimanganese heptoxide (Ref 3), 30% hydrogen peroxide in a sealed tube (Ref 4), and activated C (apparently contg adsorbed O_2) in a sealed tube at 150° for 1

hour, yield 7% (Ref 5). It has also been prepd by the action of Sb trifluorodichloride on chlorodifluoronitromethane (Ref 3)
Spectra. The IR spectrum and band assignments are given in Ref 6; in the UV there is a $n \rightarrow \pi^*$ transition at 35842^{-1} (Ref 7)
Use: A mixt of 0.151 to 1 part of ammonia is claimed as a liq rocket monoprop, Isp 218 lb-sec/lb (Ref 8)
Refs: 1) Beil **1**, ⟨105⟩ 2) W. Hückel, Nach-AkadWissGöttingen, Math-PhysikKlasse **1946**, 36 & CA **43**, 6793d (1949) 3) R.N. Hazeldine, JCS **1953**, 2075 4) J. Banus, JCS **1953**, 3755 5) J. Jander & R.N. Hazeldine, JCS **1954**, 919 6) J. Mason & J. Dunderdale, JCS **1956**, 769 7) A. Balasubramian & C.N.R. Rao, Chem&Ind **1960**, 1026 & CA **55**, 1412c (1961) 8) H.W. Bost & R.C. Doss, USP 3127736 & CA **61**, 5445a (1964)
Chloronitromethane. This article supplements the material in Vol **3**, C258-Rff under Chloromethane and Derivatives. Bp at 60mm 58–60°, d at 20° 1.472g/cc, RI at 20°, 1.4450 (Ref 3); CA Registry No 1794-84-9

It is prepd by the action of w on 2,3-dichloro-3,3-difluoro-2-nitropropionyl chloride at 45–50° for 4 hours, yield 61% (Ref 3). It undergoes the ter Meer reaction with Na nitrite to give dinitromethane (Ref 2). The IR and Raman spectral peaks are assigned in Ref 6. The pK_a at 25° was found to be 7.20 (Ref 4). In polarographic analysis it gives two breaks in the curve, indicating a two electron reduction probably by the eqn $ClCH_2NO_2 + 2e^- = CH_2NO_2^- + Cl^-$ (Ref 5)
Refs: 1) Beil **1**, ⟨106⟩ 2) H. Feuer, "Recent Advances in the Chemistry of Polynitro Compounds" in T. Urbański, Ed, "Nitro Compounds", ProcInternSymp, Warsaw **1963**, Tetrahedron **20**, Supp 1, 103 3) I.V. Martynov & Yu.L. Krugylak, ZhObshchKhim **35**, 248 (1965) & CA **62**, 14490b (1965) 4) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966) 5) J. Armand, BullFr **1966**, 546 & CA **64**, 17040e (1966) 6) P. Gluzinski & Z. Eckstein, SpectrochimActa **24A**, 1777 (1968)
Chlorofluoronitromethane. $ClCHFNO_2$, mw 113.49, N 12.34%; OB to CO_2 −7.05%; bp 79–81°; d at 20°, 1.532g/cc. RI at 20° 1.3840 (Ref 2). It is prepd by the decarboxylation of chlorofluoronitroacetic acid with hot w (Ref 3), or anhyd K fluoride (Ref 2). Its pK_a in w is given as 10.14 in Ref 4
Refs: 1) Beil – not found 2) I.V. Martynov et al, ZhObshchKhim **33**, 3384 (1963) & CA **60**, 4000a (1964) 3) Yu.L. Krugylak et al, USSRPat 159821 & CA **60**, 11897b (1964) 4) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966)
Chlorodifluoronitromethane. $ClCF_2NO_2$, mw 131.48, N 10.66%; bp 24–25° (Ref 2). It is prepd by the oxidn of the nitroso compd with dimanganese heptoxide, yield 15% (Ref 2), or by the interaction of difluorodiazirine with nitryl chloride, yield 15% (Ref 3)
Refs: 1) Beil **1**, ⟨106⟩ 2) R.N. Hazeldine, JCS **1953**, 2075 3) R.A. Mitch, JHeterocyclicChem **1**, 233 (1964)
Dichloronitromethane. This article supplements the material in Vol **5**, D1213-R under Dichloromethane and Derivatives. In polarographic analysis it shows a complex curve indicating two 2-electron reductions giving finally NMe and two Cl^- ions (Ref 1). Its pK_a at 25° was found to be 5.99 (Ref 2)
Refs: 1) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966) 2) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966)
Trichloronitromethane. This article supplements the material in Vol **3**, C256-R under Chloroform and Derivatives; CA Registry No 76-06-2. The IR spectrum and assignment of peaks are given in Ref 2; and in the UV there is a $n \rightarrow \pi^*$ transition at $35907cm^{-1}$ (Ref 3). A procedure is described in Ref 5 for its spectrophotometric detn in w. The thermodynamic props are calcd in Ref 4
Refs: 1) Beil **1**, ⟨106⟩ 2) J. Mason et al, JCS **1959**, 2014 3) A. Balasubramanian & C.N.R. Rao, Chem&Ind **1960**, 1025 & CA **55**, 1413c (1961) 4) A.H. Castelli & F. Pristera, "The Thermodynamic Properties of Nitrotrichloromethane" **PA-FRL-TN-91** (Sept 1961) 5) J.A. Castro & H. Godoy, AnalChimActa **33**, 679 (1965)
Bromonitromethane. This article supplements the material in Vol **2**, B312-R under Bromomethane and Derivatives; CA Registry No 563-70-2. The IR and UV spectra are given in Ref 3. In polarographic analysis a two electron reduction to $CH_2NO_2^-$ and Br^- is indicated (Ref 4). It can be quanty detd by treatment with concd sul-

furic acid, then resorcinol, to give a colored complex which can be measured spectrophotometrically (Ref 2)

Refs: 1) Beil **1**, {115} & ⟨106⟩ 2) L.R. Jones & J.A. Riddick, AnalChem **24**, 1533 (1952) 3) V.I. Slovetskii et al, IzvestAkadNOtdel-KhimNauk **1961**, 683 & CA **55**, 23048 (1961) 4) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966)

Bromodifluoronitromethane. $BrCF_2NO_2$, mw 175.94, N 7.96%; CA Registry No 354-42-7. It has been patented as an insecticide, fungicide, and nematocide

Refs: 1) Beil – not found 2) E.E. Kenaga, USP 3445575 (1969) & CA **71**, 37905r (1969)

Bromodichloronitromethane. $BrCCl_2NO_2$, mw 208.86, N 6.71%; bp at 22mm, 52°; d at 20°, 2.073g/cc. It is prepd by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 33.2%

Refs: 1) Beil – not found 2) G.A. Burk & R.A. Davis, USP 3159686 (1965) & CA **62**, 3937d (1965)

Dibromonitromethane. Br_2CHNO_2, mw 218.86, N 6.40%; a liq; bp at 13mm, 58.5–60° (Ref 2); RI at 25°, 1.5757 (Ref 4); CA Registry No 598-91-4. It was first prepd by the action of Br on bromonitromethane in basic soln (Ref 2), and later by the similar bromination of nitroacetamide (Ref 3). In polarographic analysis a two electron reduction to $BrCHNO_2^-$ and Br^- is indicated (Ref 5)

Salts, Ammonium Salt. It is formed with Amm bromide by the action of liq ammonia on tribromonitromethane. The crude salt mixt is obtd as a yellow powd which gives free dibromonitromethane by the action of aq hydrobromic acid (Ref 4)

K salt. It is obtained as an orange powd which decomps suddenly on heating with formation of K bromide, but does not deton (Ref 3)

Refs: 1) Beil **1**, 57, [43] & ⟨106⟩ 2) R. Scholl, Ber **29**, 1822 (1896) 3) R.C. Schreyer, JACS **73**, 2962 (1951) 3) S.K. Brownstein, JOC **23**, 113 (1958) 4) J. Armand, BullFr **1966**, 574 & CA **64**, 17040e (1966)

Dibromofluoronitromethane. $FCBr_2NO_2$, mw 236.86, N 5.91%. It is claimed to reduce hydrocarbon emissions from automobile exhaust when added to the fuel at 3.3% by vol

Refs: 1) Beil – not found 2) C.P. Parsons & C.T. Pumpelly, USP 3413105 (1969) & CA **70**, 30633w (1969)

Chlorodibromonitromethane. $ClCBr_2NO_2$, mw 253.30, N 5.53%; a heavy oil; bp at 22mm, 67–69°; d at 25°, 2.398g/cc (Ref 3). It is prepd by the action of Br on chloronitromethane in aq K hydroxide (Ref 2), or by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 35.4% (Ref 3)

Refs: 1) Beil **1**, 77 2) J. Tscherniak, Ber **8**, 610 (1875) 3) G.A. Burk & R.A. Davis, USP 3159686 (1965) & CA **62**, 3937d (1965)

Tribromonitromethane. This article supplements the material in Vol **2**, B312-L under Bromoform and Derivatives; CA Registry No 464-10-8. The IR and UV spectra are given in Ref 4. In polarographic analysis a two electron reduction to $Br_2CNO_2^-$ and Br^- is indicated (Ref 5). It adds to olefins to form 1,1,1-tribromo-2-nitroalkanes. The authors found that it is the only halonitroalkane to react in this way (Ref 3). When added to liq ammonia it forms a mixt of the Amm salt of dibromonitromethane and Amm bromide (see above) (Ref 2)

Refs: 1) Beil **1**, {115} & ⟨106⟩ 2) S.K. Brownstein, JOC **23**, 113 (1958) 3) Yu.A. Baskakov & N.M. Mel'nikov, ZhObshchKhim **29**, 1233 (1959) & CA **54**, 8599i (1960) 4) V.I. Slovetskii et al, IzvestAkadNOtdelKhim-Nauk **1961**, 683 & CA **55**, 23048g (1961) 5) J. Armand, BullFr **1966**, 547 & CA **64**, 17040e (1966)

Iodonitromethane. ICH_2NO_2, mw 186.95, N 7.49%; OB to CO_2 –8.56%, an unstable, lacramatory oil, odor unpleasant (Refs 2 & 3); CA Registry No 25538-43-6. It is prepd by the action of Ag nitrite on methylene iodide in the presence of a trace of I (Ref 2), or by the action of I on NMe in cold alkali (Ref 3). It is reduced electrolytically to iodide and NMe (Ref 4). A Na salt has been prepd as a white solid which explds on heating (Ref 2).

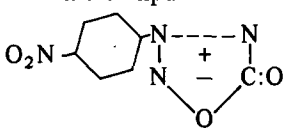
Refs: 1) Beil **1**, 77 & {115} 2) A. Russanow, Ber **25**, 2632 (1892) 3) C.D. Nenitzescu & D.A. Isacescu, Ber **63**, 2484 (1930) 4) S. Tribalat & M. Grall, CR Series C **269**, 83 (1969) & CA **71**, 97712k (1969)

Dinitromethane (DNMe). $CH_2(NO_2)_2$, $CH_2N_2O_4$, mw 106.04, N 26.42%, OB to CO_2 +15.09%. It

is stored and handled in the form of salts, but has recently been obtd as an unstable oil, mp −15° (Ref 3); bp at 4mm, 39–40°; d at 20°, 1.524g/cc, RI at 20°, 1.4480 (Ref 16); CA Registry No 625-76-3. It was first prepd by the action of aq Amm sulfide on bromodinitromethane (Ref 2); and by the action of cold concd sulfuric acid on the di-K salt of symdinitroethane (Ref 4), isolated as the K salt. It is best prepd by the reduction of dibromodinitromethane with As trioxide in cold aq K hydroxide and isolated as the K salt (Ref 3). The pure material has been regenerated from the K salt by treatment with anhyd hydrogen fluoride in abs eth (Ref 16)

Ionization. The pK_a at 25° in w is 3.60, 50% aq et alc 4.11, et alc 7.5, and me alc 7.2 (Ref 17)

Reactions. It reacts with benzenediazonium chloride to give yellow crysts, mp 75° with gas evolution, whose structure was first thought to be $(PhN{:}N)_2C(NO_2)_2$ (Ref 3). More recently the reaction with p-nitrobenzenediazonium fluoroborate was examined in greater detail (Ref 11). The first prod isolated was the hydrazone $p\text{-}O_2NC_6H_4NHN{:}C(NO_2)_2$, orange-red crysts, mp 120–25° with decompn. It deflagrates when heated on a spatula, and its solns decomp slowly in the cold and more rapidly on heating, with evolution of oxides of N. From the mother-liquor was obtained another compd, mp 164°, which was considered to be a meso-ionic compd:



For a discussion of these type compds see Ref 12. The chemistry and technology of DNMe has been reviewed in Ref 9 with emphasis on its use as an intermediate for the prepn of nitropolymers, especially thru 2,2-dinitro-1,3-propanediol (code name A-diol)

Spectra. The UV spectra in w, acid, and base are given in Ref 5. The proton nuclear magnetic resonance spectrum shows a sharp singlet at 3.90ppm from tetramethylsilane (Ref 15)

Salts. **Ammonium Salt.** Obtained as bright yellow fine needles, expl at 105° (Ref 3). It is completely ionized in w at 25° (Ref 20)

Ba salt. Bright yellow needles, insol in w or et alc (Ref 3)

Cs Salt. Its IR and UV spectra are given in Ref 19

Li Salt. Its IR spectrum is given in Ref 13

HgCl+ Salt. It is prepd by the action of Hg(II) chloride on the K salt in w (Ref 6)

Phenylhydrazine Salt. It is prepd by the action of phenylhydrazine on dinitromethane in anhyd eth and obtd as intense yellow needles, mp 101° with gas evoln (Ref 3)

Piperidine Salt. The ionization constant in w at 25° is 3.37±0.01 (Ref 20)

K Salt. DNMe is stored and handled as the K salt which is obtd as brown-yellow feathery crysts, expln temp 218° (Ref 4). It is also prepd by the action of excess K cyanide or K thiosulfate on dibromodinitromethane (Ref 7). Best lab prepn: K nitrite (25g) in 40ml of w is added to 24g of chloronitromethane in 50g of me alc at 0°. To this soln is added with good stirring 16.5g of K hydroxide in 50g of me alc as the temp is held betw 0 and −5°. The stirring is contd for 5 hours, the pptd solid filtered off, and recrystd from w to give 8.4g of K dinitromethane, yield 23.3%, expln temp 208° (Ref 8). More recently it is conveniently prepd on a lab and comml scale by the interaction of NMe and Na nitrite with a Ag salt, most commonly the nitrate. This reaction, developed by Shechter and Kaplan of the Purdue Research Foundation, is called the Shechter-Kaplan reaction (Ref 14). The IR spectrum is given in Ref 13. The ionization constant in w at 25° is 2.26±0.01 (Ref 20). It readily adds to activated olefins (Ref 10)

Rb Salt. Its IR and UV spectra are given in Ref 18. The ionization constant in w at 25° is 0.602±0.004 (Ref 20)

Ag Salt. It is formed from the K salt and Ag nitrate in w, decomps at 135° (Ref 3). The IR and UV spectra are given in Ref 18. It reacts with Me iodide to give 1,1-dinitroethane (Ref 3)

Na Salt. The IR spectrum is given in Ref 13. It is estimated to be 100% ionized in w at 25° (Ref 20)

Refs: 1) Beil **1**, 77, (24), [44], {115} & ⟨107⟩ 2) S.M. Losanitsch, Ber **16**, 51 (1884) 3) P. Duden, Ber **26**, 3003 (1893) 4) R. Scholl & A. Schmidt, Ber **35**, 4288 (1902) 5) A. Hantzsch & K. Voigt, Ber **45**, 112 (1912) 6) W. Prager, Monatsh **33**, 1285 (1912) & CA **7**, 589 (1913) 7) R.A. Gotts & R. Hunter,

JCS **125**, 449 (1924) 8) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and their Application to Solid Smokeless Propellants", AerojetEngrgCorp, Azusa, Calif, Quarterly Report 345, Contr No N7-onr-462 (4 Jan 1949), p 54 9) L. Herzog & K. Klager, "A Review of Dinitromethane and 2,2-Dinitroethanol", AerojetEngrgCorp, Special Report 461, Contr No N7-onr-462 (20 July 1950) 10) L. Herzog et al, JACS **73**, 749 (1951) 11) S. Hünig & O. Boes, Ann **579**, 46 (1953) & CA **49**, 7518i (1955) 12) W. Baker & W.D. Ollis, QuartRevs **11**, 15 (1957) 13) V.I. Slovetskii et al, IzvestAkadNOtdelKhimNauk **1963**, 57 & CA **57**, 10874e (1963) 14) H. Shechter & R.B. Kaplan, USP 2997504 (1963) & CA **58**, 5515h (1963) 15) W. Hofman et al, JACS **86**, 555 (1964) 16) G.Ya. Legin et al, IzvestAkadNSerKhim **1965**, 2220 & CA **64**, 11073e (1966) 17) V.I. Slovetskii et al, TetrahedronLett **1966**, 1746 18) V.I. Slovetskii et al, ZhOrganKhim **2**, 1445 (1966) & CA **66**, 59654v (1967) 19) I.N. Shokhor et al, ZhOrganKhim **3**, 489 (1967) & CA **67**, 81695p (1967) 20) V.I. Slovetskii et al, IzvestAkadNSerKhim **1968**, 1004 & CA **69**, 54836v (1968)

Halogen Dinitro Derivatives of Methane

All 14 possible halogen derivs of dinitromethane have been reported in the literature. They are sens to friction, shock, and impact, as well as being toxic and skin irritants (Ref 5)

Fluorodinitromethane. $FCH(NO_2)_2$, $CHFN_2O_4$, mw 128.04, N 21.88%, OB to CO_2 18.74%, fr p −24.5°; bp at 20mm 35–38°, d at 20°, 1.5955 g/cc; RI at 20°, 1.4054 (Ref 4); pK_a at 20° 7.70 (Ref 2); CA Registry No 7182-87-8. It is prepd by the fluorination of the Amm salt of dinitromethane at 2–3° in w, yield 90% (Ref 4); by the action of H peroxide and K hydroxide on fluoronitroform in me alc; or by the fluorination of the K salt of ethyl dinitroacetate (Ref 5)

Hg Salt. It is prepd by the action of Hg(II) monoxide in eth on the free nitro compd, yield 86%, mp 147° (Ref 6). It reacts with K hydroxide or K iodide to give the K salt of fluorodinitromethane, and with H chloride or w to regenerate the free nitro compd (Ref 3)

Refs: 1) Beil – not found 2) H.G. Adolph & M.J. Kamlet, JACS **88**, 4761 (1966) 3) L.V. Okhlobystina et al, DoklAkadN **176**, 1086 (1967) & CA **68**, 78397h (1968) 4) L.T. Eremenko & F.Ya. Natsibullin, IzvestAkadNSerKhim **1968**, 912 & CA **69**, 35315b (1969) 5) M.J. Kamlet & H.G. Adolph, JOC **33**, 3073 (1968) 6) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50160p (1969)

Difluorodinitromethane. $F_2C(NO_2)_2$, $CF_2N_2O_4$, mw 146.03, N 19.19%; bp 34°; d at 10°, 1.5644 g/cc; RI at 10°, 1.3640 (Ref 4); CA Registry No 1185-11-1. It is prepd by the reaction of di-N tetroxide with difluorodiazirine (Ref 2); by the fluorination of a mixt of K nitroform and Na fluoride at −12 to −6° in a Cu vessel (Ref 4); or by the action of anhyd K fluoride on fluoronitroform in sulfolane at 150°, yield 58.7% (Ref 5). A mixt of 0.249p to one p of ammonia has been claimed as a liq rocket proplnt (Ref 3)

Refs: 1) Beil – not found 2) R.A. Mitsch, JHeterocyclicChem **1**, 233 (1964) 3) H.W. Bost & R.C. Doss, USP 3127736 (1964) & CA **61**, 5445a (1964) 4) L.T. Eremenko et al, IzvestAkadNSerKhim **1968**, 429 & CA **69**, 18508f (1968) 5) M.J. Kamlet & H.G. Adolph, JOC **33**, 3073 (1968)

Chlorodinitromethane. This article supplements the material in Vol **3**, C259-L under Chloromethane and Derivatives; CA Registry No 921-13-1. Its pK_a in w at 20° is 3.53–3.80 (Refs 1 & 3). The K salt has a mp of 85° with decompn (Ref 2). The Hg salt is prepd from chlorodinitromethane and the Hg salt of fluorodinitromethane. It reacts with aniline to form $PhNHC(NO_2)_2Cl$, yield 59.1%, mp 125° with decompn (Ref 4)

Refs: 1) T.N. Hall, JOC **29**, 3587 (1964) 2) V.I. Erashko et al, IzvestAkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 3) A.I. Ivanov et al, ZhFizKhim **40**, 2298 (1966) & CA **66**, 14512v (1966) 4) L.V. Okhlobystina et al, DoklAkadN **176**, 1086 (1967) & CA **68**, 78397h (1968)

Chlorofluorodinitromethane. $FCCl(NO_2)_2$, $CClFN_2O_4$, mw 158.49, N 17.68%; OB to CO_2 20.19%, bp at 752mm 85–87°; d at 20°, 1.6162 g/cc, RI at 20°, 1.3992 (Ref 5); CA Registry No 19845-51-3. It is prepd by the action of di-N tetroxide on chlorofluoronitroacetic acid in an autoclave at 80–90° (Ref 3); by the action of Li

chloride in dimethylformamide on fluoronitroform, yield 35% (Ref 4); or by the action of Cl in anhyd eth on the Hg salt of fluorodinitromethane, yield 72% (Ref 5). The thermal decompn has been studied betw 170 and 240°. The plot of log k vs 1/T was found to be a straight line from which the activation energy was calcd to be 41.5kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) I.V. Martynov et al, USSR-Pat 20788 & CA **69**, 35407q (1968) 4) A.A. Fainzil'berg et al, IzvestAkadNSerKhim **1969**, 476 & CA **70**, 114505u (1969) 5) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50169p (1969)

Dichlorodinitromethane. This article supplements the material in Vol **5**, D1213-R under Dichloromethane and Derivatives; bp at 50mm, 54–56°; d at 20°, 1.6643g/cc; RI at 20°, 1.5460 (Ref 2); CA Registry No 1587-41-3. It is prepd by refluxing trichloroethylene with a 3 mole excess of 70% nitric acid (Ref 1); or by the action of Cl on the K salt of dinitromethane in aq K hydroxide (Ref 2). The thermal decompn betw 115 and 150° was found to be 1st order and homogeneous, the plot of log k vs 1/T gave a straight line (Ref 3). It is a useful herbicide for water weeds (Ref 1).

Refs: 1) H. Johnston, USP 3054828 (1963) & CA **58**, 3315e (1963) 2) V.I. Erashko et al, IzvestAkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 3) G.M. Nazin et al, Combstn-&Flame **12**, 102 (1968)

Bromodinitromethane. This article supplements the material in Vol **2**, B312-R under Bromomethane and Derivatives; the pK_a in w at 20° is 3.47–3.60 (Refs 4 & 6); in the UV the λ_{max} is at 385mμ (Ref 6); CA Registry No 996-67-8. The Amm salt is formed by the action of liq ammonia on dibromodinitromethane (Ref 2). The K salt is a yellow solid, mp 152° with decompn (Ref 5). It is formed by the action of phenylhydrazine in aq K hydroxide on dibromonitromethane (Ref 2)

Refs: 1) Beil **1**, {115} 2) A.K. Macbeth & W.B. Orr, JCS **1932**, 540 3) F.C. Schmidt et al, JOC **9**, 421 (1944) 4) T.N. Hall, JOC **29**, 3587 (1964) 5) V.I. Erashko et al, Izvest-AkadNSerKhim **1965**, 2060 & CA **64**, 6477g (1966) 6) A.I. Ivanov et al, ZhFizKhim **40**, 2298 (1966) & CA **66**, 14514v (1966)

Bromfluorodinitromethane. $BrCF(NO_2)_2$, $CBrFN_2O_4$, mw 202.94, N 13.81%; bp at 40mm, 35–36°; d at 20°, 1.8722g/cc; RI at 20°, 1.4351 (Ref 3); CA Registry No 22632-20-8. It is prepd by the action of Br in anhyd eth on the Hg salt of fluorodinitromethane, yield 76.4% (Ref 3). The thermal decompn was studied betw 170 and 210°. The plot of log k vs 1/T was a straight line from which the activation energy was calcd as 39.5kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50160p (1969)

Bromochloronitromethane. $BrCCl(NO_2)_2$, $CBrClN_2O_4$, mw 219.41, N 12.77%; a heavy oil, suffocating odor; mp 9.2–9.3°, bp at 15mm, 75–76°; d at 10°, 2.0394g/cc; RI at 20°, 1.4739 (Ref 4); CA Registry No 33829-48-0. It is prepd by the action of aq Cl on the K salt of bromodinitromethane (Ref 2), yields are improved by the addn of Na acetate (Ref 3)

Refs: 1) Beil **1**, 78, [45] & ⟨115⟩ 2) S.M. Losanitsch, Ber **17**, 848 (1884) 3) R.A. Gotts & L. Hunter, JCS **125**, 447 (1924) 4) F.C. Schmidt et al, JOC **9**, 421 (1944)

Dibromodinitromethane. $Br_2C(NO_2)_2$, $CBr_2N_2O_4$, mw 262.87, N 10.66%; a heavy yellow oil, solidifies to white leaflets; fr p 6°, mp 10° (Ref 5); bp at 19mm, 78–80° without decompn, expl at 158° (Ref 6); d at 25°, 2.3946 g/cc; RI at 20°, 1.5215 (Ref 9). It is insol in w, miscible with et alc, and volat in steam (Ref 2); CA Registry No 2973-00-4. It has been prepd by the action of Br in w (Ref 7) or aq K hydroxide (Ref 11) on the K salt of dinitromethane; or by the introduction of Br vapors into a w soln of equal parts of the di-K salt of sym-tetranitroethane and Na acetate (Ref 8). It is one prod isolated from the action of concd nitric acid on Br-contg compds such as ethylene dibromide (Ref 3), sym-tribromoaniline (Ref 2), p-bromophenol, and dibromo-p-toluidine (Refs 3 & 4). The experimental details for its prepn from sym-tribromoaniline and concd nitric acid are given in Ref 10

Reactions. For reactions see above under Dinitromethane and Bromodinitromethane

Refs: 1) Beil **1**, 78 & [44] 2) S.M. Losa-

nitsch, Ber **15**, 472 (1883) 3) S.M. Losanitsch, Ber **16**, 51 (1884) 4) S.M. Losanitsch, Ber **16**, 2731 (1884) 5) L. Wolff, Ber **26**, 2217 (1893) 6) R. Scholl & M. Brenneisen, Ber **31**, 651 (1898) 7) R. Scholl & A. Schmidt, Ber **35**, 4291 (1902) 8) L. Hunter, JCS **125**, 1483 (1924) 9) E. Schmidt et al, Ber **59**, 1887 (1926) 10 F.C. Schmidt et al, JOC **9**, 420 (1944) 11) V.I. Erashko et al, Izvest-AkadNSerKhim **1965**, 2060 & CA **64**, 6447g (1966)

Iodonitromethane. $ICH(NO_2)_2$, $CHIN_2O_4$, mw 231.96, N 12.08%, OB to CO_2 10.35%; CA Registry No 29610-14-8. The K salt is formed by the action of I in aq K hydroxide on dinitromethane (Ref 2). It is obtained as yellow tablets which darken on standing and expl at 154° (Ref 3). The Ag salt is obtd as pale yellow leaflets which expl at 109–10° (Ref 3)

Refs: 1) Beil **1**, 79 & [45] 2) S.M. Losanitsch, Ber **16**, 51 (1884) 3) R.A. Gotts & L. Hunter, JCS **125**, 443 (1924)

Fluoroiododinitromethane. $FCI(NO_2)_2$, $CFIN_2O_4$, mw 249.96, N 12.08%; it is a liq which decomps slowly on standing in the dark, rapidly in light; bp at 27mm, 59–9.5°; d at 20°, 2.3541g/cc; RI at 20°, 1.4998 (Ref 3); CA Registry No 22632-21-9. It is prepd by the action of I in anhyd eth on the Hg salt of fluorodinitromethane, yield 74% (Ref 3). The thermal decompn was studied betw 160 and 197°. The plot of log k vs 1/T gave a straight line from which the activation energy was calcd as 39.7kcal/mole (Ref 2)

Refs: 1) Beil – not found 2) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 2801 & CA **70**, 77061y (1969) 3) L.V. Okhlobystina et al, IzvestAkadNSerKhim **1969**, 708 & CA **71**, 50169p (1969)

Chloroiododinitromethane. $ClCI(NO_2)_2$, $CClIN_2O_4$, mw 265.42, N 9.05%; a colorl oil, characteristic odor; d at 12°, 2.1424g/cc; CA Registry No 40956-65-8. It is prepd by the action of aq Cl on the K salt of iododinitromethane

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Bromoiododinitromethane. $BrCI(NO_2)_2$, $CBrIN_2O_4$, mw 310.88, N 8.01%; an unstable oil, odor disagreeable; CA Registry No 40956-66-9. It is prepd by the action of aq Br on an ice cold soln of the K salt of iododinitromethane

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Diiododinitromethane. $I_2C(NO_2)_2$, $CI_2N_2O_4$, mw 357.87, N 7.83%; an extremely unstable oil, odor disagreeable; CA Registry No 40956-64-7. It is prepd by the acidification of an ice cold soln of the K salt of iododinitromethane. It decomps on standing with the evolution of I and oxides of N

Refs: 1) Beil **1**, [45] 2) R.A. Gotts & L. Hunter, JCS **125**, 448 (1924)

Trinitromethane (Nitroform, TNMe). Trinitromethan or nitroform (Ger), Nitroforme (Fr); $CH(NO_2)_3$, CHN_3O_6, mw 151.04, N 27.82%, OB to CO_2 +37.08%; a colorl to pale yellow solid, a pale yellow liq; mp 26.3 ± 0.1° (Ref 46). It can also be obtained in a higher melting form, mp 50°, which was assumed by the authors to be the aci-form (Ref 15); bp at 22mm, 45–7° (Ref 16); d at 24.3°, 1.5967g/cc; RI at 24.3°, 1.44174 (Ref 11). The pH of a satd soln in w was measured with a glass electrode and found to be 0.6 (Ref 25, p 2); CA Registry No 517-25-9. The Hercules Powder Co of Wilmington, Del has been granted a trademark for *Nitroform*®, a synthetic w-insoluble compd for controlled release of N for agricultural use (Ref 40). This should not be confused with TNMe

Historical. It was first prepd by the action of nitric acid (d 1.52 g/cc) on acetylene (Ref 5), and this is the basis for one industrial process for mfg TNMe (Refs 10, 29 & 35). This reaction was first examined on a large scale in Ger during WWII, where it was used to prepare TNMe and TeNMe for use as intermediates for the prepn of expls (Ref 18)

Preparation. A continuous process is described in Ref 26 for its prepn from nitric acid and acetylene. Other prepns on both lab and industrial scales are by the action on Tetranitromethane (TeNMe) of K hydroxide in aq glycerol (Ref 16), aq $HOCH_2SO_3Na$, or 30% aq H peroxide (Ref 19a) to give the K salt which is treated with sulfuric acid (Ref 16), syrupy phosphoric acid (Ref 20), or best by passing gaseous HCl thru a suspension of the K salt in anhyd eth (Ref 19a). It has also been prepd by the action of nitric acid on malonamide,

yield 58% (Ref 34); Ac_2O (Ref 27); the di-K salt of dinitroacetic acid, yield 54% (Ref 28); or ethylene (Ref 12)

Laboratory Preparation. A soln of 168g of K hydroxide in 350ml of w is cooled to 5° and 120g of 30% aq H peroxide added with stirring. Next is added, with stirring, 189g of TeNMe at a rate which keeps the temp at 20–5°. It is then allowed to rise to 30° over 15min, the bright yellow solid collected on a glass frit, washed with anhyd me alc, then anhyd eth, and air dried to give 100% of the K salt of TNMe. The salt is suspended in anhyd eth and anhyd HCl passed in until the yellow color disappears. The white ppt of KCl is filtered off and washed with anhyd eth. The eth is evapd from the filtrate and addnl washings at reduced press give 85–95% of crude TNMe which can be purified by sublimation (Ref 19a, p 79)

Chemical Reactions. TNMe is a strong acid and forms salts with metals and bases (see below). It readily reacts with formaldehyde to form trinitroethanol (Ref 16). It adds to activated double bonds, such as α,β-unsaturated carbonyl compds and vinyl ethers (Ref 19b). It forms a complex with dioxane contg 2 moles of TNMe to one of dioxane, mp 44–4.5°, bp at 8mm, 61–2° (Ref 19a, p 33). It reacts with aromatic diazonium salts to give compds of the type $ArN{:}NC(NO_2)_3$. The compds are relatively unstable and their expl props have not been examined (Ref 12). It reacts with N-hydroxymethyl compds to form adducts of the type $RNHCH_2C(NO_2)_3$. The same compds are formed from TNMe, formaldehyde, and the amine; or from trinitroethanol and the amine (Ref 31). It forms complexes with N-contg heterocyclics whose expl props have not been examined (Ref 42). It forms complexes with benzene and methylbenzenes. The formation constants for these complexes vary from 8.46 for the benzene complex to 279.4 for the hexamethylbenzene complex (Ref 49)

Analytical. It can be titrated with std base to a salmon colored phenolphthalein endpoint; and can be quanty pptd from aq solns with tetraphenylarsonium chloride; K_{sp} of the complex in w is 6.9×10^{-9} (Ref 22). This procedure can be adapted to the analysis of compds, such as bis-(trinitroethyl) urea, which regenerate TNMe on alkaline hydrolysis. In an ion exclusion-partition chromatographic method for the sepn of acids, TNMe emerged from the column betw citric and itaconic acids (Ref 36)

Impact Sensitivity. On the BRL machine (1kg wt), using a noisemeter to detect explns, the 50% expln height was found to be 218cm. A 50/50 mixt with kerosene had a 50% expln height of 130cm (Ref 21)

Power by Ballistic Mortar. 125–37% of TNT (Ref 24)

Spectrum, Ultraviolet. It shows a plain shoulder in eth, and in w shows a broad maximum at 3400Å (Ref 7)

Stability. It may be stored indefinitely at 0° in sealed glass ampules (Ref 20)

Toxicity. The toxic concns in air for mice are: LD (minimum) 0.7, LD50 0.8, and LD100 1.0mg/ℓ; the max acceptable concn is suggested to be 0.0005mg/ℓ (Ref 37). There is a large amt of toxicological info on the effects of TNMe in this Ref

Uses. It was found to be a poor gelling agent for NC (Ref 14). Its principal use is as an intermediate for the prepn of other expl compds.

Salts, **Ammonium Salt.** Yellow needles from w (Ref 6). It is prepd by the action of w or et alc on trinitroacetonitrile (Ref 2), or by the action of ammonia on TeNMe (Ref 6). The Q_c was found to be 1108.6 ± 1.3cal/g. From this was calcd the Q_f as −47.3 ± 0.2kcal/mole at 1 atm and 25°, and the energy of the bond betw Amm and the nitroformate ion to be 24.8 ± 0.7kcal/mole (Ref 47). It is 100% ionized in w at 25° (Ref 50). It has been patented as an ingredient in high energy proplnts (Ref 32)

Ba Salt. Fine pale yellow crysts, prepd by the action of Ba oxide on TeNMe in aq glycerol (Ref 13). A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

Ca Salt. A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

2,4-Dinitrophenylhydrazine Salt. It is prepd by the addn of the hydrazine in iso-Pr alc to TNMe in the same solv, mp 120–23° (Ref 48)

Guanidine Salt. It was first prepd in Ger during WWII by the addn of a guanidine salt to the K salt of TNMe in w. The hydrate is obtained as needles, mp 122–24°; the anhyd salt mp 128°. Impact sensy (2.5kg wt) 50% expln height,

17cm; deton vel at a loading d of 1.66g/cc, 8200m/sec; cryst d 1.643g/cc; vacuum stability: gas evoln 1.39cc/g in 48 hours at 90°; mixed with Al powd, 1.70cc/g in 48 hours at 90°. It detond after 30 hours at 100° (Ref 25)

Hydrazine Salt. Fine yellow crysts, mp 123° with decompn (Ref 25). It is prepd by the addn of hydrazine hydrate to TNMe in w (Ref 25), or by the addn of anhyd hydrazine to TNMe in iso-Pr alc (Ref 48). The cryst structure and X-ray diffraction pattern of the pure salt are given in Ref 45. Impact sensy (2.5kg wt), the 50% expln height was found to be 10cm (Ref 25). It is stable to 100° (Ref 48). It is claimed as an ingredient in a thixotropic proplnt formulation (Ref 41)

Li Salt. A complex with 2 moles of hydrazine is obtained as an orange-yellow solid, mp 70° with decompn (Ref 39). It is claimed as an oxidizer in proplnt formulations (Ref 39). It is 100% ionized in w at 25° (Ref 50)

Hg Salt. Colorl crysts, slightly sol in org solvs; prepd by the action of Hg oxide on an eth soln of TNMe (Ref 4). It reacts with olefins to form adducts contg one or 2 trinitromethyl groups, depending on reactant ratios (Ref 33). The ionization const in w at 25° is 6.04×10^{-3} (Ref 50)

Mg Salt. It forms an orange-yellow complex with hydrazine, mp 88° with decompn, d 1.68 g/cc, impact sensy 11.7cm (2kg wt). The salt has been patented as a proplnt ingredient (Ref 39)

Methylamine Salt. A yellow solid; mp 126–28° with decompn; ign temp 112°; vacuum stab 1.64cc/g of gas evolved at 60° in 2 hours, 2.04cc/g at 60° in 48 hours (Ref 43). It has been patented as an expl ingredient (Ref 44) and a proplnt ingredient (Ref 41)

K Salt. A yellow cryst solid, prepd by the action of basic K salts on TeNMe in the presence of reducing agents (see also above under TNMe). Some which have been used are: K methoxide in me alc (this proc is subject to dangerous explns) (Ref 8); K cyanide in me alc (Ref 23); a satd aq soln of K ferrocyanide (Ref 9); or K nitrite in w, yield 80% (Ref 38). It has also been prepd by the action of K nitrite on dibromodinitromethane (Ref 13). Its expln temp is 97–98° (Ref 3); and its impactg sensy, using a noisemeter to detect explns, was found to be 44.3cm (50% expln height, 1 kg wt) (Ref 21). The soly in w and et alc was detd betw 0 and 60° (Ref 13). It is 100% ionized in w at 25° (Ref 50). It is claimed as a corrosion inhibitor when added at a level of 0.05–0.1% to liq rocket proplnts (Ref 30)

Piperidine Salt. Its ionization constant in w at 25° is 0.288 ± 0.001 (Ref 50)

Rb Salt. It is prepd from TNMe and Rb hydroxide in w, decomps at 157–59°. The ionization constant in w at 25° is 0.613 ± 0.003 (Ref 50)

Ag Salt. It is prepd by the action of Ag oxide on TNMe in eth, mp 100° (Ref 3). It reacts with benzyl halides to form trinitroethyl derivs (Ref 17). Explodes mildly on rapid heating (Ref 3)

Na Salt. It is prepd by the action of Na nitrite on TeNMe in me alc or et alc (Ref 38). It is completely ionized in w at 25° (Ref 50). A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

Refs: 1) Beil **1**, 79, (21), [45], {116} & ⟨107⟩ 2) L. Schiskoff, Ann **101**, 216 (1857) 3) A. Hantzsch & A. Rinckenberger, Ber **32**, 631 (1899) 4) H. Ley & H. Kissel, Ber **32**, 1366 (1899) 5) Baschieri, AttiRealeAccadLincei-(Rendiconti) [5] **9**, I, 392 (1900) 6) E.C. Franklin & C.A. Kraus, JACS **27**, 213 (1905) 7) E.P. Hedley, Ber **41**, 1200 (1908) 8) A.K. Macbeth, Ber **46**, 2537 (1913) 9) F.D. Chattaway & J.M. Harrison, JCS **109**, 171 (1916) 10) K.J.P. Orton & P.V. McKie, JCS **117**, 283 (1920) 11) K. vonAuwers & L. Harres, Ber **62**, 2287 (1929) 12) A. Quilico, Gazz **62**, 912 (1932) & CA **27**, 1348 (1933) 13) A.K. Macbeth & W.B. Orr, JCS **1932**, 543 14) L. Médard, MP **25**, 451 (1932–33) & CA **28**, 5660 (1934) 15) L.W. Andrew & D.L. Hammick, JCS **1934**, 244 16) C.D. Hurd, "Report on the Preparation and Properties of Nitroform", OSRD **144**, 20 Sep 1941 (ATI-29966), p 11 17) W.S. Reich et al, JCS **1947**, 1235 18) K.F. Hager, IEC **41**, 2169 (1949) 19a) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and their Application to Solid Smokeless Propellants", Aerojet Engrg Corp Quarterly Summary Report 371, Contr N7onr-462 (15 Apr 1949) 19b) R.D. Geckler & M.H. Gold, Quarterly Summary Report 404 (12 Sep 1949), p 53 20) W.L.

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Halogen Derivatives of Trinitromethane

Fluorotrinitromethane. $FC(NO_2)_3$, mw 169.03, N 24.85%. A colorl to pale yellow liq, bp 84.2°; d at 20°, 1.795g/cc; RI at 25°, 1.3944; Q_f at 25°, −51.99kcal/mole (Ref 3); CA Registry No 1840-42-2. It has been prepd by the action of F in N 1:6 on a mixt of 20g of solid K salt of TNMe, 40g of K fluoride, and 50g of Cu turnings at −12 to −6° in a Cu vessel (Ref 4); by the action of 10% F in He on the K salt of TNMe in w, yield 48%, purity by gas chromatography 99.42 mole% (Ref 3); by the action of F on the Na salt of TNMe in aq Na hydroxide (Ref 5); or by the action of KF on TeNMe in dimethylformamide (Ref 6). It could not be detond with a hammer blow (Ref 2). It is a useful oxidizer in monoproplnts or hypergolic biproplnts (Ref 6). Calcd Isp with fuels are as follows: 0.304:1 with ammonia, 265; 0.469:1 with hydrazine, 281; 0.151:1 with triptane, 270; 0.262:1 with acetonitrile, 267; 0.313:1 with me alc, 261; and 0.185:1 wt ratio with 1,2-bis(dimethylamino)propane, 271 lb-sec/lb (Ref 2). It does not react at ambient temp with acetonitrile, triptane, acet, me alc, benzene, nitrobenzene, and cyclohexane (Ref 2)

Refs: 1) Beil – not found 2) H.W. Bost & R.C. Doss, USP 3127736 (1964) & CA **61**, 5445a (1964) 3) M.F. Zimmer et al, JChemEngrgData **11**, 577 (1966) 4) L.T. Eremenko et al, IzvestAkadNSerKhim (1968), 429 & CA **69**, 18565 (1968) 5) V. Grakaus-

kas & K. Baum, JOC **33**, 3080 (1968) 6) R.C. Doss, USP 3419625 (1969) & CA **70**, 77293 (1969)

Chlorotrinitromethane. $ClC(NO_2)_3$, mw 185.46, N 22.65%. A very pale yellow oil, freezes to a white solid, insol in w, sol in org solvs (Ref 3). Its odor is penetrating and unpleasant, resembling chloropicrin; and it is a lacrymator (Ref 3). Mp 5.75° (Ref 8); bp at 9mm, 35° (Ref 3); d at 20° 1.6769g/cc (Ref 6); RI at 20°, 1.4471 (Ref 8); dipole moment at 25°, 2.17 debye (Ref 5); heat capacity 0.21cal/g/deg; Q_v 10.86kcal/mole; Q_f at 25 , −5.57 ±0.18 cal/mole (Ref 8); CA Registry No 1943-16-4. It is prepd by the action of Cl on the K salt of TNMe in ice cold eth (Ref 2), or in w (Ref 3); or by the slow addn of acet to a mixt of nitric acid and HCl (Ref 4). Its IR and UV spectra are given in Ref 7. It reacts with K hydroxide in w or et alc to give the K salt of TNMe (Ref 4). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen chloride, and Cl (Ref 9)

Refs: 1) Beil **1**, [46] & {116} 2) E. Schmidt et al, Ber **54**, 1483 (1921) 3) A.K. Macbeth & D.D. Pratt, JCS **119**, 354 (1921) 4) W.J. Boyd, JSCI **44**, 222T (1925) & CA **19**, 2188 (1925) 5) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 15036b (1961) 6) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 22096i (1961) 7) V.I. Slovetskii et al, IzvestAkadNOtdKhimNauk **1961**, 683 & CA **55**, 23048g (1961) 8) M.F. Zimmer et al, JChemEngrgData **9**, 527 (1964) 9) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 315 & CA **69**, 66758j (1968)

Bromotrinitromethane. $BrC(NO_2)_3$, mw 229.95, N 18.23%. A faintly greenish yellow liq; mp 9.5–10°; bp at 8mm, 59° (Ref 4); d at 20°, 2.0313g/cc; RI at 20°, 1.4808 (Ref 7); dipole moment at 25°, 2.56 debye (Ref 6); CA Registry No 560-95-2. It has been prepd by the action of Br on TNMe in sunlight (Ref 2); in nitric acid (Ref 4); on the K salt of TNMe in ice cold eth, yield 90% (Ref 7); or on the Hg salt of TNMe in acet, yield 87% (Ref 5). It reacts with K hydroxide in et alc to give the K salt of TNMe (Ref 3), and with olefins to form 2-bromo-1-nitronate esters which can be hydrolyzed to the bromoalcohols (Ref 8). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen bromide, and Br (Ref 9)

Refs: 1) Beil **1**, 79, (21), [46] & {116} 2) L. Schischkoff, Ann **119**, 247 (1861) 3) A.K. Macbeth & D.D. Pratt, JCS **119**, 355 (1921) 4) A.K. Macbeth & D.D. Pratt, JCS **119**, 1356 (1921) 5) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1960**, 669 & CA **54**, 22331e (1960) 6) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 22331e (1961) 7) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 22096i (1961) 8) K. Torssel & R. Ryhage, ArkivKemi **23** 525 (1965) & CA **63**, 6893b (1965) 9) V.I. Slovetskii et al, IzvestAkadNSerKhim **1968**, 80 & CA **69**, 35191g (1968)

Iodotrinitromethane. $IC(NO_2)_3$, mw 276.46, N 15.19%. Bright yellow leaflets, insol in w, sol in hot et alc, benzene, or ligroin (Ref 2); mp 55–56°; bp at 13mm, 48–8.5° (Ref 3); dipole moment 3.79 debye (Ref 4); CA Registry No 630-70-6. It is prepd by the reaction betw I and the Ag salt of TNMe (Ref 2); or by the action of I on the K salt of TNMe in ice cold eth, yield 50% (Ref 5). It may expld violently on standing (Ref 3). It gives TeNMe on treatment with Ag Nitrite and the K salt of TNMe on treatment with aq K hydroxide (Ref 2). It reacts with ethylene and cyclohexene to form 2-iodonitronate esters which react further to form oxazolidines (Ref 6). The thermal decompn was studied at 170° and 400mm. The decompn prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxide, C monoxide, C dioxide, cyanogen iodide, and I (Ref 7)

Refs: 1) Beil **1**, 79 & [47] 2) A. Hantzsch, Ber **39**, 2478 (1906) 3) J. Mesenheimer & M. Schwarz, Ber **39**, 2551 (1906) 4) A.N. Shidlovskaya et al, DoklAkadN **132**, 1376 (1960) & CA **55**, 15036b (1961) 5) S.S. Novikov et al, IzvestAkadNOtdKhimNauk **1961**, 672 & CA **55**, 15036b (1961) 6) V.A.

Tartakovskii et al, IzvestAkadNSerKhim **1966**, 1290 & CA **65**, 16808 (1966) 7) G.M. Nazin et al, IzvestAkadNSerKhim **1968**, 315 & CA **69**, 66758j (1968)

Tetranitromethane (TeNMe). Tetranitromethan (Ger), Tétranitrométhane (Fr), Tetranitrometano (It), Tetranitrometan (Russ); $C(NO_2)_4$, mw 196.04, N 28.57%; OB to CO_2 +49%; a colorl to pale yellow liq, freezes to a colorl solid. Its odor is described as pungent (Ref 21). Pure TeNMe is said to be colorl, but becomes yellow on contact with w, due to hydrolysis to TNMe (Ref 5). Mp 14.2° (Ref 26); bp 125.7° (Ref 10); d at 25°, 1.62294g/cc; RI at 25°, 1.43822 (Ref 18). The dipole moment is essentially zero, indicating the structure to be symmetric, instead of $(O_2N)_3CONO$ as had been postulated to account for its reactivity (Ref 18); CA Registry No 509-14-8

Historical. It was first prepd by the action of nitric acid on TNMe (Ref 2). This reaction is the basis of large scale prepn in which acetylene is nitrated to TNMe and the latter treated with an excess of nitric acid to give TeNMe (Ref 26). As stated above under TNMe, in Ger during WWII, the prepn of TeNMe by this process was scaled up for use as an intermediate and as a substitute for nitric acid in the V-2 rocket (Ref 26). A pilot plant was built at Newark, NJ for prodn using this procedure. It was destroyed by an expln in 1953 and not rebuilt (Refs 33 & 44). Other prepns of lesser importance are by the action of Ag nitrite on iodotrinitromethane (Ref 3); by the action of 90% nitric acid and 25% oleum on malononitrile, yield 45% (Ref 40); by the action of mixed acid on a number of aromatic nitrocompounds, of which nitrobenzene, dinitrobenzene, and nitronaphthalene gave the best yields (Ref 13a); and by the action of nitryl chloride on salts of TNMe. The best yield, 95%, was obtained with the K salt (Ref 38). It is formed in small amts during the nitration of toluene to prepare TNT (Refs 37 & 38), and has been held responsible for explns which have occurred in TNT mfg plants. It has been postulated that mixts of TeNMe and toluene, which are as sensitive as NG, have condensed in off gas lines and detonated (Ref 37). Crude TNT, therefore, contains varying amts of TeNMe which, being highly toxic, accounts for conflicting reports as to the toxicity of TNT (Ref 37). By the use of C^{14}-labeled TNT, it was shown that 54.2% of the TeNMe came from the aromatic C attached to the Me group, 8.3% from each of the C atoms connected to nitro groups, 7.4% from each of the C atoms attached to H, and 6.1% from the Me group (Refs 37 & 38)

Laboratory Preparation. Anhydrous nitric acid (31.5g) in a 250ml 2-necked flask fitted with a dropping funnel and thermometer reaching to its bottom is cooled to 10°, and 51g of Ac_2O is added slowly at a rate which keeps the temp below 10°. After all is added, the funnel is removed and the flask allowed to warm slowly to room temp, allowed to stand a week, the contents poured into 300ml of w in a 500ml flask, and the TeNMe removed by steam distn. The lower layer of the distillate is sepd, washed with dil alkali, w, and dried over anhyd Na sulfate; yield 57–65% (Ref 32). *TeNMe should not be distd as it can expl with great violence, and distn residues are especially dangerous* (Ref 46). A continuous process using this reaction is described in Ref 34. A similar prepn is by heating acetyl nitrate with acet ac or Ac_2O (Ref 4)

Chemical Reactions. TeNMe gives TNMe or salts of TNMe under a variety of conditions (see above under TNMe). It is a mild oxidizing agent, converting hydroquinone to quinhydrone, N,N-dimethylaniline into crystal violet (Ref 8), and thiourea into $(H_2NCS)_2$ (Ref 14). It is



a nitrating and nitrosoating agent (Ref 26), converting triethylamine into diethylnitrosamine (Ref 12). It is reduced to guanidine and ammonia with Zn (Ref 14) or Fe (Ref 13) and aq HCl

Analytical. A proc is described for the quant titrimetric analysis of TeNMe in nitric acid (Ref 35); and a spectrophotometric method is described in Ref 41 for the detn of small amts of TeNMe in air and w

Critical Diameter. The crit diam for deton propagation of TeNMe thickened with poly(methyl acrylate) and loaded with up to 75% inert solids was detd and found to decrease with increasing solids loading. It was postulated that the solids acted as reaction foci ahead of the deton front (Ref 45)

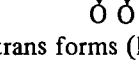
Explosion Temperature. It does not expl below 360° (Ref 21)
Heat of Combustion. 102.9kcal/mole (Ref 22)
Heat of Explosion. From a differential therm analysis exotherm at 310° the Q_e at 227° was calcd to be 557cal/g (Ref 39)
Heat of Formation. −8.9kcal/mole (Ref 22)
Impact Sensitivity. Described as "similar to TNT" (Ref 21). On BM app (2kg wt) the 50% expln height was found to be over 100cm (Ref 25)
Shock Wave Sensitivity. A test is described to detn the shock wave sensy of liq expls. A crit thickness is detd for which an impressed shock wave causes a deton. For TeNMe this was detd to be 3mm. An eqn is developed to relate this thickness with other parameters such as press and deton vel (Ref 42)
Spectra, Infrared. The IR spectra in the gas, liq, and solid states are in Ref 30
Ultraviolet. λ_{max} ca 275mμ, log ε 2.2 (Ref 19)
Thermal Stability. At 100° it evolves acid fumes in 30min, at 135° there is no expln after 300min (Ref 21)
Toxicity. It is a lacrymator and irritates the skin mucous membranes, especially of the respiratory tract (Ref 26). Prolonged exposure to vapors causes damage to liver, kidneys, and other organs. Concn in air of 0.1ppm is fatal and 3.3ppm or higher are rapidly fatal (Ref 47, p 1156). Its threshold limit value in air is set at 1ppm (Ref 47, p 22)
Trauzl Test. 21.4% of TNT when pure (Ref 26); for mixts see below
Uses. It does not gelatinize NC (Ref 15). It improves the octane rating of diesel fuels (Ref 26). It decreases the polymerization rate of methyl methacrylate (Ref 24), and styrene (Ref 23), but does not inhibit the reaction. A review of its use as an oxidizer in rocket proplnts is given in Ref 33. TeNMe gives yellow to orange colors with olefins and aromatic compds. This is used as a diagnostic test for the presence of these groups in org analysis (Refs 6, 9, 16, 17 & 29)
Explosive Mixtures with Organic Compounds. Mixts with org compds are more powerful and sensitive expls than TeNMe. Those whose expl props have been detd are listed below:
Benzene. A mixt of 2 moles of TeNMe and one of benz gave an expln temp of 163.3° (Ref 11). An 87:13 mixt with benz gave a Trauzl test of 134% of TNT (Ref 26). Mixts of from 65 to 90% by wt in benz had a card gap test of over 300 cards, indicating them to be very sens (Ref 36). The sensy of mixts with benz was found to be due to the formation and collapse of cavitation bubbles in the liq (Ref 43)
Ethylene Glycol. A 50% soln by wt had a card gap test of 270 cards (Ref 36)
Gasoline. Mixts with gasoline and diesel fuel were found to be powerful, but sens expls (Ref 26)
Hydrocarbons. Addn of metallo-org compds lowers the burning rate of TeNMe/hydrocarbon mixts to the point where they are useful monoproplnts (Ref 27)
Naphthalene. A mixt of 2 moles of TeNMe to one of naphthalene gave an expln temp of 160.4° (Ref 11)
Nitromethane. A mixt of 4 moles of NMe to one of TeNMe gave a maximum expansion of 30.62 in the Pb block expansion test (Ref 20). A mixt contg 40% TeNMe had a card gap test of 75 cards (Ref 36)
Paraffins. Mixts of 10–40% paraffins and 69–90% TeNMe are liq expls which are readily detond by expl shock, but are resistant to mech shock (Ref 28)
Sodium Methoxide. TeNMe explds violently in its presence (Ref 7)
TNT. The power by BalPend of mixts with TNT was 171, TNB 151, RDX 167, and EDNA 160% of TNT (Ref 31)
Toluene. A mixt with toluene expld at the Kaiser Wilhelm Inst in 1917, and in 1920 at the Univ of Münster a massive iron gas burner containing a residue of 10g of a TeNMe/toluene mixt decompd suddenly. The deton splintered the container, and of 300 students in the area, 10 were killed and 20 injured (Ref 13b). A mixt with toluene which has an OB of zero is called "Panclastite" in Fr. It has a deton vel of 8000 m/sec (NG 7000m/sec) and is more shock sensitive than NG (Ref 31)
Refs: 1) Beil **1**, 80, (21), [47], {116} & ⟨107⟩ 2) L. Schischkoff, Ann **119**, 246 (1861) 3) A. Hantzsch, Ber **39**, 2479 (1906) 4) A. Pictet & E. Khotinsky, Ber **40**, 1136 (1907) 5) F.D. Chattaway, JCS **97**, 2099 (1910) 6) I. Ostromisslenskii, JPraktChem (2) **84**, 489 (1911) & CA **6**, 1287 (1912) 7) A.K. Macbeth, Ber **46**,

2537 (1913) 8) J.N. Rakshit, JACS **36**, 1221 (1914) 9) A.K. Macbeth, JCS **107**, 1826 (1915) 10) A.W.C. Menzies, JACS **41**, 1337 (1919) 11) G. Tammann, NachGesWissGöttingen **1919**, 220 & CA **14**, 3532 (1920) 12) E. Schmidt & R. Schumacher, Ber **54**, 1418 (1921) 13) T. Henderson et al, JCS **123**, 1136 (1925) 13a) P.V. Mckie, JSCI **44**, 430T (1925) & CA **19**, 3373 (1925) 13b) A. Stettbacher, SS **25**, 439 (1930) & CA **25**, 1647 (1931) 14) A.K. Macbeth & W.B. Orr, JCS **1932**, 542 15) L. Médard, MP **25**, 451 (1932–33) & CA **28**, 5660 (1934) 16) T.T. Davies & D.L. Hammick, JCS **1938**, 763 17) H. Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen", Springer (1938), p 773 18) G.L. Lewis & C.P. Smyth, JACS **61**, 3067 (1939) 19) G. Kortüm, ZPhysChem(Leipzig) **B43**, 271 (1939) & CA **33**, 8115 (1939) 20) H.B. Hass, "The Synthesis of Certain Aliphatic Nitro Compounds", OSRD **154** (18 Oct 1941), p 19 21) R. McGill, "Evaluation of Explosives Submitted to the Explosives Research Laboratory in 1941", OSRD **830** (25 Aug 1942), p 56 22) W.A. Roth & K. Isecke, Ber **77**, 537 (1944) 23) G.V. Schulz et al, JMakrChem **2**, 127 (1944) 24) G.V. Schulz, Ber **80**, 241 (1947) 25) A.J. Clear & W.R. Tomlinson, Jr, "Development of Standard Tests, Application of the Impact and Sand Tests to the Study of Nitroglycerin and Other Liquid Explosives", PATR **1738** (13 June 1948), Table I 26) K.F. Hager, IEC **41**, 2185 (1949) 27) J.A. Hannum, USP 2559071 (1951) & CA **45**, 9836d (1951) 28) J.A. Hannum, USP 2560439 (1951) & CA **46**, 739b (1951) 29) E. Heilbronner, Helv **36**, 1121 (1953) & CA **47**, 11980i (1947) 30) P.H. Lindenmeyer & P.M. Harris, JChemPhys **21**, 408 (1953) 31) H. Muraour, MAF **28**, 520 (1954) & CA **49**, 2753b (1955) 32) P. Liang, "Tetranitromethane" in OrgSynColl Vol **3** (1955), p 803 33) J.G. Tshinkel, IEC **48**, 732 (1956) 34) F.C. Anderson et al, "Explosives Research", AGC **1200**, Contr N7onr-46208 (21 Dec 1956), p 10 35) I. Sakamaki et al, BunsekiKagaku **6**, 626 (1957) & CA **52**, 13540e (1958) 36) J.G. Tshinkel & C.R. Morrison, Chem & Eng Data Series **3**, 350 (1958) 37) F.S. Holahan et al, "The Use of Carbon-14 as a Tracer to Study the Origin of Tetranitromethane in TNT Manufacture", PATR **2695** (July 1960) (AD 241129 & PB 148304) 38) F.S. Holahan et al, JACS **84**, 756 (1962) 39) R.S. Bohon, AnalChem **35**, 1845 (1963) 40) H.G. Clark et al, USP 3067261 (1963) & CA **58**, 8904b (1963) 41) D.J. Glover & S.G. Landsman, AnalChem **36**, 1690 (1964) 42) I.M. Voskoboinikov et al, DoklAkadN **167**, 610 (1966) & CA **64**, 19366a (1966) 43) V.E. Gordeev et al, DoklAkadN **172**, 383 (1967) & CA **66**, 77920v (1967) 44) Urbański **3** (1967), 299 45) R.Kh. Kurbangalina, ZhPriklMekhTekhFiz **1969**, 133 & CA **71**, 126697s (1969) 46) Houben **X/1** (1971), p 11 47) Sax (1975)

METHANE, NITROSO. CH_3NO; mw 45.04, N 31.10%, OB to CO_2 –88.81%. It is a blue gas at room temp, its solns in hydrophobic solvs are blue, in w and hydrophilic solvs are colorl (Ref 2); CA Registry No 865-40-7

Preparation. It was first prepd by the irradiation of tert-butyl nitrite with a Hg-vapor lamp and isolated as a colorl dimer which, when heated above its mp of 122.0–2.2°, is converted to the blue monomer; prolonged heating of the dimer converts it to the insoluble trimer of formaldehyde oxime (Ref 2). It has also been prepd in varying yield by the irradiation of compds capable of producing Me radicals, such as dimethyl mercury (Ref 5), tert-butyl peroxide (Ref 8), azomethane, or Me iodide (Ref 10) in the presence of nitric oxide

Reactions. Monomeric nitrosomethane is condensed out at liq N temp to a pale blue solid which converts to the colorl dimer upon warming to room temp (Refs 6 & 7), and to formaldehyde oxime at higher temps (Ref 7). The structure proposed for the dimer is



which can exist in cis and trans forms (Ref 6). The low yield of nitrosomethane in irradiation expts has been explained by its reactn with excess nitric oxide to form N dioxide, N, and polymeric prods (Ref 9)

Spectroscopic Data. Freshly prepd nitrosomethane has an IR absorption band at 6.3–6.4μ which slowly decays and is replaced by a band at 11μ characteristic of formaldehyde oxime (Ref 8). The visible absorption λ_{max} is 287mμ in eth and at 266–7mμ in w (Ref 4)

Refs: 1) Beil **1**, {105} & ⟨99⟩ 2) C.S. Coe

& T.F. Doumani, JACS **70**, 1516 (1948) 3) J.R. Raley et al, JACS **70**, 88 (1948) 4) H.T.J. Chilton & B.G. Gowenlock, JCS **1954**, 3174 5) W.A. Bryce & K.U. Ingold, JChemPhys **23**, 1968 (1955) 6) B.G. Gowenlock & J. Trotman, JCS **1955**, 4190 7) L. Batt & B.G. Gowenlock, TrFaradSoc **56**, 682 (1960) 8) J.G. Calvert et al, JACS **82**, 1 (1960) 9) M.I. Christie et al, JCS **1964**, 3147 10) M.I. Christie et al, TrFaradSoc **61**. 674 (1965)

Nitroso Halogen Derivatives of Methane

Difluoronitrosomethane, F_2CHNO, mw 81.03, N 17.29%; prepd by the photolysis of a mixt of chlorodifluoromethane & nitric oxide

Refs: 1) Beil – not found 2) M.G. Bellas et al, CanJChem **43**, 1022 (1965)

Trifluoronitrosomethane. F_3CNO; mw 99.01, N 14.15%; a deep blue solid, liq, or gas. The color of the liq is described as that of a concd ammoniacal Cu soln (Ref 2). The odor is described as earthy or similar to sewage sludge (Ref 2). Mp $-196.6°$, bp $-84°$ (Refs 1 & 2); CA Registry No 334-99-6

Preparation. It was first isolated as a by-prod from the fluorination of Ag cyanide. Its formation was attributed to the presence of Ag nitrate or Ag oxide in the tech grade Ag cyanide used (Ref 2). The first prepn in good yield was by the irradiation in a sealed tube of a mixt of nitric oxide and trifluoromethyl iodide plus a small amt of Hg with the light from a Hg vapor lamp, yield 75% (Ref 3). The same workers also prepd trifluoronitrosomethane by the reaction of Ag trifluoroacetate with nitrosyl chloride (ClNO), yield 13% (Ref 5). More recent work indicated that this reaction proceeds thru the intermediate formation of the mixed anhydride of nitrous and trifluoroacetic acids (F_3CCONO) (Ref 11).

$$F_3C\overset{\displaystyle O}{\overset{\|}{C}}ONO$$

Another prepn reported is by heating trifluoroacetohydroxamic acid ($F_3CCONHOH$) to $85°$ at 30–40mm of Hg, yield 63% (Ref 10)

Chemical Reactions. It is readily oxidized with hydrogen peroxide to the nitro compd (Ref 4). It is stable in the absence of light or air for 3–5 years; but sunlight or irradiation with UV light converts it to o-nitroso-N,N-bis(trifluoromethyl)-hydroxylamine, $(F_3C)_2NONO$ (Ref 8). It reacts with perfluoroethylene to give a mixt of perfluoro-2-methyl-1,2-oxazetidine and a linear copolymer (Ref 6). This polymer, whose structure was shown to be $(CF_2CF_2NO)_x$, has

$$\begin{array}{c} \\ | \\ CF_3 \end{array}$$

been been found to be an elastomer with very good chem resistance and low temp props. For a review of this type of elastomer see Ref 11

Heat of Vaporization. 4133cal/g, Trouton const 21.9 (Ref 7)

Spectra. Infra Red. The IR spectrum of a highly purified sample in the gas phase with assignment of bands is given in Ref 7

Visible. The intense blue color of the compd is due to a broad absorption band at 6800–40Å, $\varepsilon_{max} = 19.0$ (Ref 4). This band is present in the gas phase and in solns (Ref 9)

Toxicity. Its inhalation causes headaches and an unwell feeling (Ref 2)

Refs: 1) Beil **1**, {105} & ⟨99⟩ 2) O. Ruff & M. Giese, Ber **69**, 598 (1936) 3) R.N. Hazeldine, JCS **1953**, 2075 4) J. Banus, JCS **1953**, 3755 5) R.N. Hazeldine & J. Jander, JCS **1953**, 4172 6) D.A. Barr & R.N. Hazeldine, JCS **1955**, 1881 7) J. Mason & J. Dunderdale, JCS **1956**, 754 8) R.N. Hazeldine & B.J.H. Mattison, JCS **1957**, 1741 9) J. Mason, JCS **1957**, 3904 10) I.L. Knunyants & G.A. Sokol'skii, DoklAkadN **132**, 602 (1960) & CA **54**, 24366f (1960) 11) M.C. Henry et al, "Synthesis, Compounding, and Properties of Nitroso Rubbers" in P.R. Tarrand, ed, Fluorine Chemistry Reviews **1**, 1 (1967)

Chloronitrosomethane. See Chloromethane and Derivatives in this Vol

Chlorodifluoronitrosomethane. $ClCF_2NO$, mw 115.47; N 8.24%; a dark blue liq or gas; bp ca $-35°$ (Refs 1, 2 & 6); CA Registry No 421-13-6

Preparation. It has been prepd by reactions analogous to those for prepn of trifluoronitrosomethane (Refs 2 & 5). It has also been prepd by the action of 33% aq nitric acid on chlorodifluorosulfenyl chloride ($ClCF_2SCl$) (Ref 3), and by the action of hot concd HCl on difluoronitroacetic acid (Ref 4). Its props and reactions are similar to trifluoronitrosomethane

Refs: 1) Beil **1**, ⟨99⟩ 2) R.N. Hazeldine, JCS **1953**, 1075 3) N.N. Yarovenko & S.P. Moronyi, ZnObsKhim **30**, 4066 (1960) & CA **55**, 20928e (1961) 4) A.V. Fokin et al,

ZhObshchKhim **36**, 540 (1966) & CA **65**, 613e (1966) 5) R.N. Hazeldine, USP 3083327 (1964) & CA **60**, 1588d (1964) 6) C.W. Taylor, USP 3342874 (1968) & CA **68**, 21546b (1968)

Dichlorofluoronitrosomethane. $FCCl_2NO$, mw 131.93, N 10.61%; a blue liq, bp 12° (Ref 2); CA Registry No 1495-28-9. It is prepd by the action of 33% nitric acid on $FCCl_2SCl$, yield 8% (Ref 2); and by the action of K chloride on fluorochloronitroacetic acid (Ref 3)

A soln of the compd in eth was treated overnight with hydrogen sulfide in a sealed tube to give FClC:NOH which polymerized in a few days (Ref 2)

Refs: 1) Beil – not found 2) N.N. Yarovenko & S.P. Motornyi, ZhObshchKhim **30**, 4066 (1960) & CA **55**, 20928e (1961) 3) I.V. Martynov & Yu.L. Krugylak, ProblOrganSinteza-AkadNaukSSSR, OtdObshchITeknKhim **1965**, 56 & CA **64**, 8022h (1964)

Trichloronitrosomethane. Cl_3CNO, mw 148.39, N 9.51%, OB to CO_2 −10.78%; a deep blue liq, comparable in color to ammoniacal Cu solns; freezes at liq N temp to a violet-blue solid; bp 57–58°; d at 20°, 1.500g/cc (Refs 1, 2 & 3); CA Registry No 3711-49-7

Preparation. It was first prepd by the action of 10% nitric acid on Na trichloromethanesulfonate (Cl_3CSO_2Na) (Ref 2). It has also been prepd by the reduction of chloropicrin (Cl_3CNO_2) at a Pt cathode in 40% aq sulfuric acid contg et alc (Ref 4); by heating trichloroacetohydroxamic acid ($Cl_3CCONHOH$) to 90° and 20–30mm, yield 62% (Ref 5); and by the interaction of Na trichloromethanesulfonate and nitrosyl chloride in a sealed tube (Ref 7). Most interesting is the report that when nitric oxide was passed thru C tetrachloride while being irradiated with high-energy electrons, the soln turned dark blue, and a 50% yield of trichloronitrosomethane was obtd (Ref 6)

Chemical Reactions. It decomps slowly on standing, more rapidly on heating in the absence of air to form nitrosyl chloride, nitric oxide, chloropicrin, & trichloromethyldichloromethyl-eneimine ($Cl_3CN{:}CCl_2$) (Ref 2). It deflagrates in the presence of O_2 at 120° to give N dioxide, chloropicrin, and hexachloroethane (Ref 2). It is reduced to Me amine with Fe turnings and acet ac (Ref 2); and to phosgene oxime ($Cl_2C{:}NOH$) with hydrogen sulfide in Me alc (Ref 2), or Sn dichloride and HCl (Ref 3)

Solubility. It is insol in w, sol in org solvs (Ref 2)

Refs: 1) Beil **1**, [39], {105} & ⟨99⟩ 2) W. Prandtl & K. Sennewald, Ber **62**, 1754 (1929) 3) W. Prandtl & W. Dollfus, Ber **65**, 754 (1932) 4) H. Brintzinger et al, ZElektrochem **53**, 109 (1949) & CA **43**, 8915 (1949) 5) I.L. Knunyants & G.A. Sokol'skii, DoklAkadN **132**, 602 (1960) & CA **54**, 23466f (1960) 6) A. Hengleim, LargeRadiationSourcesInInd, ProcCong-Warsaw **2**, 139 (1959) & CA **55**, 19762c (1961) 7) H. Sutcliffe, JOC **30**, 3221 (1965)

Bromodifluoronitrosomethane. $BrCF_2NO$, mw 159.93, N 8.76%; it is a dark blue solid & liq; bp ca −12°. It is prepd by the irradiation of a mixt of bromodifluoroiodomethane and nitric oxide in a sealed tube in the presence of Hg, yield 50%

Refs: 1) Beil **1**, ⟨100⟩ 2) R.N. Hazeldine, JCS **1953**, 2075

Bromodichloronitrosomethane. $BrCCl_2NO$, mw 192.84, N 7.26%; it is a dark blue liq of unpleasant odor, fr p −80°, bp 21° at 24mm. It is prepd by the action of Br and Na acetate on phosgene oxime ($Cl_2C{:}NOH$). It decomps on attempted distn at atm press. It is reduced to phosgene oxime with hydrogen sulfide in Me alc, and warming with Br produces dichlorodibromomethane

Refs: 1) Beil **1**, {105} 2) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

Chlorodibromonitrosomethane. $ClCBr_2NO$, mw 237.31, N 5.90%; it is a dark blue liq of unpleasant odor, it freezes at −80°, bp 24° at 20mm; it can only be distd in a vacuum. It is prepd by action of Br and Na acetate in w on bromochloroformoxime (BrCCl:NOH). Heating with Br forms chlorotribromomethane

Refs: 1) Beil **1**, {105} 2) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

Tribromonitrosomethane. Br_3CNO, mw 281.77, N 4.97%; it is a dark blue liq of unpleasant odor; bp 36–38° at 14mm, decomps above 50°. It is prepd by the action of K hypobromite on MF (Ref 2), or by the action of KBr and Na acetate on MF (Ref 3). Upon warming with w forms tetrabromomethane and cyanogen bromide (Ref 3)

Refs: 1) Beil **1**, {106} 2) G. Endres & H. Bottmann, Ber **65**, 67 (1932) 3) L. Birkenbach & K. Sennewald, Ber **65**, 546 (1932)

Written by: **C. H. McDONNELL**

Methanites. Safety expls used in coal mining. Pelant (Ref) details eight compn variations, of which Methanites VII and VIII proved to be the safest. They were gallery tested in methane-air-coal dust atms in 200 to 500g charges, and produced about 1.8% ignitions. In actual use in gaseous and dusty coal mines, no ignitions or explns occurred. The formulations for the eight Methanites, results of output tests, calcd expl temps, and results of gallery tests are given below:

Table 1

Methanites	I	II	III	IV	V	VI	VII	VIII
Formulation, %								
Nitroglycerin	28.60	28.40	26.0	25.0	25.0	25.0	25.0	25.0
Nitrocellulose	1.05	1.04	1.0	1.0	1.0	1.0	0.8	0.8
Centralite	–	–	–	0.5	0.5	0.25	–	–
Liquid DNT	0.70	0.69	–	–	–	–	–	–
Wood flour	–	–	–	0.5	–	–	–	–
Glycerin	2.20	2.17	2.1	–	–	–	–	–
Dextrin	2.20	2.17	2.1	–	–	–	–	–
Ca nitrate in 50% soln	–	–	–	–	4.0	4.0	4.0	3.0
Amm nitrate	27.75	27.53	29.4	32.0	23.0	23.1	23.25	25.0
Na chloride	31.10	36.80	38.5	40.0	46.5	46.65	46.65	45.9
Fe_2O_3	0.40	0.40	0.4	–	–	–	–	–
Water	–	0.80	0.5	1.0	–	–	–	–
Palatino A	–	–	–	–	–	–	0.2	0.3
Output Tests								
Trauzl test, cc [a]	240	230	225	190	170	170	165	170
Kast test, mm [b]	0.91	0.86	0.85	0.82	0.68	0.67	0.50	0.66
Gap test, cm [c]	5–6	4–5	2–4	2	2	1–2	0	0
Expln Temp (calcd), °C, by method of:								
Mallard & LeChatelier	2571	2502	2401	2168	2021	1962	1939	2019
Berthelot & Vieille	2176	2103	2002	1778	1631	1576	1555	1633
Pier & Bjerrum	3294	3229	3048	2707	2513	2431	2380	2504
Gallery Test (% of explns)	22.7	21.2	19.8	11.6	5.5	4.2	1.8	1.8

a Trauzl Pb block test, 10g sample, No 6 cap
b Kast's crusher test, 10g sample, Cu cylinder
c Transmission of detonation

Ref: V. Pelant, Chem&Ind(Paris), Special No (June 1933), 888–901

Methanol (Methyl alcohol, wood alcohol). CH_3OH, mw 32.04; OB to CO_2 −149.81%; clear, colorl, mobile, highly polar liq; mp −97.8°, bp 64.5°, d 0.7913g/cc at 20/4°, flash p 54°F, autoign temp 867°F, vap press 100mm at 21.2°C; miscible with w, alc & eth. Can be prepd by the high press catalytic synthesis from carbon monoxide and hydrogen, or by partial oxidn of natural gas hydrocarbons. Other methods of prepn and properties are given in Ref 1. It is used in the manuf of formaldehyde and dimethyl terephthalate, chemical synthesis (methyl amines, methyl chloride, methyl methacrylate, etc), aviation and rocket fuel (Ref 3), automotive antifreeze, solv for NC, ethyl cellulose, polyvinyl butyral, shellac, resin, manila resin, dyes; denaturant for alc; dehydrator for natural gas (Ref 4). Nobel used methanol as an additive to NG to reduce its sensitivity for transportation purposes. In this case it was removed by w wash prior to use (Ref 2). Methanol can be nitrated directly to form Methyl Nitrate (see in this Vol), a powerful expl compd

Methanol is a dangerous *fire hazard* when exposed to heat or flame, and a moderate *expl hazard* when exposed to flame. It is a dangerous *disaster hazard* upon exposure to heat or flame, and can react vigorously with oxidizing materials. Methanol possesses distinct narcotic props, and is also a slight irritant to the mucous membranes. Its main toxic effect is exerted upon the nervous system, particularly the optic nerves and possibly the retinae. In the body the products formed by its oxidn are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methanol should be regarded as a cumulative poison (Ref 5)

Methanol is available in Technical, C.P. (99.85% purity) and electronic (used to cleanse and dry components) grades. US Spec 0-M-232E (July 30, 1968) with Amd 1 (Sept 11, 1970), covers the requirements and tests for methanol used by all Federal agencies (see below)

Refs: 1) Beil **1**, 273, (131) & [252] 2) Naoúm (1928), 261 3) S. Krop, JetPropn **24**, 225 (1954) 4) CondChemDict (1971), 564-L 5) Sax (1968), 911-L

METHANOL, **Analytical Procedures**

Methanol, Federal Specification 0-M-232E (July 30, 1968) entitled *Methanol (Methyl Alcohol)* requirements and tests, supplemented by *Amendment 1* (Sept 11, 1970)

1.1 Scope. This Spec and Amd 1 covers methanol of synthetic grades and a denaturing grade

1.2 Classification. Methanol shall be of the following grades:

Grade A – Synthetic, 99.85% by wt (solvent use)

Grade AA – Synthetic, 99.85% by wt (hydrogen–carbon dioxide generation use

Grade C – Wood alcohol (denaturing grade)

2.1 Applicable Documents – Listed among them are:

a) Fed Test Method Std **No 791**, "Lubricants, Liquid Fuels, and Related Products; Methods of Testing", available from the Superintendent of Documents, US Government Printing Office, Washington, DC, 20402

b) Military Specification **MIL-G-10157**, "Generator and Charging Plant, Hydrogen and Carbon Dioxide, Semitrailer-Mounted"

c) Military Standard **MIL-STD-147** "Palletized and Containerized Unit Loads 40″ x 48″ 4-Way (Partial) Pallet Skids, Runners, or Pallet-Type Base"

d) Military Standard **MIL-STD-290**, "Packaging, Packing, and Marking of Petroleum and Related Products", Publications b, c and d, required by contractors in connection with specific procurement functions, should be obtained from the procuring activity or as directed by the contracting officer

e) Internal Revenue Service Regulations **26-CFR-212**, "Formulas for Denatured Alcohol", available from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402

f) American Society for Testing and Materials (ASTM) Standards **D1078**, "Distillation Range of Volatile Organic Liquids"; **D1209**, "Color of Clear Liquids (Platinum-Cobalt Scale)"; **D1296**, "Residual Odor of Lacquer Solvents and Diluents"; **D1353**, "Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products"; **D1363**, "Permanganate Time

of Acetone and Methanol"; **D1364**, "Water in Volatile Solvents (Fischer Reagent Titration Method)"; **D1612**, "Acetone in Methyl Alcohol (Methanol)"; **D1613**, "Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products". The above publications can be obtained from the American Society for Testing and Materials, 1916 Race St, Philadelphia, Pennsylvania 19103

3. **Requirements.**

3.1 Grades A and AA. Shall conform to Table 1

3.2 Grade C. Grade C wood alcohol (denaturing grade) shall comply with Internal Revenue Service Regulations **SDAI of 26-CFR-212**, "Formulas for Denatured Alcohols"

4. **Quality Assurance Provisions**, which include:

4.1 Responsibility for Inspection

4.1.1 Material Inspection

4.2 Classification of Inspection

4.3 Quality Conformance Inspection

4.3.1 Lot

4.3.2 Drums and Small Containers

4.3.3 Tank Cars

4.3.4 Lot Acceptance

are discussed on p 3 of Spec 0-M-232E

4.4 Quality Conformance Inspection.

4.4.1 Chemical Reagents. Wherever chemical reagents are specified in the following tests, analytical reagent grade shall be used

4.4.2 Acetone and Aldehydes. Determine the acetone and ethanol content in accordance with **ASTM D1612.** The sample is reacted with Nessler's reag and the turbidity that is produced is compared to a standard contg the equivalent of 0.003 weight % acet

4.4.3 Acetone and Ethanol (Grade AA only). Determine the acetone and ethanol content by the elution method of gas chromatography using internal standards

4.4.3.1 Apparatus and Operating Conditions. A conventional chromatographic technique utilizing an instrument at least equal in performance to the highest sensitivity range of the Perkin Elmer Vapor Phase Fractometer Model 154 shall be used. A two meter elution column

Table 1

Characteristics	Grade A Requirement	Grade AA Requirement
Acetone and aldehydes, % max	0.003	0.003
Acetone, % max	–	0.001
Ethanol, % max	–	0.001
Acidity (as Acetic Acid), % max	0.003	0.003
Alkalinity, % max as NH_3	0.003	0.003
Appearance	Clear and free from suspended matter or sediment	
Carbonizable substances	No discoloration	No discoloration
Color	Not darker than color standard No 5 of ASTM platinum-cobalt scale	
Distillation range	Not more than 1° and shall include 64.6° ± 0.10° at 760mm	
Hydrocarbons	No cloudiness or opalescence	No cloudiness or opalescence
Specific gravity, max	0.7928 at 20°/20°	0.7928 at 20°/20°
% Methanol by weight, min	99.85	99.85
Nonvolatile content, g/100ml, max	0.0010	0.0010
Odor	Characteristic, nonresidual	Characteristic, nonresidual
Permanganate test	No discharge of color in 30 minutes	No discharge of color in 30 minutes
Water, % max	0.15	0.10

using tetraethylene glycol dimethyl ether (TEDME) or equal as the liquid phase shall be used under the following operating conditions: temp, +55°; press, adjust to produce He flow rate of 80 ± 10ml; sample size, 0.20ml

4.4.3.2 Quantitative Analysis.

(a) Internal standards for quant analysis curves shall be run on standard specimens prepd by adding pure ethanol or acet in 0.001% by vol increments. The area under the peak is equivalent to the concn of ethanol or acet in the specimen. Using a simple ratio, the concn of ethanol or acet can be calcd

(b) The area under the ethanol or acet curve of the unknown sample, when calcd utilizing the internal standardization method, shall be no more than specified in Table 1

4.4.4 Acidity. Determine the acidity in accordance with **ASTM D1613**. The sample is mixed with an equal vol of w and titrated with aq NaOH soln to the phenolphthalein end point

4.4.5 Alkalinity. To 25ml of w, add 1 drop of 0.1% methyl red indicator soln (60% alc) and 0.01N acid or base until the soln is just pink. Add 25ml of specimen, mix well, then titrate with 0.01N sulfuric acid until the pink color is restored. Calc the % NH_3 by wt as follows:

$$\% \text{ alkalinity as } NH_3 = \frac{(\text{ml of } H_2SO_4)(\text{Normality of } H_2SO_4)(1.703)}{(\text{ml of specimen})(0.79)}$$

4.4.6 Appearance. The specimen shall be thoroughly mixed and shall be examined by transmitted light for clarity, suspended matter, or sediment. This is most readily done by pouring some of the specimen into a test tube or Nessler tube

4.4.7 Carbonizeable Substances. Pipette 5ml of the sample into a 20x150mm test tube. Slowly and carefully add 5ml of concd H_2SO_4 and swirl the tube gently during the addition. The H_2SO_4 used must be no darker in color than the methanol. *Do Not Cool The Mixt.* Allow the tube and contents to stand for 5 minutes at room temp. Examine the contents visually for any evidence of discoloration

4.4.8 Color. Det color in accordance with **ASTM D1209**. The sample is compared spectrophotometrically against platinum-cobalt standard solns

4.4.9 Distillation Range. Det the distn range in accordance with **ASTM D1078**, with the following exceptions: (a) measure the 100ml of specimen and distillate at room temp (without w bath); (b) det temp using JL-4 type thermometer having a range of 45° to 70° in increments of 0.1°. In this method a 100ml sample is distd under conditions equiv to a simple batch differential distn. The temp of the Hg in the thermometer is equilibrated with that of the refluxing liq before the distillate is taken over. Boiling temps observed on a partial immersion thermometer are corrected to std atmos press to give true boiling temps

4.4.10 Hydrocarbons. Dil 15ml of the specimen to 45ml with distd w in a Nessler tube. Visually examine for cloudiness or opalescence during 30 minutes of standing

4.4.11 Specific Gravity (Methanol Content). Det the sp gr with a pycnometer of about 50ml capacity or by any other method accurate to the fourth decimal place. In the temp range 15 to 25°, the sp gr changes 0.00094 per degree. This correction factor shall be multiplied by the number of °C difference between 20° and the temp of the specimen. This resulting number shall be added to the detd sp gr of the specimen when the temp is greater than 20° and subtracted when the temp is lower than 20°. Det the methanol content from the sp gr based on the following:

Table 2

% by Weight	Specific Gravity at 20/20°
99.7	0.79330
99.8	0.79298
99.85	0.79283
99.9	0.79267
100.0	0.79236

4.4.12 Nonvolatile Content. Det nonvolatile content in accordance with **ASTM D1353**, except that specimen shall be 500ml (see Vol **6**, p E158-L)

4.4.13 Odor. Det odor in accordance with **ASTM D1296**. In this test strips of filter paper are dipped into specimen and reference standards, and odor comparisons are made of "characteristic" odor when the strips are wet, and "residual" odor remaining after the strips appear dry. If an odor persists on the sample paper after the point in time when no odor is detectable on the standard paper, the odor is reported as "residual"

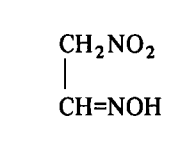
4.4.14 Permanganate Test. Det permanganate time in accordance with **ASTM D1363**. Substances reacting with K permanganate in neutral solns reduce it to Mn dioxide which colors the soln yellow. In this test the time required for the color of the test soln to change to that of a standard soln is measured. The color of the test soln changes from pink-orange to yellow-orange

4.4.15 Water Content. Det w content in accordance with **ASTM D1364** (see Vol **6**, p E158-R)

Written by **S. M. KAYE**

METHAZONIC ACID AND ITS SALTS

Methazonic Acid (Nitroacetaldoxime). $C_2H_4N_2O_3$, mw 104.07, N 26.92%, OB to CO_2 −46.12%; leaflets from eth, prisms from benz and plates from chlf; mp 79° (decompn), bp (explds at 150°); sol in w, alc, eth, acet, warm benz and chlf. Can be prepd by heating nitromethane with alc NaOH or by treating nitromethane with aq ammonia at a temp below 10° (Refs 2, 3 & 4)



Methazonic acid is an expl, less powerful than TNT (Trauzl block expansion 240cc vs 290cc for TNT) but more sensitive to impact (comparable to PA). It is unstable in storage

Methazonic acid forms numerous salts, some of which are expl (Ref 1). The salts were prepd either by treating the acid with carbonates or oxides of the corresponding metals, or from Na or K methazonates by double decompn

Ammonium Methazonate. $NH_4C_2H_3O_3N_2$. Cryst; sol in methanol, less in alc; nearly insol in eth and chlf. Deflagrates on rapid heating

Lead Methazonate. $Pb(C_2H_3O_3N_2)_2$. Cryst; explds on impact or when heated to 220°

Mercury Methazonates. Forms two salts; *mercuric*, $Hg(C_2H_3O_3N_2)_2$ and *mercurous*, $HgC_2H_3O_3N_2$. The former explds at 160°, the latter at 170°. Both salts explode on impact

Potassium Methazonate. $KC_2H_3O_3N_2$. Needles; explds violently when heated to 195°. Urbański and Kowalczyk (Ref 5) considered it the best expl of all the methazonates examined by them

Silver Methazonate. $AgC_2H_3O_3N_2$. Yellowish powd, darkening slowly by action of light. Explds violently when heated to about 160°

Sodium Methazonate. $NaC_2H_3O_3N_2$. Cryst; explds mildly at 245°

Thallium Methazonate. $TlC_2H_3O_3N_2$. Cryst; explds violently when heated to about 235°. It was the most sensitive to impact (4cm with a 2kg weight) of all the methazonates (Ref 5)

Refs: 1) Beil **1**, 627, (331) & [684] 2) P. Friese, Ber **9**, 394 (1876) 3) W.R. Dunstan & E. Goulding, JCS **77**, 1262 (1900) 4) W. Steinkopf & C. Kirchoff, Ber **42**, 617–21 & 2026–31 (1909) & CA **3**, 1155 & 2438 (1909) 5) T. Urbański & M. Kowalczyk, SS **32**, 42 (1937) (This is an abstract of a paper in the Polish journal, Wiadomosci Techniczne Uzbrojenia **4**, 22–34 (1935)

Methilites. Liq expls developed in the USA during WWII for use in linear charges for mine field clearance. Typical of these were:

Methilite 20: NG/EGDN 75/25 80, DMePh 20 & EtCent 0.8% (added)

Methilite 25: NG/EGDN 75/25 75, DMePh 25 & EtCent 0.75% (added)

EL-389A: NG/EGDN 75/25 55, DNT oil/TNT 70/30 45 & DPhA 0.55% (added)

EL-389B: NG/EGDN 75/25 60, DNT oil/TNT 70/30 40 & DPhA 0.6% (added)

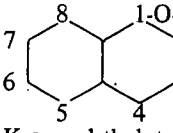
Storage stability problems were encountered with all of these expls

Ref: L.H. Eriksen, "Properties of Liquid Explosives", PATR **1542** (2 July 1945)

METHOXY NAPHTHALENES AND DERIVATIVES

Methoxynaphthalenes. $C_{10}H_7.O.CH_3$, mw 158.21. There are two isomers: 1-methoxy- & 2-methoxy naphthalene

1-Methoxy-Naphthalene (Methyl-α-naphthyl-ether)



liq, mp <−10°, bp 269°, d 1.0964g/cc at 14/2°, RI 1.6940 at 25°; sol in alc, eth & benz. Prepn from K-α-naphthalate by heating with methylchloride at 280°

Ref: Beil **6**, 606, (306), [578] & {2922}

2-Methoxy-Naphthalene (Methyl-β-naphthyl-ether). Cryst, mp 73–74°, bp 274°. Sol in eth, chlf & benz. Prepn from K-β-napthalate by heating with methyl chloride at 300°
Ref: Beil **6**, 640, (312), [615] & {2926, 2969}

2,4-Dinitro-5-Methoxy-1-Acetoxy-Naphthalene (Acetic acid-(2,4-dinitro-5-methoxy-naphthyl-(1)-ester); [2,4-Dinitro-5-methoxy-naphthyl-(1)] acetate). $(O_2N)_2C_{10}H_4(C_2H_3O_2).O.CH_3$, mw 306.25, N 9.15%, OB to CO_2 −125.39%, gold cryst, mp 154° (decompn). Prepn from 2,4-dinitro-5-methoxy-naphthol by refluxing with Ac_2O & concd sulfuric acid
Ref: Beil **6**, {5274}

4,6-Dinitro-5-Hydroxy-1-Methoxy-Naphthalene (2,8-Dinitro-5-methoxy-naphthol-(1), methyl-[4,6-dinitro-5-hydroxy-naphthyl-(1)]-ether). $(O_2N)_2C_{10}H_4(OH).O.CH_3$, mw 278.24, N 10.07%, OB to CO_2 −132.26%, gold needles from alc, mp 183° (decompn). Sol in alc. Prepn from 5-methoxy-1-acetoxy-naphthalene by reaction with an excess of nitric acid (d 1.42 g/cc) at 0°
Ref: Beil **6**, {5274}

5,7-Dinitro-8-Hydroxy-1-Methoxy-Naphthalene (Methyl-[5,7-dinitro-8-hydroxy-naphthyl-(1)]-ether, 2,4-Dinitro-8-methoxy-naphthol-(1)). $(O_2N)_2C_{10}H_4(OH).O.CH_3$, mw 264.21, N 10.61%, OB to CO_2 −121.12%, gold plates from alc, mp 179–80° (decompn). Sol in dil alkali & alc. Prepn from 2,4-dinitro-1,8-dimethoxy-naphthalene by reaction with 2N NaOH
Ref: Beil **6**, {5284}

6,8-Dinitro-5-Hydroxy-1-Methoxy-Naphthalene (2,4-Dinitro-5-methoxy-naphthol-(1), methyl-[6,8-Dinitro-5-hydroxy-naphthyl-(1)]-ether). $(O_2N)_2C_{10}H_4(OH).O.CH_3$, mw 264.21, N 10.61%, OB to CO_2 −121.12%, orange needles from CCl_4, mp 173° (decompn). Sol in CCl_4. Prepn from 2,4-dinitro-naphthalenediol-(1,5) by reacting with an excess of dimethyl sulfate in dil NaOH
Ref: Beil **6**, {5273}

2-Methoxy-1-Chloromethyl-Naphthalene (Methyl-[1-chloromethyl-naphthyl-(2)]-ether). $(ClCH_2)C_{10}H_6.O.CH_3$, mw 206.78, OB to CO_2 −220.52%, cryst from petr ether plus benz or from alc, mp 120–23° (decompn). Sol in alc & petr eth plus benz. Prepn from an AcOH soln of 2-methoxy-naphthalene reacted with a HCl satd suspension of paraformaldehyde in AcOH
Ref: Beil **6**, {3020}

Methyl Abietate (Methyl resinate or Methyl sylvate). (The commercial product, contg about 90% of MeAb, manufd by the Hercules Powder Co, is named "Abalyn"). $C_{19}H_{29}COOCH_3$, mw 316.47, colorl to faintly amber liq with pleasant, ester-like, odor; mp, does not freeze, even at −40°, but becomes very viscous; bp 360–65° (with sl decompn), d 1.040g/cc at 20° (1.020–1.030 for Abalyn); RI 1.5295 at 20°, flash p 180° and fire p 218° (Cleveland open cup); viscosity 28–30 poises at 25°; saponification No 20–25; acid No 6 or less; sp ht 0.395 between 25–27°. Can be obtained commercially by esterification of either abietic acid, or of rosin with methanol at high temps. In the lab, it is possible to prepare it by heating an alkali resinate with a methyl halide. It is miscible with most org solvents. Has been proposed as a plasticizing resin for lacquers, including those of NC, and as a coating for some progressive burning proplnts. It is v sl volatile (5.6mm Hg at 200°, compared with 22.4mm Hg for dibutyl phthalate), and possesses very satisfactory thermal stability, being stable up to 350°. It is practically noncorrosive and does not develop acid on hydrolysis

Being an unsatd compd with one double bond, it is markedly subject to oxidn, and when left in air, dries and turns yellow. As this property reduces its usefulness in some applications, methods were developed whereby the reactive double bond was satd with H_2. The resulting compd is:

Methyl Dihydroabietate (Commercial product developed by Hercules Powder Co under name "Hercolyn". Another product is "Hercolyn-D", which is Hercolyn deodorized by steam-blowing), $C_{19}H_{31}COOCH_3$, mw 318.48, colorl to faintly amber colored liq; mp, does not freeze at −40°, but becomes very viscous; bp 356–70° with sl decompn; d 1.020–1.030g/cc for Hercolyn; flash p 183° and fire p 218° (Cleveland open

cup); RI 1.517 to 1.519 at 20°; viscosity 28–34 poises at 20°; acid No 6 or less; saponification No 20–25

Can be prepd by catalytic hydrogenation of methyl abietate. "Hercolyn" possesses excellent thermal stability. It does not corrode metals and does not develop acid on hydrolysis. Its volatility is very low (4.5mm Hg at 200°)

Both "Hercolyn" and "Abalyn" combine the solvent power of abietic acid with that of a methyl ester. Thus, they may act as resins and as plasticizers. Both possess excellent wetting ability, even for nonporous materials such as glass and metals. Hercolyn was proposed (Refs 2 & 3) as a coating for NC proplnt grains

Refs: 1) Beil – does not list abietic acid (abietinsäure) or "methyl-abietate" 2) E.S. Goodyear, USP 2147698 (1939) & CA **33**, 4040 (1939) 3) H.M. Spurlin & G.H. Pfeiffer, USP 2198746 (1940) & CA **34**, 6078 (1940) 4) R.S. Morell, "Synthetic Resins and Allied Plastics", Oxford Univ Press, London (1943), 253 5) R.L. Wakeman, "The Chemistry of Commerical Plastics", Reinhold Pub Corp, NY (1947) 6) R. Houwink, "Elastomers and Plastomers", Elsevier Pub Co, Amsterdam (1949), **2**, 385 7) Hercules Powder Co, Pamphlet on "Hercolyn" and "Abalyn" 8) CondChemDict (1971), 562–63

Methyl Acetate (Essigsäuremethylester in Ger), CH_3COOCH_3, mw 74.08, OB to CO_2 −151.19%, colorl, vol liq, mp −98.05°, bp 54.05°, flash p 15°F, d 0.924g/cc, RI 1.3619 at 20°, autoign temp 935°F. Can be prepd by heating methanol with acet ac in the presence of sulfuric acid. Sol in w, miscible with alc, eth and common hydrocarbon solvents

Good solv and plasticizer for cellulose esters, including NC's, except for those with very high N contents

Refs: 1) Beil **2**, 124, (52) & [125] 2) CondChemDict (1971), 563-L

Methyl Acetoacetate (Acetessigsäuremethylester in Ger), $CH_3COCH_2COOCH_3$, mw 116.11, OB to CO_2 −151.58%, colorl liq, mp −80°, bp 171.7°, d 1.0785g/cc at 20/20°, flash p 158°F, vap press 0.7mm at 20°. Can be prepd by treating methylacetate with metallic Na and decomp the resulting Na compd with acet ac. Sl sol in w (38p at RT), sol in alc, eth and et acet. Used as a solv for cellulose ethers or as an ingredient of solv mixts for cellulose esters

Refs: 1) Beil **3**, 632, (223) & [414] 2) CondChemDict (1971), 563-L

Methyl Acetone. Commercial product; a water-white, anhydr liq, consisting of various mixts of acet (45 to 65%), methyl acetate (20 to 30%) and methanol (20 to 40%). Density about 0.83g/cc, boiling range 50 to 70°, flash p near 0°F. Miscible with hydrocarbons, oils and w. Obtained as a by-product in the manuf of acet and methanol from wood distn, representing fractions which cannot be economically sepd. The mixt can be used as such, being an excellent solv and plasticizer for NC and other cellulose esters, such as the acetate. It also dissolves rubber, gums, resins, lacquers, paint and varnish

Refs: 1) T.H. Durrans, "Solvents", Van-Nostrand, NY (1938), 122 2) CondChemDict (1971), 563-L

Methyl Alcohol. See Methanol

Methylacetylene (Allylene, Propyne). $CH_3C{\equiv}CH$, mw 40.07, colorl liquified gas; bp −23.1°, fr p −101.5°; flammable, dangerous fire and expl risk. It is self-reactive, and can decomp explosively at 4.5 to 5.6 atms press (Ref 2). An expln occurred at Dow's Freeport, Texas plant in 1960 while workers were loading a small tank of methyl acetylene. Following this expln, a 2000 gal tank blew up and burned for 1½ hours. The cause of the blasts were not detd (Ref 1)

Refs: 1) Anon, C&EN **38**, 17 (May 1960) 2) T.F. Rutledge, "Acetylenic Compounds", Reinhold, NY (1968) 3) Sax (1968), 386-L 4) CondChemDict (1971), 563-R

Methylaluminum Diazide. $CH_3Al(N_3)_2$, mw 126.08, N 66.67%, white powd. When a frozen eth soln of $Al(CH_3)_3$ and excess HN_3 is thawed, reaction begins at room temp with evolution of CH_4 and pptn of a fine white powd, methylaluminum diazide. The reaction is completed

in two hours. It is sol in tetrahydrofuran; evolves CH_4 on addition of HCl; is oxidized to $CH_3OAl(N_3)_2$ on exposure to air; effloresces in moist air; is not sensitive to percussion; sputters in a flame with white light and emission of Al oxide snow; decomposes in excess w with evolution of methane; reacts with dil sulfuric acid with bright fire and occasional expl, and reduces Ag nitrate to metallic Ag in tetrahydrofuran soln
Refs: 1) Beil – not found 2) E. Wiberg & H. Michaud, ZNaturforsch **9b**, 497 (1954) & CA **49**, 767 (1955)

METHYLAMINE AND DERIVATIVES

Methylamine. This article supplements the one in Vol **1**, A225–7 under Aminomethane and Derivatives; CA Registry No 74-89-5
Uses in Explosives. Gaseous methylamine is passed into solid Amm Perchlorate below –6.3° to give useful monoproplnts. A mixt so prepd of 85% Amm Perchlorate and 15% methylamine has an Isp of 230 lbsec/lb at 20atm (Ref 1). A paste of 90.36% AN, 7.78% methylamine, and 1.85% inert is a blasting expl (Ref 2). Mixts of AN with 6–9% methylamine are blasting expls, and with 15–40% are proplnts. A mixt of 65.5% AN, 14.5% methylamine and 20% unsymmetrical dimethylhydrazine has an Isp of 161 lbsec/lb and gives 25.4cuft of gas/sec at 1475°F. Similarly a mixt of 65.5% AN, 28.5% methylamine, and 5% hydrazine gives 23cuft of gas/sec; and a mixt of 72.1% AN and 27.9% methylamine gives an Isp of 181 lbsec/lb at 300 lbs press (Ref 3)
Refs: 1) L.A. Stengel, USP 2958182 (1960) & CA **55**, 5958c (1961) 2) Ibid, USP 2976137 (1961) & CA **55**, 13851g (1961) 3) Ibid, USP 2978864 (1961) & CA **55**, 19245e (1961)

Methylamine 5-Aminotetrazole Salt, $CH_3NH_2.CH_3N_5$, $C_2H_8N_6$, mw 116.13, N 72.37%. It is prepd by the interaction of the components in the min quant of hot ethyl alc, softens at 95°; mp 112–17°. Its expl props are unknown
Refs: 1) Beil – not found 2) R.A. Henry, JACS **74**, 6303 (1952)

Methylamine Azide, $CH_3NH_2.HN_3$, CH_6N_4, mw 74.09, N 75.63%. It is prepd by heating $MeNHCON_3$ with w (Ref 2), or by the action of hydrazoic acid on aq methylamine (Ref 3). It is obtd as delq crysts which do not melt. It is slightly sol in w and ethyl alc; insol in eth (Ref 3). Its expl props are unknown
Refs: 1) Beil **4**, [318] & {90} 2) E. Oliveri-Mandala, Gazz **43**, I, 538 (1913) & CA **7**, 3755 (1913) 3) A. Cirulis & M. Straumanis, JPraktChem **161**, 65 (1942) & CA **37**, 5022 (1943)

Methylamine Complex with Cupric Azide, $(MeNH_2)_2Cu(N_3)_2$, $C_2H_{10}CuN_8$, mw 209.74, N 53.40%. It is prepd by the interaction of the components, mp 126–28° (Ref 2). It is insol in inert solvs, decomps in hot w, explds at 180–90°, and is not shock sens (Ref 2)
Refs: 1) Beil **4**, {91} 2) M. Straumanis & A. Cirulis, ZAnorgChem **251**, 341 (1943) & CA **37**, 6574 (1943)

Methylamine Cupric Bromate Complex, $(MeNH_2)_4Cu(BrO_3)_2$, $C_4H_{20}Br_2CuN_4O_6$, mw 443.64, N 12.63%. It is prepd by the interaction of methylamine and Cu(II)bromate and is obtd as blue crysts which expld in 30secs at 88°
Refs: 1) Beil **4**, {91} 2) J. Amiel, CR **200**, 672 (1935) & CA **29**, 2469 (1935)

Methylamine Cupric Chlorate Complex, $(MeNH_2)_4Cu(ClO_3)_2$, $C_4H_{20}Cl_2CuN_4O_6$, mw 354.61, N 15.80%. It is prepd by satg an aq soln of Cu(II)chlorate with methylamine and is obtd as dark blue crysts which are hydrolyzed in w. When heated in a glass tube at 4°/min, it explds at 122°
Refs: 1) Beil **4**, {91} 2) J. Amiel, CR **199**, 51 (1934) & CA **28**, 5361 (1934)

Methylamine Cupric Perchlorate Complex. $(MeNH_2)_4Cu(ClO_4)_2$, $C_4H_{20}Cl_2CuN_4O_8$, mw 386.72, N 14.49%. It is prepd by the interaction of methylamine and Cu(II)perchlorate and is obtd as blue crysts which expld in 30secs at 247°
Refs: 1) Beil **4**, {91} 2) J. Amiel, CR **200**, 672 (1935) & CA **29**, 2469 (1935)

Methylamine Salt of 3,6-Dinitrophthalic Acid, $2CH_3NH_2.C_8H_4N_2O_8$, $C_{10}H_{14}N_4O_8$, mw 318.24, N 17.61%, OB to CO_2 –95.6%. Prepd

by the addn of an ethyl alc soln of the acid to the amine in ethyl alc; mp 157.5°. It is a solid deriv useful for the identification of methylamine

Refs: 1) Beil – not found 2) T. Momose & M. Nakamura, ChemPharmBull(Tokyo) **10**, 553 (1962) & CA **59**, 5242a (1963)

Methylamine Salt of Ethyl Nitroacetate, $MeNH_2.O_2NCH_2COOEt$, $C_5H_{12}N_2O_4$, mw 164.16, N 17.07%, OB to CO_2 –78.0%. Prepd by the interaction of its components; mp 110–11°

Refs: 1) Beil – not found 2) M. Kocór et al, RoczChem **31**, 1037 (1957) & CA **52**, 8281f (1958)

Methylamine MEDINA Salt, $2MeNH_2.(O_2NNH)_2CH_2$, mw 198.19, N 42.14%, OB to CO_2 –72.7%. It is prepd by the action of methylamine on MEDINA in ethyl alc and is obtd as hygr crysts, mp 120° with decompn

Refs: 1) Beil **4**, {93} 2) F. Chapman et al, JCS **1949**, 1641

Methylamine Hydrobromide Cupric Azide Complex, $(MeNH_3+)Cu(N_3)_2-Br-$, CH_6BrCuN_7, mw 259.61, N 37.77%. Dark violet crysts, mp 116°. It detonates with a hammer blow

Refs: 1) Beil **4**, {**91**} 2) M. Straumanis & A. Cirulis, ZAnorgChem **252**, 9 (1943) & CA **38**, 3563 (1944)

Methylamine Nitrate, bp 230° with yellowing (Ref 2), Q_p^0 218.4kcal/mole (Ref 1), max d obtainable under a press of 500kg/sqin is 1.41 g/cc (Ref 2); CA Registry No 22113-87-7

Gap Test. When 2g of MF were detond 0.5cm from Methylamine Nitrate, there was no transmission of the deton, but in contact with the MF there were 3 transmissions in 3 trials (Ref 2)

Hygroscopicity. When exposed to 50% humidity it absorbs 100% by wt of w in 21 days (Ref 2)

Impact Sensitivity. The 50% expln height is 2.5m (10kg wt) (Ref 2)

Power by Lead Block Expansion. 100% of PA (Ref 2)

Shock Sensitivity. It is detond by 2g of MF when pulverized and packed to a d of 1.20g/cc. It is also detond by 20g of PA when packed to a d of 1.4g/cc in glass tubes (Ref 2)

Thermal Sensitivity. At 375–90° it decomps with burning in 6–8secs (Ref 2). In a 20mm tube combstn is difficult. It melts and boils before burning and only the heated material burns without propagation to unheated material. When unconfined it melts and boils without burning (Ref 1)

Mixtures of Methylamine Nitrate with Compounds which have Explosive Properties. A mixt with 70–80% AN is called "Nitramite No 2" in Fr (Ref 2). When detond with 2g of MF in 30mm tubes it has a deton vel of 2550m/sec at a d of 1.00g/cc and 3250m/sec at 1.25g/cc (Ref 2). Mixts of Methylamine Nitrate with AN, Ca nitrate, or Na nitrate form low melting eutectics which are castable expls (Ref 1). A soln of 200g of Methylamine Nitrate in 800 lbs of methyl alc is a useful fuel for turbojets (Ref 3). A 50/50 mixt by wt with hydrazine is a gas generator proplnt (Ref 4). Mixts with hydrazine and methylhydrazines are stable and hypergolic with liq O, N dioxide, red fuming nitric acid, white fuming nitric acid, and F (Ref 5). A compn of 46.8% AN, 33.3% Methylamine Nitrate, 16.7% w, 2.0% resin, and 1.2% guar gum, when boosted with 0.5 lb of Comp B, has a deton vel of 21000ft/sec and is a useful mining expl (Refs 6 & 7)

Refs: 1) T.L. Cottrell & J.E. Gill, JCS **1951**, 1799 2) A. LeRoux, MP **34**, 129 (1952) & CA **48**, 4839a (1954) 3) L.A. Stengel, USP 2947618 (1960) & CA **54**, 21714g (1960) 4) C. Rose, USP 3081595 (1963) & CA **58**, 11163d (1963) 5) L.A. Stengel & E.E. Toops, USP 3088272 (1963) & CA **59**, 377c (1963) 6) J.J. Minnick, USP 3409484 (1968) & CA **70**, 21467t (1969) 7) C. Dunglinson & W.M. Lylerly, USP 3431155 (1969) & CA **70**, 116788n (1969)

Methylamine Perchlorate, mp 255° with decompn (Ref 2); it can be recrystd from et alc/chlf mixts (Ref 4). The crystal structure by X-ray diffraction of the solid is given in Refs 2 & 5. There is a phase transition at 178°; d of phase II at 77°, 1.58g/cc; d of phase I at 200°, 1.58g/cc (Ref 2). The temp of expln is 338° (Ref 1); formn const in acetonitrile is 35 (Ref 3). By mass spectral analysis it was shown

that the vaporization, then thermal decompn betw 150° and 275° is primarily by dissocn into methylamine and perchloric acid plus a small amt by a more complex path leading to C and N oxides (Refs 4 & 6)
Refs: 1) R.L. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919) 2) M. Stammler et al, "Rotational Polymorphism of Methyl-Substituted Ammonium Perchlorates" in "Advances in X-Ray Analysis" **9**, 170–89, Plenum Press, NY (1966) 3) J.F. Coetzee et al, Talanta **11**, 93 (1964) 4) J.L. Mack & G.B. Wilmot, JPhChem **71**, 2155 (1967) 5) P.F. Zanazzi, ActaCryst **B24**, 499 (1968) 6) W.A. Guillory & M. King, JPhChem **73**, 4367 (1969)

Methylamine Picrate, $CH_3NH_2.C_6H_3N_3O_7$, $C_7H_8N_4O_7$, mw 260.17, N 21.54%, OB to CO_2 –67.7%; yellow crysts, 3 cryst forms: a trimorphous form at low temp which changes at 58° to a rhombic form, and at 63° to a 3rd form (Ref 2), mp 211° (cor) (Ref 4); nα 1.473, β 1.878, γ 1.987 (Ref 4). It is prepd by the addn of methylamine to a satd (6%) soln of PA in w, recrystd from aq ethyl alc (Ref 4); soly is 1.33p in 100p of w, fairly sol in ethyl alc (Ref 1). It behaves as a weak electrolyte in ethanolamine, but the conductivity is high (Ref 3)
Refs: 1) Beil **6**, 280, [266] & {920} 2) E. Ristenpart, Ber **29**, 2530 (1896) 3) H.T. Briscoe & T.P. Dirkse, JPhChem **44**, 388 (1940) 4) J. Mitchell & W.M.D. Bryant, JACS **65**, 128 (1943)

Methylamine Picrolonate, $CH_3NH_2.C_{10}H_8N_4O_5$, $C_{11}H_{13}N_5O_5$, mw 295.25, N 23.72%, OB to CO_2 –127%; pale yellow crysts from w, decomps at 244° (Ref 3); soly at 16°, 1p in 1073p of w, 4717p of ethyl alc; at bp, 1p in 369p of w, 133p of ethyl alc (Ref 3); it explds on rapid heating (Ref 2)
Refs: 1) Beil **24**, 51 2) L. Knorr, Ber **30**, 914 (1897) 3) J. Otobi, ZPhysiolChem **43**, 305 (1904) & JCS (Abstr) **88** (Pt 1), 126 (1905)

Methyl Ammonium Chloride Complex with Cupric Azide, $MeNH_3Cl.Cu(N_3)_2$, CH_6ClCuN_7, mw 215.15, N 45.58%; dark violet crysts, mp 150° with decompn
Refs: 1) Beil **4**, {91} 2) M. Straumanis & A. Cirulis, ZAnorgChem **252**, 9 (1943) & CA **38**, 3563 (1944)

Methylnitramine, reacts with diazonium salts to form $ArN{:}NNMeNO_2$ which are yellow solids that ignite below their mp and decomp on standing at room temp (Ref 1). It reacts with activated olefins to form adducts of the type $XCH_2CH_2NMeNO_2$ where "X" is an activating group (Ref 2)
Refs: 1) N.M. Baranchik et al, DoklAkadN **94**, 701 (1954) & CA **49**, 6158h (1955) 2) L.W. Kissinger & M. Schwarts, JOC **23**, 1342 (1958)

Written by **C. H. McDONNELL**

N-Methylaniline and Derivatives

N-Methylaniline (Methylaminobenzene or Benzeneamine, N-Methyl). $CH_3NHC_6H_5$, mw 107.15, N 13.07%, OB to CO_2 –277%. Colorl oily liq which rapidly darkens in contact with air, fr p –57°, bp 196.25°, d_4 at 20° 0.98912 g/cc, RI at 20° 1.5684 (Ref 10), Q_C^V –973.5 kcal/mole, Q_f liq 7.7, gas 20.4kcal/mole (Ref 7), crit press 51.3 ± 0.5atm (Ref 4, UV peak at ca 3650Å (Ref 2), IR spectrum is given in Ref 5; CA Registry No 100-61-8

Prepd by the action of methylating agents (methyl chloride, bromide, iodide, or sulfate) on aniline. This procedure gives a mixt with dimethylaniline which is difficult to separate by distn (see below for sepn procedure) (Refs 1, 6 & 9). Pure samples are best prepd by the methylation of acetanilide or benzanilide to the N-methyl compds followed by acid hyd. It has been prepd commercially by the action of methyl alc on aniline in an autoclave under press and by the action of methyl amine on halobenzenes. For a summary of prepns see Refs 6 & 9. It may be separated from aniline and dimethylaniline by treatment of the mixt with benzenesulfonyl chloride. Dimethylaniline fails to react and is extd out with dil acid. Aniline forms benzenesulfonanilide which is acidic and is removed by washing with dil base, leaving the N-methylbenzenesulfonanilide. Purified N-methylaniline is obtd by acid hyd (Ref 8). N-Methylaniline is used as an additive to raise the octane no of motor fuels (Ref 6), as a dyestuff intermediate (Ref 3), in the prepn of Tetryl (see below), and in the prepn of Methylcentralite (Encycl, Vol **2**, C137-R)

Refs: 1) Beil **12**, 135, (149), [79] & {240} 2) H. Ley & G. Pfeiffer, Ber **54**, 369 (1921) 3) R.N. Shreve, "Dyes Classified by Intermediate" (Chemical Catalog Co, 1922), 336 4) W. Herz & E. Neukirch, ZPhysChem **104**, 363 (1923) & CA **17**, 2979 (1923) 5) J.W. Ellis, JACS **49**, 350 (1927) 6) E.C. Hughes et al, IEC **42**, 787 (1950) 7) G.N. Vriens & A.G. Hill, IEC **44**, 2733 (1952) 8) Shriner, Fuson, & Curtin (1956), 119 9) Houben **11/1** (1957) 10 ChemRubHdb (1974–51), C-119

Salts and Complexes of N-Methylaniline with Inorganic Compounds:

Complex with Cypric Nitrate, $(MeNHPh)_2-Cu(NO_3)_2$, $C_{14}H_{18}CuN_4O_6$, mw 401.86, N 16.66%, OB to CO_2 −148%; blue crysts, prepd by the interaction of the components in hot methyl alc

Refs: 1) Beil **12**, {240} 2) A. Cirulis & M. Straumanis, Ber **76**, 828 (1943)

Complex wtih Dicupric Pentaazide Ion, $MeNH_2Ph^+.Cu(N_3)_5^-$, $C_7H_{10}Cu_2N_{16}$, mw 445.29, N 50.13%; fine brown needles which decomp at 80° and deton sharply at 203°; prepd by the action of Na azide on the above nitrate complex

Refs: 1) Beil **12**, {240} 2) A. Cirulis & M. Straumanis, Ber **76**, 828 (1943)

Perchlorate Salt, $MeNHPh.HClO_4$, mw 207.62, N 6.75%, OB to CO_2 −116%; needles from ethylene dichloride/eth, mp 79° (Ref 2). It is prepd by the action of 57% aq perchloric acid on the amine in w. The burning rate betwn 1 and 400atm is in Ref 3

Refs: 1) Beil – not found 2) N.J. Leonard & J. Klainer, JHeterocyclChem **8**, 215 (1971) & CA **75**, 5854q (1971) 3) A.E. Fogel'zand et al, FizGorenyiVzryva **8**, 257 (1972) & CA **78**, 45833a (1973)

Salts and Complexes of N-Methylaniline with Organic Compounds:

3-Bromopicrate, $C_{13}H_{11}BrN_4O_7$, mw 415.15, N 13.50%, OB to CO_2 −94.5%; a yellow solid from et alc, mp 171–72° with decompn (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961) 3) J.W. Elder & R.P. Mariella, JChemEngData **9**, 402 (1964)

3-Chloropicrate, $C_{13}H_{11}ClN_4O_7$, mw 370.70, N 15.15%, OB to CO_2 −105%; a yellow solid from et alc, mp 165–66° with decompn (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961) 3) J.W. Elder & R.P. Mariella, JChemEngData **9**, 402 (1964)

3-Iodopicrate, $C_{13}H_{11}IN_4O_7$, mw 462.10, N 12.12%, OB to CO_2 −84.8%; a yellow solid from et alc, mp 158–59° with decompn (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961) 3) J.W. Elder & R.P. Mariella, JChemEngData **9**, 402 (1964)

2,4-Dinitrobenzoate, $C_{14}H_{13}N_3O_6$, mw 319.27, N 13.16%, OB to CO_2 −143%; a brown solid, mp 102.6–3.8°; prepd by the interaction of the components in hot abs ethyl alc. The salt is used to isolate and identify N-methylaniline

Refs: 1) Beil **12**, {245} 2) C.A. Buehler & J.D. Calfee, IEC, AnalEd **6**, 351 (1934)

3,5-Dinitrobenzoate; light yellow crysts, mp 121.8°; prepd by the interaction of the components in hot abs ethyl alc. It is also used to isolate and identify N-methylaniline

Refs: 1) Beil **12**, {245} 2) C.A. Buehler et al, IEC, AnalEd **5**, 277 (1933)

m-Ethylpicrate, $C_{15}H_{16}N_4O_7$, mw 364.31, N 15.38%, OB to CO_2 −136%; yellow crysts from methyl alc, mp 114–15° with decompn; prepd by the interaction of the components in methyl alc or ethyl alc

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961)

Ethyl-2,4,6-trinitrobenzene Complex, $C_{15}H_{16}N_4O_6$, mw 348.31, N 16.09%, OB to CO_2 −147%; red prisms, mp 44°

Refs: 1) Beil **12**, 140 2) G. Schultz, Ber **42**, 2635 (1909)

Picrate, $C_{13}H_{12}N_4O_7$, mw 336.26, N 16.66%, OB to CO_2 −119%; yellow crysts from methyl alc, mp 144.5°; CA Registry No 14953-19-6

Refs: 1) Beil **12**, (151) 2) J. Meisenheimer, Ber **52**, 1673 (1919)

2,2',6,6'-Tetranitro-4,4'-biphenol Complex, $MeNHPh.[HOC_6H_2(NO_2)_2-2,6-4-]_2$, $C_{16}H_{15}N_5O_{10}$, mw 437.32, N 14.80%, OB to CO_2 −120%; bright yellow crysts, prepd by the interaction of the components in hot benz

Refs: 1) Beil – not found 2) G. Saito &

Y. Matsunaga, BullChemSocJapan **46**, 1609 (1973) & CA **79**, 52431s (1973)

α,α,α-Trifluoro-2,4,6-trinitrotoluene Complex, $C_{14}H_{11}F_3N_4O_6$, mw 388.26, N 14.42%, OB to CO_2 −108%; violet needles, mp 56–57°; prepd by mixing equimolar amts of the components in ethyl alc

Refs: 1) Beil – not found 2) D.N. Gray et al, JCS **1960**, 2243

2,4,6-Trinitrobenzoate, $C_{14}H_{12}N_4O_8$, mw 364.27, N 15.38%, OB to CO_2 −114%; colorl crysts which lose CO_2 on heating to form the colored trinitrobenzene complex; prepd by mixing equimolar amts of the components in acet

Refs: 1) Beil – not found 2) M. Hirota, BullChemSocJapan **33**, 1046 (1960) & CA **55**, 8346 (1961)

2,4,6-Trinitro-m-cresol Complex, $C_{14}H_{14}N_4O_7$, mw 350.28, N 15.38%, OB to CO_2 −128%; yellow crysts from ethyl alc, mp 127–28° with decompn; prepd by the interaction of the components in ethyl alc; CA Registry No 51010-15-2

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961)

2,4,6-Trinitrotoluene Complex, $C_{14}H_{14}N_4O_6$, mw 334.28, N 16.76%, OB to CO_2 −138%; prepd by mixing the components in hot ethyl alc, recrystd from ethyl alc

Refs: 1) Beil – not found 2) A.K. Dwivedy et al, JChromatog **29**, 129 (1967)

Trinitro-3,5-xylenol Complex, $C_{15}H_{16}N_4O_7$, mw 364.31, N 15.37%, OB to CO_2 −136%; yellow crysts from methyl alc, mp 165–66° with decompn; prepd by the interaction of the components in ethyl alc; CA Registry No 51010-34-5

Refs: 1) Beil – not found 2) R.P. Mariella et al, JOC **26**, 3219 (1961)

Azido and Azo Derivatives of N-Methylaniline

p-Azido-N-Methylaniline, p-$MeNHC_6H_4N_3$, $C_7H_8N_4$ mw 148.17, N 37.82%; crysts, mp 52°; prepd by the action of hydroxylamine hydrochloride on N-methyl-p-nitrosoaniline in aq Na carbonate. Upon exposure to light in thin layers, it turns red, then violet

Refs: 1) Beil **12**, {429} 2) A. Angeli & A. Pieroni, AttiAccadLincei v **32**, i, 151 (1923) & CA **17**, 3487 (1923)

4-Methylamino-2',3,4'-Trinitroazobenzene, $C_{13}H_{10}N_6O_6$, mw 346.26, N 24.27%, OB to CO_2 −116%; yellow platelets, mp 274.5–5.0° with decompn; prepd by the action of methyl amine hydrochloride on 4-fluoro-2',3,4'-trinitroazobenzene in eth, yield 95.8%

Refs: 1) Beil – not found 2) O. Neunhoffer & W. Ruske, Ann **610**, 143 (1957)

Nitro Derivatives of N-Methylaniline

Nitro-N-Methylanilines, $C_7H_8N_2O_2$, mw 152.15, N 18.41%, OB to CO_2 −168%. The following isomers are described in the literature:

N-Nitro-N-methylaniline, needles or leaflets from eth, mp 38.5–9.5°, volatile in steam without decompn (Ref 1); CA Registry No 7119-93-9

2-Nitro-N-methylaniline, red needles with blue/violet reflections from petr eth, mp 37° (Ref 2), decomps above the mp (Ref 13); CA Registry No 612-28-2

3-Nitro-N-methylaniline, reddish yellow needles or prisms from ethyl alc, mp 68° (Ref 3); CA Registry No 619-26-1

4-Nitro-N-methylaniline, brownish yellow prisms with violet reflections, mp 150–51° (Ref 4), decomps above the mp (Ref 13), Q_C^V 924.3 kcal/mole (Ref 9); CA Registry No 100-15-2

It is prepd by the action of methylamine on 4-chloro-1-nitrobenzene (Ref 5); by the action of methyl iodide (Ref 6), or methyl sulfate on 4-nitroaniline (Ref 7); or by the hydrolysis of 4-nitro-N-methylformanilide with hot concd aq HCl (Ref 8). In a study of the effect of nitric acid concn on the prods of the nitration of N,N-dimethylaniline to form Tetryl, it was isolated in low yield by the action of nitric acid, d 1.046g/cc, plus Na nitrite on N,N-dimethylaniline (Ref 10). A eutectic mixt with N-ethyl-4-nitroaniline has been patented as a stabilizer for NC (Ref 12). Studies at NPF indicate that 4-nitro-N-methylaniline is superior to Centralite, 2-nitrodiphenylamine, or Acardite in stabilizing NC

Refs: 1) Beil **12**, 586, (295) & {1125} 2) Beil **12**, 689, [369] & {1516} 3) Beil **12**, 700, [377] & {1544} 4) Beil **12**, 714, (350), [385] & {1584} 5) E. Bamberger, Ber **27**, 379 (1894) 6) J.J. Blanksma, Rec **21**, 270 (1902) 7) F. Ullman, Ann **327**, 113 (1903) 8) G.T. Morgan & W.R. Grist, JCS **118**, 690 (1918) 9) W.E. Garner & C.L. Abernethy, PrRoySoc **99** [A], 213 (1921) & JCS (Abstr) **120** ii, 435 (1921) 10) M.A. Phillips & H. Shapiro, JCS**1942** , 584

11) Anon, NPF Semiannual Rept 1 (July-Dec 1950) ATI-101324, pp 2–3 12) J.A. Gallaghen & I. Pincus, USP 2696430 (1954) & CA **49**, 5846a (1955) 13) ChemRubHdb (1974–75), C-111

Dinitro-N-methylanilines, $C_7H_7N_3O_4$, mw 197.15, N 21.32%, OB to CO_2 –110%. The following isomers are described in the literature:

N,2-Dinitro-N-methylaniline, bright yellow prisms, mp 70° (Ref 1)

N,4-Dinitro-N-methylaniline, bright yellow needles from benz, mp 142.5° (Ref 2); CA Registry No 16698-03-6. It is prepd by the alkylation of N,p-dinitroaniline with methyl iodide in alk soln (Refs 8 & 9). It is one compd isolated from aged NC proplnts stabilized with N-methyl-p-nitroaniline. Hollingsworth at ERDE examined the reaction of nitrogen dioxide with this stabilizer in order to elucidate the mechanism of the formation of the compds isolated. He found that after 7 days at 35°, a good yield of N,4-dinitro-N-methylaniline was obtd; and postulated that it arose from the oxidn of N-nitroso-4-nitroaniline (Ref 16)

2,4-Dinitro-N-methylaniline, canary yellow needles or monoclinic prisms from acet ac, mp 178° (Ref 3), Q_C^V 885.5kcal/mole (Ref 10), a UV peak is at 3600Å which may be used to detect and determine it in crude Tetryl (Ref 13); CA Registry No 2044-88-4. It is one intermediate in the series of reactions which occur when N,N-dimethylaniline is treated with nitric acid resulting in the formation of Tetryl (see in the Encycl under Tetryl). If N,N-dimethylaniline is allowed to stand overnight in the presence of nitric acid (d 1.254–1.340g/cc), an almost quanty yield of 2,4-dinitro-N-methylaniline is obtd (Ref 11). In addn Clarkson isolated it in 93% yield by the action of dilute nitric acid on 2,4-dinitro-N,N-dimethylaniline, and he treated it in 75% sulfuric acid with 98% nitric acid and obtd a 91.9% yield of Tetryl (Ref 17). As a possible raw material for an improved prepn of Tetryl, its prepn from methyl amine and 1-chloro-2,4-dinitrobenzene was studied in detail, including kinetics and economics of the reaction (Refs 12 & 18). It can be sepd from commercial Tetryl and identified by thin layer chromatography (Ref 19). Specs for material used by the US Armed Forces for the prepn of Tetryl are in **MIL-D-20309** (23 Nov 1951) and include the following requirements:

Color – Yellow to orange-yellow
Moisture – Maximum, 0.2 percent
Acidity or alkalinity – Maximum, 0.10 percent
Acetone insoluble – Maximum, 0.20 percent
Ash – Maximum, 0.20 percent
Inorganic chloride – Maximum, 0.07 percent
Melting point – Minimum, 176.5°
Granulation – Thru No 10 US Std sieve, minimum, 99.5 percent

2,5-Dinitro-N-methylaniline, red needles from EtOH, mp 163° (Ref 4)

2,6-Dinitro-N-methylaniline, orange needles, mp 106–07° (Ref 5). Q_C^V 895.35kcal/mole, Q_f^V 2.45kcal/mole, Q_f^p 6.55kcal/mole (Ref 15). It has been found as a by-prod in the prepn of the 2,4-isomer (Ref 15). It has been sepd from other compds related to Tetryl by thin layer chromatography (Ref 19)

3,4-Dinitro-N-methylaniline, mp 156° (Ref 6)

3,5-Dinitro-N-methylaniline, orange-yellow needles, mp 158° (Refs 7 & 14)

Refs: 1) Beil **12**, 697 2) Beil **12**, 728 3) Beil **12**, 749, (361), [406] & {1681} 4) Beil **12**, 757, [413] & {1704} 5) Beil **12**, 758 & (365) 6) Beil **12**, [414] 7) Beil **12**, {1705} 8) J. Pinnow, Ber **30**, 837 (1897) 9) E. Bamberger & R. Dietrich, Ber **30**, 1254 (1897) 10) W.E. Garner & C.L. Abernethy, PrRoySoc **99** [A], 213 (1921) & JCS (Abstracts) 120 ii, 435 (1921) 11) H.H. Hodgson & G. Turner, JCS **1942**, 584 12) A.G. Hill & K.H. Klipstein, AIChETransactions **42**, 527 (1946) & CA **40**, 4883 (1946) 13) I.A. Brownlie & W.M. Cumming, JSCI **67**, 206 (1948) & CA **43**, 1189 (1949) 14) J.C. Roberts & K. Selby, JCS **1949**, 2786 15) L. Médard & M. Thomas, MP **39**, 199 (1957) & CA **53**, 718a (1959) 16) B.L. Hollingsworth, JCS **1959**, 2420 17) C.E. Clarkson et al, JCS **1950**, 1561 18) J. Issoire & G. Burlet, MP **40**, 47 (1958) & CA **55**, 1484c (1961) 19) S.K. Yasuda, JChromatog **50**, 455 (1970) & CA **73**, 94387p (1970)

Trinitro-N-methylanilines, $C_7H_6N_4O_6$, mw 242.15, N 23.14%, OB to CO_2 –72.7%. The following isomers have been reported in the literature:

N,2,4-Trinitro-N-methylaniline (2,4-dinitrophenylmethylnitramine), light yellow hexagonal crysts

from EtOH, mp 115° (Ref 14), Q_c^v 869.2kcal/mole, Q_f^v −5.3kcal/mole, Q_f^p −0.7kcal/mole (Ref 16); CA Registry No 19092-03-6. It has been shown to be an intermediate in the prepn of Tetryl from N,N-dimethylaniline as it can be prepd from N,N-dimethylaniline or 2,4-dinitro-N-methylaniline by the action of 70% nitric acid in 90% yield (Refs 13 & 14); and can be nitrated to Tetryl with a mixt of 64% sulfuric acid, 15% nitric acid, and 21% w; yield 91.9% (Ref 14). It can be isolated from commercial Tetryl and identified by thin layer chromatography (Ref 21)

N,2,6-Trinitro-N-methylaniline (2,6-dinitrophenylmethylnitramine), mp 110.8°, Q_c^v 874.9kcal/mole, Q_f^v −10.8kcal/mole, Q_f^p −6.10kcal/mole (Ref 17)

2,3,4-Trinitro-N-methylaniline, mp 190°, prepd by the oxidn of 2,3,4-trinitro-N,N-dimethylaniline (Encycl, Vol **5**, D1315) with Cr trioxide (Ref 2)

2,4,5-Trinitro-N-methylaniline, mp 199°, prepd by the action of 80% nitric acid on 2,5- or 3,4-dinitro-N,N-dimethylaniline (Refs 3 & 6); also in low yield by the nitration of 3-nitro-N,N-dimethylaniline at 30° (Ref 9)

2,4,6-Trinitro-N-methylaniline (N-methylpicramide), yellow needles from EtOH contg acid, mp 114.8° (Refs 4 & 7); the UV spectrum has a peak at 340 and a shoulder at 410–20m (Ref 19); CA Registry No 1022-07-7. It is prepd by the hydrolysis of the N-nitroso compd (see below) at 70–80° (Ref 5); by the action of concd sulfuric acid (Ref 8) or UV light (Ref 12) on Tetryl; by the action of methyl amine on Ethyl Picrate (Ref 18) or Tetryl (Ref 7); or by the action of nitric acid (d 1.42g/cc) at 0° on N,N-dimethylaniline (Ref 10). It is present in crude Tetryl and is the active dermatitic agent in the latter (Ref 12). It can be isolated from crude Tetryl and identified by thin layer chromatography (Ref 21)

Thermodynamic properties, Q_c^v 853.6kcal/mole, Q_f^v 10.45kcal/mole, Q_f^p 15.1kcal/mole (Ref 15)

Explosive properties, impact sensy 120% of PA, power by Pb block expansion 74% of PA (Ref 11)

Use, RDX (60g) is stirred into 40g of molten N-methylpicramide at 120° to give a castable expl, deton rate 7750m/sec, vacuum stab better than Cyclotol (Ref 20)

Refs: 1) Beil **12**, {1704} 2) Beil **12**, [419] 3) Beil **12**, [420] 4) Beil **12**, 764, (368) & [420] 5) E. Bamberger & J. Müller, Ber **33**, 108 (1900) 6) H. Swann, JCS **117**, 3 (1920) 7) T.C. James et al, JCS **117**, 1275 (1920) 8) T.L. Davis & C.F.H. Allen, JACS **46**, 1046 (1924) 9) H.H. Hudson & E.W. Smith, JCS **1931**, 1509 10) H.J. Hodgson & G. Turner, JCS **1942**, 584 11) Blatt, OSRD **2014** (1944) 12) I.A. Brownlie & W.M. Cumming, BiochemJ **40**, 20 (1946) & CA **40**, 4146 (1946) 13) F.M. Lang, CR **226**, 1381 (1948) & CA **42**, 7263g (1948) 14) C.E. Clarkson et al, JCS **1950**, 1561 15) L. Médard & M. Thomas, MP **37**, 138 (1955) & CA **51** 716g (1957) 16) L. Médard & M. Thomas, MP **38**, 62 (1956) & CA **51**, 13553g (1957) 17) L. Médard & M. Thomas, MP **39**, 196 (1957) & CA **53**, 718a (1959) 18) K. Satake et al, BullChemSocJapan **34**, 1316 (1961) & CA **56**, 8621f (1962) 19) M.J. Kamlet et al, JOC **33**, 3070 (1968) 20) État Français, BritP 1134564 (1968) & CA **70**, 39437t (1969) 21) S.K. Yashuda, JChromatog **50**, 455 (1970) & CA **73**, 94387p (1970)

Tetranitro-N-methylanilines (except Tetryl), $C_7H_5N_5O_8$, mw 287.15, N 24.39%, OB to CO_2 −47.4%. The following isomers have been reported in the literature, but their expl props have not been examined

N,2,3,4-Tetranitro-N-methylaniline (2,3,4-trinitrophenyl-N-methylnitramine), mp 122.5°; prepd by the nitration of 2,3,5-trinitro-N-methylaniline with nitric acid (concn unspecified) (Refs 1 & 3)

N,2,4,5-Tetranitro-N-methylaniline (2,4,5-trinitrophenyl-N-methylnitramine), needles from nitric acid; mp 143.5°; prepd by nitration of 2,4,5-trinitro-N-methylaniline, or by the action of 90% nitric acid on 2,4,5-trinitro-N,N-dimethylaniline (Refs 1 & 3)

2,3,4,6-Tetranitro-N-methylaniline, mp 127°; prepd by the action of sulfuric acid on N,2,4,5-tetranitro-N-methylaniline (Refs 2 & 3)

Refs: 1) Beil **12**, [420] 2) Beil **12**, [428] 3) A. Forester & W. Coulson, JCS **121**, 1990 (1922)

Pentanitro-N-methylanilines, $C_7H_4N_6O_{10}$, mw 332.15, N 25.31%, OB to CO_2 −28.9%

N,2,3,4,6-Pentanitro-N-methylaniline (2,3,4,6-Tetranitro-N-methylnitramine, m-Nitrotetryl);

needles or monoclinic prisms, mp 145–46° with decompn (Ref 2); Q_c^v 2551cal/g, Q_f^v –29.9cal/g (Ref 4). It is prepd by heating N,N-dimethylpicramide with nitric acid (d 1.5g/cc) (Ref 2), or by nitration of N-methyl-3-nitroaniline (Ref 3). It is found in crude Tetryl as it is formed from a small amt of N-methylaniline present in commercial N,N-dimethylaniline (Ref 7). The effect of its presence on the stability of Tetryl is discussed by Knowles (Ref 6); it can be removed from Tetryl by a Na carbonate boil, being converted to Na styphnate (Ref 5). A procedure for the detn of m-Nitrotetryl in Tetryl is described in Ref 10

Explosive properties. Impact sensy by FI test (Encycl Vol **6**, F39) 48% of PA (Ref 9); by Kast app max fall of 2kg wt for 0/6 shots 19cm, min fall for 6/6 shots 36cm (51–3 and above 60cm resp for Tetryl) (Ref 6); power by Pb block expansion 120% of PA (Ref 9); by plate dent test – a mixt of 80% m-Nitrotetryl and 20% NG has the same effect as a mixt of 80% PETN and 20% NG (Ref 8); thermal stability – when heated at 20°/min it expl at 175°, at 5°/min it expl at 162°; it evolves N oxides after 2 hours at 60° (Ref 6)

N,2,3,4,5- or N,2,3,5,6-Pentanitro-N-methylaniline, mp 132° with decompn, Q_c^v 2453 cal/g, power by Trauzl test 151% of TNT, by BalMort 143% of TNT (Ref 11). According to Lothrop (Ref 11) the compd prepd by Blancksma (Ref 3) and described by him as N,Ar-hexanitro-N-methylaniline is actually one of the above-titled compds. Lothrop, however, was unable to distinguish between the two possible structures for Blancksma's compd

Refs: 1) Beil **12**, 771, (372), [428] & {1743} 2) P. vanRomburgh, Rec **8**, 274 (1889) 3) J.J. Blancksma, Rec **21**, 265 (1902) 4) P.P. Rubtzov & L.A. Sever'yanov, ZhRus-FizKhimObshch **50**, 140 (1918) & CA **18**, 1421 (1924) 5) C.L. Knowles, JIEC **12**, 246 (1920) 6) C.F. vanDuin & B.C.R. vanLennep, Rec**39** , 145 (1920) & CA **14**, 2708 (1920) 7) Davis (1943), 178 8) A. Stettbacher, TechIndSchweizChemiker-Ztg **26**, 181 (1943) 9) Blatt, OSRD **2014** (1944) 10) I.A. Brownlie & W.L. Cumming, JSCI **67**, 206 (1948) & CA **43**, 1189c (1948) 11) W.C. Lothrop et al, JACS **73**, 3581 (1951)

N,Ar-Hexanitro-N-methylaniline (N-Methyl-N-pentanitrophenylnitramine, 2,5-Dinitrotetryl). The compd prepd by Blacksma by nitration of 3,5-dinitro-N-methylaniline and claimed to be the above, was shown by Lothrop to be a pentanitro-N-methylaniline (see above)

Nitro Nitroso Derivatives of N- Methylaniline

Nitro nitroso-N-methylanilines, $C_7H_7N_3O_3$, mw 181.15, N 23.20%, OB to CO_2 –128%

2-Nitro-N-nitroso-N-methylaniline (N-methyl-2-nitrophenylnitrosamine), yellow needles from EtOH, mp 36° (Ref 1)

3-Nitro-N-nitroso-N-methylaniline (N-methyl-3-nitrophenylnitrosamine), yellow crysts from EtOH, mp 68–70° (Ref 2); CA Registry No 18600-50-5

4-Nitro-N-nitroso-N-methylaniline (N-methyl-4-nitrophenylnitrosamine), needles from hot EtOH, mp 104° (Ref 3); CA Registry No 943-41-9. It is prepd by the action of nitrous acid on 4-nitroso-N,N-dimethylaniline (Ref 4), or by the action of nitrous acid on 4-nitro-N,N-dimethylaniline (Ref 5). In his research on the prepn of Tetryl from N,N-dimethylaniline, Hodgson found that the action of nitric acid (d 1.12g/cc) in the presence of Na nitrite gave a low yield of 4-nitro-N-nitroso-N-methylaniline (Ref 6). It is probably present in aged NC proplnts stabilized with methyl centralite (Encycl Vol **2**, C138 & Ref 7). It is formed in aged NC proplnts stabilized with N-methyl-p-nitroaniline, and is formed when the latter is treated with nitric oxide in wet dioxane (Ref 8)

4-Nitro-2-nitroso-N-methylaniline, green prisms from acet/w, mp 165–67° with decompn; prepd by the photolysis of N-(2,4-dinitrophenyl)-N-methyl-leucine (Ref 9)

Refs: 1) Beil **12**, 697 & {1540} 2) Beil **12**, 710, (349) & [383] 3) Beil **12** 727, (354), [395] & {1644} 4) H.H. Hodgson & E.W. Smith, JCS **1931**, 1510 5) H.M. Halliday & T.H. Reade, JCS **1940**, 138 6) H.H. Hodgson & T.H. Reade, JCS **1942**, 584 7) C.A. Parker, "The Transformation Products of Carbamite Produced in the Ageing of Service Propellants", GtBrit AML Rept A/12(M) March 1948 8) B.L. Hollingsworth, JCS **1959**, 2420 9) D.W. Russell, JCS **1964**, 2830

Dinitronitroso-N-methylanilines, $C_7H_6N_4O_5$, mw 226.15, N 24.78%, OB to CO_2 –84.9%. The following isomers have been reported in the literature:

2,4-Dinitro-N-nitroso-N-methylaniline (2,4-dinitrophenyl-N-methylnitrosamine), yellow needles, mp 83–85° (Ref 1). It is prepd by the action of nitric acid (d 1.3g/cc) and Na nitrite (Ref 5), or 70% nitric acid (Ref 9) on N,N-dimethylaniline. It has also been prepd by the addn of solid Na nitrite to 2,4-dinitro-N-methylaniline in 65% sulfuric acid (Ref 10). It is one intermediate in the prepn of Tetryl by the nitration of N,N-dimethylaniline (Ref 11). It is decompd by heat (Ref 9), or rapidly in boiling EtOH to give 2,4-dinitro-N-methylaniline (Ref 12)

2,5-Dinitro-N-nitroso-N-methylaniline, 2,5-dinitrophenyl-N-methylnitrosamine, orange needles or plates from EtOH; prepd by the action of 50% aq Na nitrite on 2,5-dinitro-N,N-dimethylaniline in aq HCl (Refs 2 & 8)

2,6-Dinitro-N-nitroso-N-methylaniline (2,6-dinitrophenyl-N-methylnitrosamine), white needles, mp 115–16°; prepd by the action of Na nitrite in acet ac on 2,6-dinitro-N-methylaniline (Refs 3 & 6)

3,4-Dinitro-N-nitroso-N-methylaniline (3,4-dinitrophenyl-N-methylnitrosamine), mp 108–09°, prepd by the action of nitric acid (d 1.37–.40 g/cc) contg nitrous acid on 3,4-dinitro-N,N-dimethylaniline (Refs 4 & 7)

Refs: 1) Beil **12**, 757 & (364) 2) Beil **12**, [413] 3) Beil **12**, 365 4) Beil **12**, [414] 5) P. vanRomburgh & J.D. Jansen, KAkad-Wetenschappen **19**, 955 (1911) & CA **5**, 3045 (1911) 6) R. Meldola & W.F. Holley, JCS **107**, 619 (1915) 7) M.J. Smit, ProcAcad-SciAmsterdam **22**, 523 (1920) & CA **14**, 1970 (1920) 8) W.G. Macmillan & T.H. Reade, JCS **1929**, 2864 9) F.M. Lang, CR **226**, 1381 (1948) & CA **42**, 7263 (1948) 10) C.E. Clarkson et al, JCS **1950**, 1561 11) J. Glazer et al, JCS **1950**, 2662 12) B.L. Holingsworth, JCS **1959**, 2423

N-Nitroso-2,4,6-trinitro-N-methylaniline (N-methyl-N-(2,4,6-trinitrophenyl)nitrosamine, N-methyl-N-nitrosopicramide), $C_7H_5N_5O_7$, mw 271.15, N 25.83%, OB to CO_2 −56.1%. Its expl props have not been investigated. Bright yellow leaflets or needles from EtOH, mp 106.5° (Ref 1); prepd by the action of nitrous acid on N-methylpicramide suspended in acet ac (Ref 2), or by allowing Tetryl to stand for 24 hours in the presence of concd sulfuric acid (Ref 3). It is a by-prod in the prepn of Tetryl by the action of 70% (Ref 4) or concd (up to 99%) (Ref 5) nitric acid on N,N-dimethylaniline

Refs: 1) Beil **12**, 770, (371) & {1738} 2) E. Bamberger & J. Müller, Ber **33**, 103 (1900) 3) F. Reverdin, BullFr [4] **9**, 43 (1911) & CA **4**, 1089 (1911) 4) F.M. Lang, CR **226**, 1381 (1948) & CA **42**, 7263g (1948) 5) F.M. Lang, CR **227**, 384 (1948) & CA **45**, 3811e (1951)

Nitroso Derivatives of N-Methylaniline

N-p-Dinitroso-N-Methylaniline, p-ONC_6H_4NMeNO, $C_7H_7N_3O_2$, mw 165.15, N 25.45%, OB to CO_2 −150%; cryst lumps from et alc, mp 101° (Ref 2). It is prepd by the action of Na nitrite on p-nitroso-N-methylaniline in aq HCl (Ref 2). It ignites when held at 45–50° for 7 hours; a mixt of 33 of N-p-nitroso-N-methylaniline, 18.5 of Ca silicate, 33 of Amm bicarbonate, and 15.5 of w is stable at 45–50° for up to 82 hours (Ref 4). As a trade name "Elastopar" it is used as a modifier, accelerator, and cross linker for rubbers and plastics (Ref 3). It is mildly carcinogenic, but otherwise the toxicity is low (Refs 5 & 6)

Refs: 1) Beil **12**, 686, [366] & {1512} 2) O. Fischer & E. Hepp, Ber **19**, 2992 (1886) 3) H.M. Leeper et al, RubberWorld **135**, 413 (1956) & CA **51**, 8467d (1957) 4) Anon, BritP 981634 (1965) & CA **64**, 3103 (1964) 5) J.H. Weisburger et al, Naturwissenschaften **53**, 508 (1966) & CA **66**, 965y (1967) 6) Sax (1975), 284

Written by **C. H. McDONNELL**

METHYL ANISOLE AND DERIVATIVES

Methyl Anisole (Methyl methoxy benzene or Methoxytoluene). $CH_3.O.C_6H_4.CH_3$, mw 122.17, OB to CO_2 −261.93%. Three isomers exist:

Ortho (2-Methyl anisole), liq, fr p −34.1°, bp 171.8°, d 0.9798g/cc at 20/4°; RI 1.5161 (Ref 1),

Meta (3-Methyl anisole), liq, fr p −55.92°, bp 176.5°, d 0.9716g/cc at 20/4° (Ref 2);

Para (4-Methyl anisole, p-Cresyl methyl ether, p-Methoxy toluene or Methyl-p-Cresol), colorl

liq, fr p −32.05°, bp 177.05°; d 0.9702g/cc at 20/4° (Ref 3). Prepn & other props are in Beil

Refs: 1) Beil **6**, 352, (171), [328] & {1244}, ortho 2) Beil **6**, 376, (186), [351] & {1297}, meta 3) Beil **6**, 392, (1999), [375] & {1351}, para

Azido Methyl Anisole (Azido methoxy toluol, Methoxybenzazid in Ger). $CH_3.O.C_6H_4.CH_2.N_3$, mw 163.17, N 25.76%, OB to CO_2 −191.21%. Three isomers exist:

Ortho (1,1-Azido methyl anisole), liq, bp 118° at 14mm of Hg. Prepd from a mixt of N-Nitroso-N-(2-methoxy-benzyl)-hydrazine and dil sulfuric acid by steam distn (Ref 1). Explodes when heated quickly (Ref 1);

Meta (3,3-Azido methyl anisole), liq, bp 134° at 28mm of Hg (Ref 2). Prepd from a mixt of N-Nitroso-N(3-methoxy-benzyl)-hydrazine and dil sulfuric acid by steam distn (Ref 2);

Para (4,4-Azido methyl anisole); prepn & properties are in Beil

Refs: 1) Beil **6**, (181), ortho 2) Beil **6**, (195), meta 3) Beil **6**, (207), para

Mononitro Methyl Anisole (2-Nitro-4-methyl anisole, 3-Nitro-4-methoxy-1-methyl benzol or Methyl-[2-nitro-4-methyl phenyl]-ether). $CH_3.O.(NO_2)C_6H_3.CH_3$, mw 167.18, N 8.38%, OB to CO_2 −167.48%, pale yellow cryst, mp 8.5°, bp 274° (partial decompn), d 1.2025 g/cc at 25/4°, RI 1.5536; sl sol in eth (Ref 1). Prepd by heating K2-nitro-p-cresol with methyl-iodide & methylalc in a sealed tube at 100° (Ref 1). Another prepn is given in Ref 2

Refs: 1) Beil **6**, 412 2) S. Yura, A. Nagasaka, & I. Tanaka, JChemSocJapan, Sect 55, 436–38 (1952) & CA **48**, 3031 (1954)

Dinitro Methyl Anisole (4-Nitro-2-nitromethyl anisole, 3-Nitro-6-methoxynitromethyl toluol or Methyl-[5-nitro-2-nitromethyl phenyl]-ether). $CH_3.O.(NO_2)C_6H_3.CH_2NO_2$, mw 212.18, N 13.21%, OB to CO_2 −113.11%, cryst, mp 93–94°. Prepd from 4-nitro-2(iodomethyl) anisole in ether-benzene soln by treatment for 3 days at RT with Ag nitrate. The sodium salt explodes violently on heating

Refs: 1) Beil, not found 2) G. Bendy, C.C. Culvenor, L.J. Goldsworthy, K.S. Kirby & R. Robinson, JCS **1950**, 1130–8 (1950) & CA **44**, 10720–21 (1950)

Trinitro Methyl Anisole (4,6-Dinitro-2-nitro-methyl-anisole, 3,5-Dinitro-6-methoxy-nitro-methyl toluol or Methyl-[4,6-dinitro-2-nitro-methyl phenyl]-ether). $CH_3.O.(NO_2)_2C_6H_2.-CH_2NO_2$, mw 257.18, N 16.34%, OB to CO_2 −77.77%, cryst, mp 65–66°. Prepd from 4-nitro-2-(nitromethyl)anisole by slow addition to a mixt of concd sulfuric-nitric acids (2:1) at 0° (Ref 2). Explodes violently when heated quickly (Ref 2)

Refs: 1) Beil – not found 2) G. Bendy, C.C. Culvenor, L.J. Goldsworthy, K.S. Kirby & R. Robinson, JCS **1950**, 1130–8 (1950) & CA **44**, 1070–21 (1950)

2,4,6-Trinitro-5-Methyl Anisole (2,4,6-Trinitro-3-methoxy-1-methyl-benzol or Methyl-[2,4,6-trinitro-5-methyl-phenyl]-ether). $CH_3.O.(NO_2)_3C_6H.CH_3$, mw 247.18, N 17.00%, OB to CO_2 −80.91%, cryst, mp 92°, sol in conventional organic solvents (Ref 1). Prepd by nitration of methyl-m-tolyl ether using concd nitric acid (Ref 1). Other prepns are listed in Refs 2 thru 5

Refs: 1) Beil **6**, 365 & [388] 2) M. Giua, GazzChimItal **49**, 146–54 (1919) & CA **14**, 1530–31 (1920) 3) H. Barbier, HelvChimActa **11**, 157–61 (1928) & CA **28**, 1339 (1928) 4) K.I. Bogacheva, JAC(USSR) **13**, 1606-7 (1940) & CA **35**, 3985 (1941) 5) I. Wender, H. Greenfield, S. Metlin & M. Orekin, JACS **74**, 4079–83 (1952) & CA **47**, 6895–96 (1953)

Methyl Nitraminoanisole (2,4,6-Trinitro-3-methylnitraminoanisole, Tetranitroanisolemethyl-nitramine, m-Methoxytetryl or 1-Methoxy-3-methyl-nitraminopicrate). $CH_3.O.C_6H.N(CH_3)NO_2(NO_2)_3$, mw 317.2, N 22.08%, OB to CO_2 −52.96%, cryst, mp 96–97° (Ref 3). Prepd from 2,3,4,6-tetra-nitrophenylmethylnitramine and m-nitrotetryl upon heating with methyl alcohol (Refs 1 & 2). The expln temp (187°) was obtd on heating the sample at the rate of 5°/min, while a temp of 198° was detn by heating at the rate of 20°/min (Refs 2 & 3). Impact sensitivity with the Kast app, max fall for no detonation using a 10kg wt (6 shots) was 15–16cm vs 14cm for

Tetryl (Refs 2 & 3); thermal stability at 90°, evolves oxides of nitrogen in hrs (Refs 2 & 3)
Refs 1) Beil **13**, 425 2) Van Duin & Van Lennop, Rec **39**, 125 & 145–47 (1920) 3) Blatt, OSRD **2014** (1944)

Methyl Azide. See under Methane in this Vol

Methyl Borate (Trimethyl borate or Trimethoxy borine), $(CH_3.O)_3B$, mw 103.92, OB to CO_2 –115.47, colorl liq, mp –29°, bp 68°, d 0.92 g/cc at 20°; vap d 3.59. Prepn & other properties are given in Beil (Ref 1). Sax (Ref 2) lists this compd as a dangerous fire hazard when exposed to heat or flame. It reacts with w or steam to produce toxic & flammable vapors, and vigorously with oxid materials
Refs: 1) Beil **1**, 287, (143) & [275] 2) Sax (1963), 883-R; (1968) 914-R

4-Methyl-2,6-Dinitrotetramethylene-2,4,6-Triamine (Methyl-bis [methyl-nitraminomethyl] amine). $CH_3.N(NO_2).CH_2.N(CH_3).CH_2.-N(NO_2).CH_3$, mw 207.23, N 33.80%, OB to CO_2 –96.51%, mp 64.5–65.5°. Prepn from methylnitramine, formaldehyde and methylamine. Deflagrates at 305°. Thermal stability at 100°, not acid in 300min; at 135°, acid in 105min. Hydroscopicity at 25°; loses 7.2% weight at 90% RH, gains 6.9% weight at 100% RH. Impact sensitivity using Bruceton No 3 machine is 50% positive with 5Kgm weight at greater than 90cm. International heat test at 75°, loses 0.6% weight. Power by ballistic mortar is 95% TNT. Vacuum stability at 100° is greater than 12cc per 5g in 24 hours
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

Methylenediisonitrosoamine. See under **MEDNA** in this Vol

Methylenedinitramine or Methylenediisonitramine. See under **MEDINA** in this Vol

(Methylenedioxy) Dimethanol Dinitrate. $CH_2(OCH_2ONO_2)_2$, mw 198.11, N 14.14%, OB to CO_2 –8.08%, liq. Prepn from formaldehyde or trioxymethylene with mixed acid. Impact sensitivity FI is 6% of PA. Power by lead block test is 148% of PA, and the material is described as "not very powerful". Chemically unstable and reactive with moisture
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

Methyleneglycoldinitrate. $CH_2(ONO_2)_2$, mw 138.04, N 20.3%, OB to CO_2 +34.8%; oily liq, bp 75–77° at 20mm; d 1.54g/cc; insol in w, sol in org compds. May be prepd (Refs 2 & 5) by nitration of formaldehyde soln at 5°. If the temp is allowed to reach 10°, a violent decompn may take place. The resulting product separates atop the spent acid as an oil, and can be purified by washing with w to obtn a stable product

It is about 65% as powerful an expl as TNT, and nearly as sensitive to impact as MF. It is reactive with moisture and not very stable. Methyleneglycoldinitrate gelatinizes NC and cellulose acetate, and it is easily absorbed by kieselguhr. Travagli (Ref 3) proposed using it as a substitute for NG or ethyleneglycoldinitrate
Refs: 1) Beil – not found 2) G. Travagli & A. Torboli, ItalP 333080 (1935) 3) G. Travagli, GazzChimItal **68**, 718 (1938) & CA **33**, 2485 (1939) 4) A. Torboli, BullSocItalBiolSper **17**, 381–2 (1942) & CA **40**, 7388 (1946) 5) F.J. Walker, "Formaldehyde", Reinhold Publ, NY (1944), 134 & 330

N-Methylethylenedinitramine. See under **MeEDNA** in this Vol

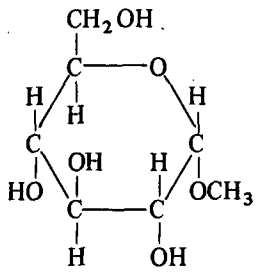
N-Bromo-N'-Methyl-Ethylenedinitramine. $Br.(O_2NN)CH_2.CH_2(NNO_2).CH_3$, mw 243.04, N 23.06%, OB to CO_2 –29.6%, pale yellow cryst, mp 118–19° (decompn); sol in acet. Prepn from N-methyl-ethylenedinitramine dissolved in aq KOH by adding liq bromine dropwise with stirring. Yield of w-washed ppt is 90%. Explosion temp is above 360°. Power is 101.2% (TNT=100%). Sensitivity to initiation is 6.6cm

(50% pt; RDX = 35cm). Stability at 135° is 4 minutes to ignition

Refs: 1) Beil – not found 2) Blomquist, OSRD **4134** (1944)

METHYLGLUCOSIDE AND ITS TETRANITRATE

α-Methylglucoside (Methyl-α-D-glucopyranoside) $C_7H_{14}O_6$, mw 194.18; orthorhombic bispheroidal crysts, mp 168°, d 1.46g/cc. Solubility in w at 17°, 63% (w/w); in 80% alc 7.3%; in 90% alc 1.6%; insol in eth. Can be prepd by refluxing finely powd glucose with methanol-HCl (Ref 2) and by other methods (Ref 3). On nitration it yields an expl tetranitrate



Refs: 1) Beil **1**, 179 2) E. Fischer, Ber **26**, 2405; **27**, 2987; **28**, 1151 (1895) 3) G.N. Bollenback, "Methyl Glucoside, Preparation, Physical Constants, Derivatives", Academic Press, NY (1958) 4) Merck (1968), 687-L

α-Methylglucoside Tetranitrate (Methyl-α-d-glucopyranoside tetranitrate). $C_7H_{10}O_2(ONO_2)_4$; mw 374.18, N 14.98%, OB to CO_2 –21.4%; quadrilateral prisms from alc; mp 49–50°; bp (decompn at 135°). Was prepd by Will and Lenze (Ref 2) by dissolving α-methylglucoside in cold concd nitric acid (d 1.52g/cc) and then adding concd sulfuric acid dropwise, with agitation and cooling

Médard (Ref 6) examined its expl properties, and noted that it required a relatively weak initiator (0.25g of MF) to detonate a sample of d 1.10g/cc. Only the cast product (d 1.65g/cc) required a strong detonator (> 1.5g of MF). Its impact sensitivity was comparable to RDX, and the Trauzl Pb block expansion was found to be 130 (PA=100). The rates of deton of 30mm diameter charges in cardboard tubes were 5630m/sec at d 1.10g/cc, 6970m/sec at 1.50g/cc, 7560m/sec at 1.60g/cc, and 7830m/sec at 1.65 g/cc. Médard concluded that Methylglucoside Tetranitrate is only slightly inferior to RDX with regard to its expl power

Médard also examined mixts of the tetranitrate with AN and DNT. He found a mixt with 52.5% AN superior to 50/50 Amatol. Trauzl test values and deton velocities for the former were 132cc and 6520m/sec (d 1.62g/cc), with the latter yielding 112cc and 6150m/sec (d 1.60g/cc), respectively

When stored at 50°, it lost 0.7% of its weight after 5 days, and 26% after 12 days (Ref 2)

Refs: 1) Beil **1**, 898 & 1900 2) W. Will & F. Lenze, Ber **31**, 68 & 80 (1898) 3) Daniel (1902), 438 & 486 4) Davis (1943), 243 5) L. Brissaud, M. Leclerq & S. Ronssin, MP **33**, 187–91 (1951) & CA **47**, 10229 (1953) (Prepn of α-methyl-d-glucoside and its nitration to the tetranitrate) 6) L. Médard, MP **33**, 193–98 (1951) & CA **47**, 10229 (1953)

α-Methylglycerol Trinitrate. See 1,2,3-Butanetriol Trinitrate in Vol **2**, B371-L

METHYLHYDANTOIN AND DERIVATIVE

5-Methylhydantoin (2,5-Dioxo-4-methylimidazolidine). $CH_3.CH.NH.CO.NH.CO$; mw 114.10, N 24.55%; mp 146–47°. Sol in w, alc, acet; sl sol in eth. Exists as monohydrate and anhydrous salts, the former is formed on slow crystn from w, and the latter on rapid crystn. Both salts are white. Can be prepd by boiling 3g of inactive α-ureidoproprionic acid, $H_2N.CO.NH.CH(CH_3)COOH$, with 50ml of w and 9ml of concd HCl for 2 hours under reflux, cooling and extrg with eth (Ref 3). Adams and Marvel (Ref 5) prepd it based on the work of Wagner and Simons (Ref 4). On nitration, it gives an expl nitromethylhydantoin (see below)

Refs: 1) Beil **24**, 279 & (305) 2) A.P.N. Franchimont & E.A. Klobbie, Rec **7**, 14 (1888) 3) H.D. Dakin, JCS **107**, 439 (1915) 4) E.C. Wagner & J.K. Simons, JChemEduc **13**, 266 (1936) & CA **30**, 6374 (1936) 5) R. Adams & C.S. Marvel, OSRD Rept No 96, Serial No 23 (Aug 24, 1941), pp 8 & 22

1-Nitro-5-Methylhydantoin (3-Nitro-2,5-dioxo-4-methylimidazolidine).

$H_3C.CH.NHCO.N(NO_2).CO$; mw 159.10, N 26.41%; OB to CO_2 –65.4%; colorl plates, mp 148–149.5°, bp, deflagrates above 225° giving a brown solid which chars on further heating, does not detonate even on heating to 360°. Sol in w, especially hot; decompd slowly in boiling w, sl sol in alc; nearly insol in eth, chlf and benz. Its aq soln is acidic (pH 4)

Can be prepd by evapg 5-methylhydantoin (15g) dissolved in white, 99% nitric acid (50 ml) to dryness on a steam cone. The resulting residue (19.5–20g or 93–95% of theory) was recrystd from hot, not boiling, w. The yield of purified product was only 65% of theory (Refs 1, 2 & 3)

Nitromethylhydantoin is an expl comparable to TNT in its sensitivity to impact. Q_c =–448.8 kcal/mole; Q_f = –99.9kcal/mole. It is slightly hygroscopic, and its stability to heat is inadequate

Refs: 1) Beil **24**, 285 2) A.P.N. Franchimont & E.A. Klobbie, Rec **7**, 13 & 237 (1888) 3) R. Adams & C.S. Marvel, "Progress Report on Nitroamides to July 24, 1941", OSRD **86** (1941), 23–5 4) A.H. Blatt & F.C. Whitmore, "A Literature Survey of Explosives", OSRD **1085** (1942), 66

N-METHYLHYDROXYACETAMIDE AND DERIVATIVE

N-Methylhydroxyacetamide (N-Methylglycolamide, N-Oxymethyl-Acetamide, Methylol-Acetamide). $CH_3.CO.NH.CH_2.OH$, mw 103.12, N 27.17%, OB to CO_2 –116.37%, very hygroscopic cryst, mp 50–52°. Very slightly sol in w, alc, chlf; sl sol in glycerin. Prepn from acetamide and KOH dissolved in formaldehyde and heated. Can be nitrated to form a powerful expl, N-Nitro-N-Methylhydroxyacetamide Nitrate (see below)

Ref: Beil **2**, 178

N-Nitro-N-Methylhydroxyacetamide Nitrate (N-Nitro-N-methylglycolamide nitrate). $O_2NO.CH_2.CO.N(NO_2).CH_3$; mw 179.09, N 23.46%, OB to CO_2 –22.3%; white needles, mp 80.82°, bp (subl at 120–21° at 6mm); d 1.65 g/cc (room temp), 1.42g/cc (at 85°). Puffs off mildly and catches fire at about 220°, but does not expl even when heated to 360°. Was prepd (Ref 2, p 31) by slowly adding 10g of N-methylhydroxyacetamide to 50ml of white nitric acid (99%), warming the soln at 50–60° for 1 hour, allowing to cool to RT, and pouring onto cracked ice. The residue was collected on a filter, washed thoroughly with cold w and dried. Yield 16–16.5g (80–83% of theory) of crude product. In order to purify it, the crude product was disd in about 150ml of 4:1, by vol, chlf-petr eth mixt

It is an expl, more powerful than TNT (about 133% by Ballistic Mortar), and comparable to Tetryl in sensitivity. Its Vel of Deton is 7420 m/sec at d 1.5g/cc, and 5490m/sec at d 1.0g/cc. Q_c is about 380kcal/mole. It is practically nonhygroscopic and its thermal stability is satisfactory. Has been used by DuPont Co as a base charge for some detonators

Refs: 1) Beil – not found 2) H. Biltz et al, JPraktChem **142**, 193–200 (1935) & CA **29**, 3652 (1935) 3) Anon, "Report on Nitroamides to July 24, 1941", OSRD **86** (1941), 11, 30, 31

α-Methyl-D-Mannosite (D-α-methylmannosite). $C_7H_{14}O_6$; mw 194.18; wh needles from 96% alc, or rhombic prisms, mp 193–94°, d 1.473 g/cc. Sol in w (24.6p/100p at 17°), sl sol in alc (1.5p/100p in abs alc and 3.2p/100p in 90% alc at 17°). On nitration, it yields the expl tetranitrate

α-Methylmannosite Tetranitrate (Nitro-α-methylmannosite). $C_7H_{10}O_2(ONO_2)_4$; mw 374.18; N 14.97%; OB to CO_2 –21.4%; fine, asbestos-like needles; mp 36°. Was prepd by Will and Lenze (Ref 2) by dissolving α-methyl-d-mannosite in cold concd nitric acid and adding concd sulfuric acid dropwise with stirring. It is an expl which is relatively stable at 50° (weight loss 1.3% in 10 days, 7% in 12 days)

Refs: 1) Beil **1**, 907 & 908 2) W. Will & F. Lenze, Ber **31**, 80 (1898) 3) Daniel (1902), 438 & 486 4) Davis (1943), 243

METHYLMERCURIC SALTS

Several salts contg the CH_3Hg–group were prepd by various investigators, and the following proved to be expl:

Methylmercuric Azide (Mercuric methylazide). CH_3HgN_3; crysts from alc; mp 130.5°; decompn explosively ca 200°. Was prepd by Perret & Perrot (Ref 3) by treating methyl mercuric hydroxide, CH_3HgOH (Ref 1) with hydrazoic acid

Methylmercuric Chromate. CH_3HgCrO_4; crysts; decomps explosively ca 255–60°. Was prepd by the reaction of chromic acid with methylmercuric hydroxide (Ref 3)

Methylmercuric Nitrate. CH_3HgNO_3; leaflets; mp 100°; v sol in w. Was prepd by Strecker (Ref 2) by treating methylmercuric hydroxide with nitric acid. It has to be handled with care, being a severe skin irritant

Methylmercuric Perchlorate. CH_3HgClO_4; crysts; deflagrates ca 180°. Was prepd by treating methylmercuric hydroxide with 60% perchloric acid (Ref 3)

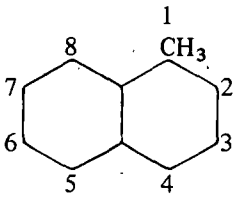
Refs: 1) Beil **4**, 681, (613) 2) A. Strecker, Ann **92**, 79 (1854) 3) A. Perret & R. Perrot, Helv **16**, 848–57 (1933) & CA **27**, 4772 (1933)

2-Methyl-2-Methylol-1,3-Propanediol. Same as **Metriol** (see in this Vol) or Pentaglycerin

METHYLNAPHTHALENE AND ITS DERIVATIVES

$C_{10}H_7.CH_3$, mw 142.19. There are two isomers, both of which may be nitrated to contain as many as four nitrogroups. The di- and trinitroisomers are weak explosives

Alpha-(or 1-) Methylnaphthalene



oil, mp −22°, bp 244.6°, d 1.0202g/cc at 20/4°, RI 1.6170 at 20°. Insol in w, v sol in alc & eth; sol in benz. Compd can be obtd from fractions of coal tar

Beta-(or 2-) Methylnaphthalene. Monoclinic cryst, mp 34.58°, bp 241.05°, d 1.0058g/cc at 20/4°, RI 1.6019 at 20°. Insol in w, v sol in alc & eth; sol in benz. Compd can be obtd from fractions of coal tar

Ref: Beil **5**, 566, 567, (265, 266), [460, 463] & {1620, 1627}

Dinitromethylnaphthalenes. $(O_2N)_2.C_{10}H_5.CH_3$, mw 232.19, N 12.07%, OB to CO_2 −151.60%. The following isomers are described by Beilstein. These compds are weaker expls than the corresponding dinitronaphthalenes (see under Naphthalene and its Derivatives in this Vol)

2,4-Dinitro-1-Methylnaphthalene, mp 161°, gold needles from alc. Prepn from [2,4-dinitronaphthyl-(1)] acetate by heating above its mp

Refs: 1) Beil **5**, [463] & {1626} 2) V. Veselý & I.A. Pastak, BullFr [4], **37**, 1448 (1925)

4,5-Dinitro-1-Methylnaphthalene, mp 142–43°, needles from alc. Prepn from 5-nitro-1-methylnaphthalene by nitration on a steam bath using nitric (d 1.52g/cc) & concd sulfuric acids in glac AcOH & Ac_2O

Ref: Beil **5**, {1626}

4,8-Dinitro-1-Methylnaphthalene, mp 122–23°, gold needles from alc. Prepn from 8-nitro-1-methylnaphthalene by nitration on a steam bath using nitric (d 1.52g/cc) & concd sulfuric acids in AcOH

Ref: Beil **5**, {1627}

4,X-Dinitro-1-Methylnaphthalene, mp 176°, brown plates from AcOH. Prepn from 4-nitro-1-methylnaphthalene by nitration in the cold with nitric acid (d 1.5g/cc)

Ref: Beil **5**, {1627}

X,X-Dinitro-1-Methylnaphthalene, mp 168°, needles from benz. Prepn from 1-Methylnaphthalene by nitration with fuming nitric acid at 0°

Ref: Beil **5**, {1627}

1,5-Dinitro-2-Methylnaphthalene, mp 131°. Sl sol in alc & AcOH. Prepn (together with 1,8-dinitro-2-methylnaphthalene) from 1-nitro-2-methylnaphthalene by heating with concd nitric & acetic acids on a w bath

Refs: 1) Beil **5**, [466] & {1635} 2) V. Veselý & J. Kapp, Rec **44**, 373 (1925)

1,8-Dinitro-2-Methylnaphthalene (1,X-Dinitro-2-methylnaphthalene; *"eso"*), mp 209°. Sl sol

in AcOH & alc. Prepn from 1-nitro-2-methylnaphthalene by heating with anhydrous nitric acid in presence of acetic & sulfuric acids
Refs: 1) Beil **5**, 568, (267), [466] & {1635} 2) R. Lesser & G. Aczel, Ann **402**, 32 (1914) 3) V. Veselý & J. Kapp, Rec **44**, 373 (1925) 4) Urbański **1**, 447 (1964)

Trinitromethylnaphthalenes, $(O_2N)_3C_{10}H_4.CH_3$. mw 277.19, N 15.16%, OB to CO_2 −112.60%. Trinitromethylnaphthalenes are supposed to be less powerful expls than trinitronaphthalenes, but comparable to dinitronaphthalenes

2,4,5-Trinitro-1-Methylnaphthalene, mp 170°, gold cryst from benz or alc. Prepn from 4,5-dinitro-1-methylnaphthalene by heating with nitric acid (d 1.5g/cc)
Ref: Beil **5**, {1627}

4,X,X-Trinitro-1-Methylnaphthalene, mp 180–81°, straw-yellow needles from CCl_4. V sl sol in alc, appreciably sol in CCl_4, chlf & AcOH. Prepn from 4-nitro-1-methylnaphthalene by nitration with mixed nitric-sulfuric acids
Refs: 1) Beil **5**, (266) 2) R. Lesser & A. Glaser, Ann **402**, 14 (1914)

X,X,X-Trinitro-2-Methylnaphthalene, mp 182°, cryst from benz. Prepn from 2-methylnaphthalene in glac AcOH by nitration at 0° with fuming nitric acid
Ref: Beil **5**, {1635}

NOTE: Nitroderivatives of 2-methylnaphthalenes have been described in detail by V. Veselý & J. Kapp in a series of articles: ChemListy **18**, 201–5, 244–9 (1924) & CA **19**, 2487 (1925); Rec **44**, 360–75 (1925) & CA **19**, 2948 (1925)

1,6,8-Trinitro-2-Methylaminonaphthalene. $(O_2N)_3C_{10}H_4.(H)N(CH_3)$, mw 292.23, N 19.18%, OB to CO_2 −109.50%, cryst, mp 257° (decompn). Prepn from 1,6,8-trinitro-2-methoxy-naphthalene by heating with methylamine in alc
Refs: 1) Beil – not found 2) E.J. Van der Kam, Rec **45**, 564–81 (1926) & CA **21**, 82–83 (1927)

Tetranitro-2-Methylnaphthalene. $(O_2N)_4C_{10}H_3.CH_3$, mw 322.21, N 17.39%, OB to CO_2 −85.04%, needles from glac AcOH, mp 262–63° (decomp). Sol in glac AcOH, acet, dioxane & py; sl sol in benz, toluene, xylene & amyl alc. Prepn from 1-nitro-2-methylnaphthalene by nitration using mixed acids of nitric (d 1.52g/cc), sulfuric (d 1.84 g/cc) & oleum (20–25% SO_3 free), and heating for one hour at 80° on a water bath. Two other isomers which do not decompose are prepd simultaneously; viz, mp (I) 230° & (II) 241–42°. Yield of the decomposed isomer is 3.23%
Refs: 1) Beil – not found 2) M. Civera & C. Torello, Gazz **86**, 350–57 (1956) & G.R. Loehr, PicArsnTrsln No **18** (1957)

1-Methyliodo Nitronaphthalene. $(I)CH(NO_2).C_{10}H_7$, mw 313.10, N 4.47%, OB to CO_2 −122.64%, cryst from alc, mp 74°. Decompn occurs at 110–35°. Prepn from 1-nitromethylnaphthalene by reacting it at 0° with a w soln of iodo K iodide & NaCl
Ref: Beil **5**, {1626}

2-Methyliodo Nitronaphthalene. $(I)CH(NO_2).C_{10}H_7$, mw 313.10, N 4.47%, OB to CO_2 −122.64%, cryst, mp 60°, decomps at 105°. Prepn from 2-nitromethylnaphthalene by reacting it at 0° with a w soln of iodo K iodide & NaCl
Ref: Beil **5**, {1635}

Methylnitramine (Nitraminomethane). $CH_3.NH.NO_2$ or $CH_3.N{:}N(:O)OH$; mw 76.06, N 36.83%, OB to CO_2 −42.1%; colorless needles from ether; mp 38°; d 1.243 at 49/4°; RI 1.4616 at 48.6°. V sol in cold w, alc, chlf and benz; less sol in eth and still less sol in petr eth. Can be prepd by nitrating n-methylurethane with abs nitric acid. The resulting soln of methyl nitrourethane is drowned in w, neutralized with Na carbonate, and extrd with eth to remove methyl nitrourethane. On passing ammonia gas thru the eth extract, a white ppt of the ammonium salt of methylnitramine is deposited and sepd by filtration. It is disd in alc and boiled to drive off the ammonia, and

to conc to a small vol. The resulting syrup is placed in a vacuum desiccator over sulfuric acid, where the final drying takes place. To obtain a purer product, the deposit may be crystd from eth

Methylnitramine explodes on heating or on contact with concd sulfuric acid. Based on tests conducted in the USA during WWII, it is more powerful than TNT (144% as detd by Trauzl lead block test) (Ref 3)

Being a strong monobasic acid, it easily forms metallic salts, some of which are expl, as for instance:

Potassium Methylnitraminate. $K.CH_3O_2N_2$; fine needles, which expl violently on heating. According to Davis (Ref 2), the heavy metal salts of methylnitramine are primary explosives, but have not been investigated extensively

Refs: 1) Beil **4**, 567, (568) & [968] 2) Davis (1943), 371–72 3) Blatt, OSRD **2014** (1944)

3-Methylnitramino-2,4,6-Trinitro-Phenetole (Methyl-[2,4,6-trinitro-3-ethoxy-phenyl] nitramin, 2,4,6-Trinitro-3-methylnitramino-phenol ethyl-ether). $O_2N.N(CH_3).C_6H(NO_2)_3.O.C_2H_5$, mw 331.23, N 21.15%, OB to CO_2 −65.21%, colorless cryst, mp 98–99°. Sol in methanol. Prepn from methyl-(2,3,4,6-tetranitro-phenyl)-nitramin by boiling with et alc. Expln temp is 192–202° (Ref 1). Ignition temp is 202°. Impact sensitivity with a 10kg weight is 16–19cm. Stability test at 90° showed decompn after 2 hours (Refs 1, 2 & 3). Decompn is shown after 20 weeks at 50° (Ref 1)

Refs: 1) Beil **13**, 425 & [218] 2) C.F. van Duin & B.C.R. van Lennep, Rec **39**, 145 (1920) 3) Urbański **3**, 64–65 (1967)

Methyl Nitrate (Methylnitrat or Salpetersäure-methylester in Ger), $CH_3.ONO_2$; mw 77.04, N 18.18%, OB to CO_2 −10.4%; colorless, mobile volatile liquid with odor of chlf; d 1.203g/cc at 25° & 1.21g/cc at 15°; fr p below −20°, bp ca 65°; vap d 2.66g/cc (Air 1.0g/cc); its vapors expl when overheated. V sl sol in w (3.85g at 20°) and miscible with alc or ether; easily gelatinizes collodion cotton. Was first prepd in 1862 by C. Lea by distilling methanol with 63% strong nitric acid in the presence of urea nitrate, but the yield was small (See Ref 1, p 284). Delépine (Ref 2) prepd it, 36% yield, by dissolving methanol in sulfuric acid (d 1.84g/cc) and adding this soln gradually to mixed nitric-sulfuric acid. A.P. Black & F.H. Baber improved Delépine's method and obtd MeN in yields up to 80% (See Ref 4, pp 62–63). A laboratory method of prepn is given in Ref 3, pp 203–04

Desseigne developed in France, after WWII, both batch and continuous methods which are claimed to give yields up to 90% (Ref 8, pp 62–63)

Procedure for Batch Method. Introduce into a 3-neck round-bottom flask of 350ml capacity (provided with an agitator and a cooling ice-water bath), 138g of mixed acid of approx compn: HNO_3 50.6, H_2SO_4 45.7 & H_2O 3.7%. The acid was prepd by mixing with stirring & cooling, calcd amts of concd nitric (94–98%) and sulfuric acids (d 1.84g/cc) After cooling the mixed acid in the flask to below 30°, introduce drop by drop 32g of methanol contg ca 1 g of urea, while stirring and cooling. Continue agitation and cooling until the temp drops to ca 18°. Transfer the mixt to a separatory funnel in which stopcock and glass stopper are carefully greased (to avoid an expln by friction to which MeN is very sensitive). After separating the layers, remove the bottom (acid) layer and discard it. Wash the contents of funnel first with 20ml of iced w and then with 20ml of 2% Na carbonate. Dry MeN with anhyd Na carbonate and transfer to weighing bottle. Desseigne obtd 69g, which is an 89.5% yield

In the continuous process, also developed by Desseigne, a special apparatus is used. A detailed description of the process together with drawings of app are given in Ref 8, pp 63–8. The product prepd by Desseigne boiled at 65.2°, its d was 1.210g/cc at 20° and soly in w 3g in 100g (Ref 8, p 63)

Roig (Ref 9) describes the method of prepn in which MeN is obtd as a 60% soln in methanol. This is done in order to avoid any risk of expln during nitration. Detailed descriptions of both laboratory and semi-plant production are given in Ref 8, p 166. The yield of MeN is 77% in lab practice and 83.7% in semi-plant production (Ref 8, p 164)

Explosive Properties of MeN (Refs 3, 5, 6, 7, 11 & 12)
Brisance by Lead Block Compression Test 132% NG
Decomposition Equations. Accdg to Berthelot, the decomposition of MeN may proceed either as:

$$2CH_3.ONO_2 = CO_2+CO+3H_2O+N_2 \quad (1)$$

or as:

$$2CH_3.ONO_2 = 2CO_2+2H_2O+H_2+N_2 \quad (2)$$

Based on the heat of formation of 39.6 kcal/mole, Berthelot calcd heats of expln at constant volume (C_v) and with H_2O liquid, as: 1609kcal/kg for equation (1) and 1616kcal/kg for equation (2). As the value detd at the same time for NG is 1595kcal/kg, it is apparent that MeN has slightly higher energy content than NG
Detonation Velocity. When detd in glass or metal tubes of small diam (3 to 5mm), the values are low, ranging from 1890 to 2482m/sec, vs 1500m/sec for NG. When detd with a glass tube 20mm diam and 1mm wall thickness, the value is 6600m/sec. Accdg to Naoûm (Ref 3, p 206), values up to 8000m/sec should be obtd in tubes 30–40mm diam. These values are comparable with those for NG (Ref 3, p 145)
FI (Figure of Insensitiveness) – 29% PA (Ref 6)
Ignition & Explosion of MeN by Flame. When MeN in an open dish is brought in contact with a flame, it ignites immediately and burns quietly with a large non-luminous flame. The vapors puff readily on ignition, and on heating them to 150°, they explode. When a small amt of MeN is ignited in a narrow glass vessel with a safety fuse, it sometimes gives a puff accompanied by breaking the glass into large pieces; sometimes a brisant detonation takes place accompanied by pulverizing the glass to a fine powder (Ref 3, pp 205–06)
Impact Sensitiveness, by Kast apparatus with 2kg wt, it explodes at 40cm drop, vs 4cm for NG. Even when mixed with kieselguhr it is less sensitive than NG (Compare with FI)
Initiation Sensitiveness. See Sensitiveness to Initiation
Power, by Ballistic Pendulum 209% PA (Ref 6)
Power, by Trauzl Test. For 10g sample with water tamping, the expansion is 615cc vs 600cc for NG, which gives ca 102.5% NG. When mixed with kieselguhr, or gelatinized with NC, MeN gives about the same values in the lead block as corresponding mixts of NG, namely 320 & 565cc. Blatt (Ref 6) gives a value of 174% PA
Sensitiveness to Flame. See under Ignition and Explosion of MeN by Flame
Sensitiveness to Initiation. MeN is more sensitive than NG. For example, when it is initiated with a No 1 cap, under w tamping, the detonation effectiveness is equal to 88% of that with a No 8 cap, while NG under the same conditions gives only 33% effectiveness
Toxicity and Fire & Explosion Hazards are briefly discussed in Refs 11 & 12
Uses: It can be used as a gelatinizer of collod cotton in commercial expls, but its high volatility is objectionable (Ref 2, p 208). Has been used in some rocket proplnts (Refs 11 & 12)

Method of analysis of MeN is described by Vandoni (Ref 10)

Written by **B.T. FEDOROFF**

Refs: 1) Beil **1**, 284, (141), [273] & {1201}
2) M. Delépine, BullFr [3] **13**, 1044 (1895) & JCS **70** I, 586 (1896) 3) Naoûm, NG (1928), 203–06 4) OrgSynthCollVol **2** (1943), 412 5) Davis (1943), 192–94
6) Blatt, OSRD **2014** (1944) 7) F.P. Bowden et al, PrRoySoc **A188**, 306–07 (1947)
8) G. Desseigne, MP **30**, 59–68 (1948)
9) F. Roig, MP **33**, 159–67 (1951)
10) R. Vandoni, MSCE **36**, 19 (1951)
11) Sax (1957), 902 12) CondChemDict (1961), 745

Methyl Nitrite (Methylnitrit or Saltpetrigsäure methylester in Ger), $CH_3.ONO$; mw 61.04, N 22.95%; colorl gas which liquefies at −12 to −16° and freezes below −19°, d 1.00g/cc at −19°; miscible with alc or ether. Was first prepd in 1854 by A. Strecker by the action of nitric acid on brucine (dimethyloxystrychnine); he also prepd it by the action of nitric acid on methanol in the presence of either Cu or As_2O_3 (See Ref 1, p 284). More recent methods include treating methanol with isoamylnitrite (drop by drop) or by treating methanol with inorganic nitrites in presence of sulfuric acid (Ref 1). Adickes (Ref 2) describes a special apparatus in which is achieved automatically the complete mixing of aq alc-$NaNO_2$ and H_2SO_4

soln in order to avoid the sudden dangerous evoln of gas during nitrification. Its toxicity and fire and expln hazards are given in Ref 3. *Severe explosion risk when shocked or heated!*
Refs: 1) Beil **1**, 284, (141), [273] & {1201} 2) F. Adickes, JPraktChem **161**, 275 (1943) & CA **38**, 65 (1944) 3) Sax (1957), 902 4) CondChemDict (1971), 579-L

METHYLNITROGUANIDINE AND ITS DERIVATIVES

N-Methyl-N′-Nitroguanidine. $H_3C.NHC(:NH).NH.NO_2$, mw 118.10, N 47.44%, OB to CO_2 −67.7%, mp 159–61°, colorl crysts. McKay and Wright (Ref 7) prepd it by heating Nitroguanidine (10.4g), disd in 30g of w containing 12g of potassium hydroxide, to 40°, and adding gradually with stirring, 13.5g of methylamine hydrochloride. This gave a viscous sludge, and some ammonia was evolved. The temp was raised steadily to 59–61° over a period of 8 minutes, and held there for 23 minutes, while stirring the mixt continuously. After the mixt was cooled to 6°, a white ppt of methylnitroguanidine (MeNGu) was filtered off, washed with 30ml of cold w and dried. The crude product weighed about 10g (84.7% yield) and melted at 151–54°. Purification of the product was achieved by crystn, first from hot w (3ml per g) and then from 95% ethanol (8ml per g)

As an expl, it is less powerful and brisant than Picric Acid (Ref 6). It has been used for the prepn of the following expl derivatives:

N-Methyl-N′-Nitroguanidine Nitrate. $H_3C.NH.C(:NH).NH.NO_2.HNO_3$, mw 181.12, N 38.67%, OB to CO_2 −22.1%, mp 87–91°, colorl crysts. McKay and Wright (Ref 7) prepd it by adding 0.355ml of 99% nitric acid, over a period of 4 minutes, to a constantly-stirred suspension of 1g of finely ground MeNGu in 10ml of carbon tetrachloride at −5°. The gummy suspension was cooled to −15° and stirred for an additional 15 minutes. This gave a granular ppt of crude nitrate, which weighed after drying, an average of 1.42g (93% yield). Its mp varied with each preparation. It is an expl which can detonate on impact

N-Methyl-N′-Nitroguanidine Perchlorate. $H_3C.NH.C(:NH).NH.NO_2.HClO_4$, mw 218.61, N 25.60%, OB to CO_2 −11.0%, mp 104°, needle-like rosettes. McKay and Wright (Ref 7) prepd it by dissolving (on heating) 6g of MeNGu in 25ml of 60% perchloric acid, and then cooling the soln to about 0°. This caused the pptn of needle-like rosettes, which were sepd by filtn, washed with 10ml of 30% perchloric acid and then with 10ml of carbon tetrachloride. The yield was 6.67g of salt, mp 98–101°. The pure product, mp 104°, was obtained on recrystn from w. The perchlorate was quite sensitive to impact, and detonated violently

Attempted Nitration of MeNGu: Various methods of nitration were attempted including nitric acid alone, or in combination with 100% perchloric acid, zinc chloride, perboric acid, boron trifluoride, etc. All of them gave MeNGu nitrate, described above, but no nitro derivatives (Ref 7, p 3029)

N-Methyl-N-Nitroso-N′-Nitroguanidine. $H_3C.N(NO).C(:NH).NH.NO_2$, mw 147.10, N 47.61%, OB to CO_2 −38.1%, mp 118° with decompn; yellow crysts; very sl sol in w, sol in methanol, decomps in alkaline soln with gas evolution. McKay and Wright (Ref 7) prepd it by dissolving 10g of MeNGu in 100ml of w to which was added 30ml of nitric acid (d 1.42 g/cc). After cooling the soln in an ice-w bath, 12.4g of Na nitrate disd in 20ml of w, were added over a 5 minute period with stirring. After stirring for an additional 20 minutes, the mixt was filtd, and the cryst crude ppt washed with cold w. The crude dried product weighed 11.25g (90.6% yield) and melted at 112–13° with decompn. It can be purified by crystn from methanol, giving a product with mp 118°, but the yield is very small. Its expl properties have not been examined
Refs: 1) T.L. Davis & A.J. Abrams, ProcAmAcadSci **61**, 437 (1926) 2) T.L. Davis & S.B. Luce, JACS **49**, 2303 (1927) (Alkyl Nitroguanidines) 3) T.L. Davis & R.C. Elderfield, ibid, **55**, 731 (1933) (Alkyl Nitro-

guanidines) 4) T.L. Davis & E.N. Rosenquist, ibid, **59**, 2112 (1937) (Transformations of Nitrosoguanidine, Alkylnitrosoguanidines and N-R, N'-R-Dialkylguanidines) 5) Davis (1943), 386 6) Blatt, OSRD **2014** (1944) 7) A.F. McKay & G.F. Wright, JACS **69**, 3028 (1947)

2-Methyl-2-Nitro-1,3-Propanediol Dinitrate (Nitroisobutylglycol dinitrate). $CH_3.C.NO_2(CH_2ONO_2)_2$, mw 225.14, N 18.67%, OB to CO_2 −24.87%, mp 38°, ignites above 240°. Prepd from the glycol by nitration with mixed acid, with 90% yield. Brisance, crushes 53g sand, equivalent to Tetryl. Q_c is 531.4cal/mole. Impact sensitivity, FI 86% relative to PA, with Bruceton No 5 machine, 50% positive with 5kg weight at 27–46cm, slightly more sensitive than TNT. Power by ballistic mortar is 134–38% TNT, 99.5% blasting gelatin; lead block expansion, 153% PA. Rifle bullet impact in welded cans gave 4/4 high order detonations. Thermal stability at 135°, acid in 15–30 minutes at 82.2°; heat test, 10 minutes at 82.2°. This material and its homologs from other aliphatic nitro compounds and aldehydes have been suggested as substitutes for NG

Refs: 1) Beil – not found 2) F.H. Bergeim, USP 1691955 (1929) & CA **23**, 708 (1929) 3) J.A. Wyler, USP 2195551 (1940) & CA **34**, 5283 (1940) 4) Blatt, OSRD **2014** (1944)

2-Methyl-2-Nitro-1-Propanol (2-Nitro-2-methyl-1-propanol, β-Nitroisobutylalcohol). $(CH_3)_2.C(NO_2).CH_2OH$, mw 119.12, N 11.76%, OB to CO_2 −127.60%, needles or plates from methanol, mp 90–91°, bp 94.5–95.5° at 10mm. Easily sol in ethyl & methyl alcs, eth and w (350p in 100p at 20°). May be prepd by treating 2-nitropropane with formaldehyde in the presence of an alkaline catalyst, such as K bicarbonate (Refs 1, 2, 3 & 4). On nitration, it yields an expl, 2-Methyl-2-Nitro-1-Propanol Nitrate (see below)

2-Methyl-2-Nitro-1-Propanol Nitrate (2-Nitro-2-methyl-1-propanol nitrate). $(CH_3)_2.C(NO_2).CH_2ONO_2$, mw 164.12, N 17.07% (nitrate N 8.54%), OB to CO_2 −68.20%, bp decomps in 5 secs at 200–05° without melting or detonation. Oily liq, insol in w & petr eth; sol in alc, eth, acet, bz & CCl_4 May be prepd by sifting 50g of dry powdered 2-methyl-2-nitro-1-propanol into a mixt of 58.5g of 90.5% HNO_3 and 241.5g of 103.1% H_2SO_4 (oleum), while stirring the mixt and maintaining it at 15°. After the addition, stirring was continued for 1 hour, and the mass was allowed to stand for ¼ hour. As no sepn took place, the mixt was poured over cracked ice. The bulk of the w was decanted and the oil transferred to a separatory funnel, where it was washed with w, Na bicarbonate, and again with w to neutrality to litmus. All the washings were mixed with the spent acid and extrd with eth. After washing the extr with w and evapg the eth, the oil was added to the main product, and it was dried under vacuum

The yield obtained by Aaronson was 34.8g (50.5% of theory), and the product contained 16.99% (theoretical 17.07%) (Ref 5)

Methylnitropropanolnitrate readily gelatinizes collodion cotton and, to a lesser extent, higher-nitrogen NC. Its explosive power is comparable to that of TNT, and about 75% of that of blasting gelatin. It is very insensitive to detonation, and for this reason its sand test value could not be detd

Impact Sensitivity. > 100cm with 2kg weight or less sensitive than TNT

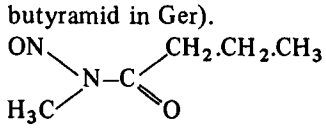
Thermal Stability. Unsatisfactory (about 6 minutes in the 82.2° Heat Test)

Toxicity. Comparable to NG

Uses. No military applications reported

Refs: 1) Beil **1**, 378 2) L. Henry, Bull-SocChim [3], **13**, 1002 (1895) 3) B.M. Vanderbilt & H.B. Hass, IEC **32**, 36 (1940) 4) C.L. Gabriel, IEC **32**, 887 (1940) 5) H. Aaronson, PATR **1125** (1941), pp 1 & 4 and Table III

Methylnitrosobutyramide (Nitroso-methyl-n-butyramid in Ger).



mw 130.15, N 21.53%, OB to CO_2 −159.81%; liq, bp 59–60°/14mm, d 1.0161g/cc at 25/4°, RI 1.4448 at 25°. Prepd by treating ethereal soln of n-methyl butyramide with nitrous anhydride, N_2O_3. Explodes when heated at atm press

Ref: R. Huisgen & J. Reinertshofer, Ann **575**, 215 (1952) & CA **47**, 3813 (1953)

N-Methyl-N'-(2-Nitroxyethyl) Ethylene Dinitramine. See *1-Methyl-N'-(2-Nitroxyethyl)-ethylenedinitramine* in Vol **5**, D1377-R

N-Methyl-N-(2-Nitroxy propyl) Nitramine. (Me_2NENA; N-(2-Nitroxypropyl) methyl nitramine. $(O_2N)N(CH_3).(CH_2CH(ONO_2).CH_3$, mw 179.16, N 23.46%, OB to CO_2 −66.80%, pale yellow oil, mp 22–23°, d 1.320g/cc at 25/4°, RI 1.478 at 25°. Prepn from 2-hydroxypropylamine after nitration with 98% nitric acid at 10° by reaction of the amine-nitric acid mixt with acetic anhydride & acetyl chloride at 35°. Reaction mixt poured on ice. Yield is 74%. No expl properties listed

Refs: 1) Beil – not found 2) Blomquist, OSRD **4134**, 45 & 119 (1944)

3-Methylol-2-Butanol (2-Methyl-1,3-butanediol or α, γ-Dioxy-β-methylbutane). $CH_3.CH(OH).CH(CH_2OH).CH_3$, mw 104.15, viscous oil, bp 200° & 98–99° at 9mm. Sol in w, v sol in alc and eth. Can be prepd either by reduction of the corresponding aldehyde, 2-methylbutanol(3)-al-(1) with Al amalgam (Ref 1), or by electrolytic reduction in 10% sulfuric acid of the corresponding ketone alc. In the latter case, methyl-2-butanone-3-ol-(1), obtained by the condensation of methylethylketone with formaldehyde, can be used. On nitration, it yields an expl dinitrate

Refs: 1) Beil **1**, 482, (250) 2) L.P. Kyriakides, JACS **36**, 535 (1914)

3-Methylol-2-Butanol Dinitrate. $CH_3.CH(ONO_2).CH(CH_2ONO_2).CH_3$, mw 194.15, N 14.43%, OB to CO_2 −74.17%, oily liq. Can be prepd in about 62% yield by gradually adding 3-methylol-2-butanol to a mixed acid containing approx HNO_3 25.3, H_2SO_4 59.6 & w 15.1%. Temp of nitration, 5–10°; total nitration time about 30 minutes; ratio of HNO_3 to methylolbutanol, 1:5

The resulting compound was an expl, very volatile and very unstable (2 minutes in the 82.2° Abel test, compared with 10–15 minutes for NG). The impact sensitivity (BurMines, 2kg weight) was 100cm+. Because of its poor stability, it was not recommended for use as a military expl

Ref: K.S. Warren, PATR **1103** (1941), p 2 and Table II

3-Methylol-2-Butanone (β-Methyl-γ-ketobutanol). $CH_3.CO.CH(CH_2OH).CH_3$, mw 102.13, colorl liq, mp does not freeze at −80°, bp 90° at 17mm, d 0.99g/cc, RI 1.4320, sol in w. Can be prepd by condensation of methyl ethyl ketone with 1 mole of formaldehyde (Refs 2 & 3). On nitration, it yields an expl

3-Methylol-2-Butanone Mononitrate (β-Methyl-γ-ketobutanol mononitrate). $CH_3.CO.CH(CH_2ONO_2).CH_3$, mw 147.13, N 9.52% (theory), 8.20% found; OB to CO_2 -114.18%; liq. Prepd by nitrating methylolbutanone with mixed acid (HNO_3 25.3, H_2SO_4 59.6 & w 15.1%). The total nitration time was 1 hour at about −5°, and the yield was 54% of product contg 8.20% N. Although the product was carefully purified to be acid-free, it underwent decompn when allowed to stand for several days at RT (Ref 4)

Refs: 1) Beil – not found 2) G.T. Morgan & E.L. Holms, JCS **1932**, 2670 3) G.T. Morgan et al, Chem&Ind **57**, 887 (1938) 4) K.S. Warren, PATR **1103** (1941), p 2 and Table I

Methyl Pentanitrophenyl Nitramine (N-Nitro-N-methyl-2,3,4,5,6-pentanitroaniline, N-Methyl-N,2,3,4,5,6-hexanitroaniline). $(O_2N)_5C_6.N(NO_2).CH_3$, mw 377.17, N 26.00%, OB to CO_2 −14.85%, colorless cryst, mp 132° (evolves gas), detonates upon heating. Sol in chlf. Prepn by nitration of a mixt of 3,5-dinitro-N-methylaniline & 3,5-dinitro-N,N-dimethylaniline. It is unstable and decomposes readily above

its mp or when boiled in w
Refs: 1) Beil **12**, 772 2) J.J. Blanksma, Rec **21**, 254 (1902) 3) Urbański **3** (1967), 65

2-METHYL-1,3-PROPANEDIOL AND ITS DERIVATIVES

2-Methyl-1,3-Propanediol (β-Methyltrimethylene-glycol). $CH_3.CH(CH_2OH)_2$; mw 90.12; liq, bp 214–214.5° at 771mm and 110–111° at 14.5mm, d 1.0297g/cc at 0/0°. Can be prepd by heating, on a w bath, methyltrimethylene-bromide [$CH_2Br.CH(CH_3).CH_2Br$] with AcOH, and saponifying the resulting diacetate with aq Ba hydroxide. It forms nitro derivatives
Refs: 1) Beil **1**, 480 & [547] 2) A. Faworsky & N. Sokownir, Ann **354**, 366 (1907)

2-Methylnitropropanediol (2-Nitro-2-methyl-1,3-propanediol). $CH_3.C(NO_2)(CH_2OH)_2$; mw 135.12, N 10.37%; monocl crysts; mp 149–51°; bp decompn. Sol in w (80p in 100p at 20°) and in alc. Can be prepd by treating a mixt of nitroethane and formaldehyde in w with a small amt of K bicarbonate as catalyst. On nitration, it yields an expl, 2-Methyl-2-nitro-1,3-propanediol dinitrate (see below)
Refs: 1) Beil **1**, 480 & [547] 2) L. Henry, BullSocChim(Fr) [3], **13**, 1002 (1895)
3) J.A. Wyler, USP 2195551 (1940)
4) B.M. Vanderbilt & H.B. Hass, IEC **32**, 36 (1940) 5) C.L. Gabriel, IEC **32**, 891 (1940)
6) H. Aaronson, "Study of Explosives Derived From Nitroparaffins", PATR **1125** (1941), pp 2 & 4

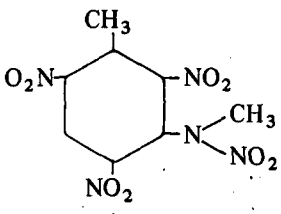
2-Methyl-2-Nitro-1,3-Propanediol Dinitrate (Nitromethylpropanediol dinitrate). $CH_3.C(NO_2).(CH_2ONO_2)_2$; mw 225.12, N 18.67%; OB to CO_2 –24.9%; waxy crysts; mp 37.4°; bp decompn at 200° within 5secs. Sl sol in w, sol in alc, acet, eth and petr eth. Prepd by gradually sifting 50g of dry, ground 2-methyl-nitropropanediol into a mixt of 300g of 4:6 HNO_3–H_2SO_4 with mechanical agitation at a temp of about 15°. After the addition, the temp was allowed to rise to 20° and kept there for ½ hour with agitation. After allowing the mixt to stand for 1 hour, it was transferred to a separatory funnel and the spent acid drawn off. The residual oil was washed twice with warm aq Na sulfite soln, and then with warm w until neutral to litmus. After drying under vacuum at 50°, the oil was chilled until it became milky in appearance and waxy crysts sepd (Aaronson, Ref 5, obtained a 76% yield). An addnl amt of material was obtained when a mixt of the washings and the spent acid was extrd with eth. The extr was washed with w, the eth evapd and the residue, after drying, gave an addnl yield of 16.2% for a total of 92.2% (Ref 5, p 7)

Methylnitropropanediol dinitrate is nearly as powerful an expl as TNT, but more brisant, comparable to Tetryl. It was prepd during WWII on a lab scale in Ger, and examined from the point of view of its gelatinizing properties on NC. Such properties were found to be rather poor, although its volatility, stability, etc were satisfactory (Ref 4)

The compound was also prepd and examined in the USA by Picatinny Arsenal, Hercules Powder Co and others, and was found to have the following characteristics:
Brisance. 53g of sand crushed in Sand Bomb Test vs 48g for TNT (110.5% of TNT)
Explosion Temperature. Ignited above 240°
Heat of Combustion. Q_v^c 531.4kcal/mole
Impact Sensitivity: 11cm with BurMines app with 2kg wt (less sensitive than NG)
Power. About 135% of TNT in BalMort Test; about 160% of TNT in Trauzl Lead Block Test
Rifle Bullet Test. High order detonations
Thermal Stability. 9 to 30 minutes in 82.2° KI test, comparable to NG; and in 15–30 minutes in 135° Heat Test; no explosion in 300 minutes
Toxicity. Similar to NG
Uses. This substance, as well as other aliphatic compds such as nitroisobutylglycol dinitrate, comprising a branched chain hydrocarbon to which one nitro and two nitrate groups are attached, has been proposed by Bergeim (Ref 2) for use in commercial expls as a partial substitute for NG
Refs: 1) Beil – not found 2) F.H. Bergeim, USP 1691955 (1928) & CA **23**, 708 (1929)
3) J. Wyler, USP 2195551 (1940) & CA **34**, 5823 (1940) 4) O.W. Stickland, "General Summary of Explosive Plants", US Office of Tech Services, PB Report No 925 (1945), p 15

5) H. Aaronson, "Study of Explosives Derived From Nitroparaffins", PATR **1125** (1941), p 4 & Table II

Methyl Tetryl or 2,4,6-Trinitrotolyl-3-Methyl-nitramine. (2,4,6-trinitro-3-methyl-nitramino-toluene or methyl-[2,4,6- trinitro-3-methyl-phenyl]-nitramine). $CH_3.C_6H(NO_2)_3.N(CH_3)NO_2$, mw 301.08, N 23.25%, OB to CO_2 −61.1%, mp 101–02°, bp expl. Colorl to yel crysts from alc; sl sol in hot w, sol in bz, acet, chlf & hot alc; sl sol in ligroin. Was first prepd by Romburgh (Ref 2) in 1884 by nitration of dimethyl-m-toluidine with mixed nitric-sulfuric acid. Blanksma (Ref 3) prepd it in 1902 by nitration of 2,4,6-trinitromethyl-aminotoluene and detd its structure



Davis (Ref 4) suggested preparing it from beta- and gamma-TNT's removed from crude TNT on purification with Na sulfite soln. The bulk of these impurities consist of Na sulfonates of DNT's, and, if treated with methylamine, the following reaction occurs:

The resulting N-methyldinitrotoluidines, when further nitrated, yield methyl Tetryl. Methyl Tetryl is a less powerful expl than Tetryl, and has not been used commercially

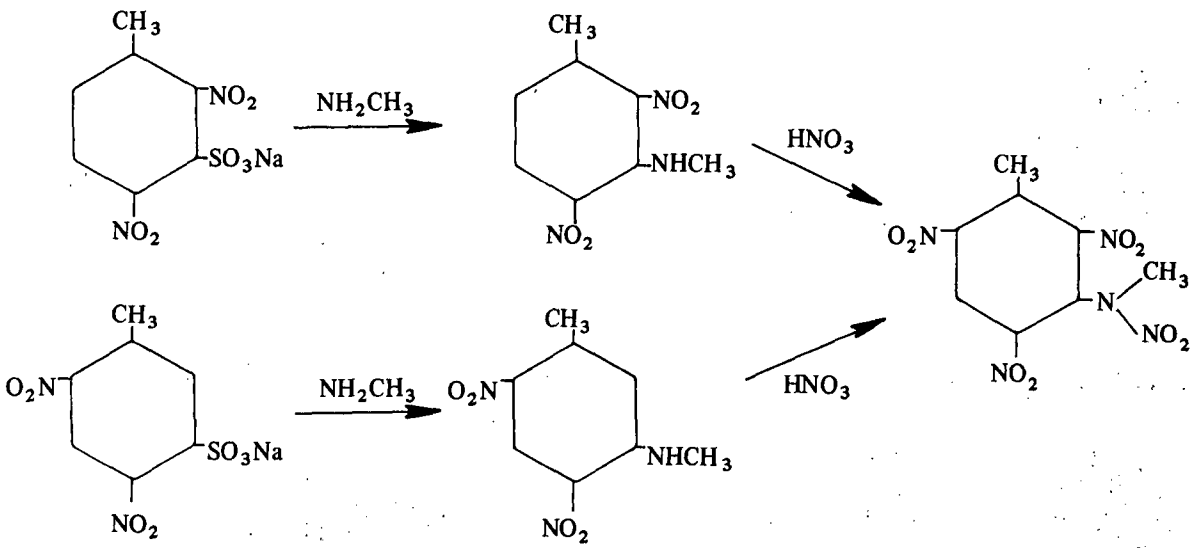
Refs: 1) Beil **12**, 880 & [482] 2) P. van Romburgh, Rec **3**, 414 (1884) 3) J.J. Blanksma, Rec**21** , 332 (1902) 4) Davis (1943), 147 5) Blatt, OSRD**2014** (1944) 6) Urbański **1** (1964), 389

Note: See also under 2,4,6-Trinitro-3-methyl-nitraminotoluene in Vol **5**, D1375-L & R

METHYL TRIMETHYLOLMETHANE AND DERIVATIVES

Methyl Trimethylol Methane (Trimethylol-methyl methane, Pentaglycerol or Trimethylol ethane). $CH_3.C(CH_2OH)_3$, mw 120.17, OB to CO_2 −173.09%, white cryst, mp 199°, bp 135–37° at 15mm, sol in dioxane, w & alc (Refs 1, 2 & 4). Prepn from propionaldehyde & formalin condensation in cold aq soln using lime; 62% yield (Refs 2 & 3)

Refs: 1) Beil **1**, 520 & {2348} 2) Blatt, OSRD **2014** (1944) 3) Blomquist, OSRD **4134** (1944) 4) Sax (1968), 1199



Methyl Trimethylnitramine Methane (Pentaglyceryl Trinitramine, PGX).
$CH_3.C(CH_2NHNO_2)_3$, mw 252.23, N 33.33%, OB to CO_2 −63.43%, white cryst, mp 130–31° (decomps); sol in ethyl acetate & nitromethane. Prepn from pentaglyceryltriurethane by nitration with a mixt of acetic anhydride & 98% nitric acid at 0–5°. Expln temp is 335° (ignition). Internation heat test at 75° shows 0.0% loss. Power using ballistic mortar is 111.8 (TNT=100). Sensitivity to initiation is 30cm at the 50% point. Stability at 135°; ignition in 10mins. Vacuum stability at 100° is 12cc in 25 hours
Refs: 1) Beil – not found 2) Blomquist, OSRD **4134** (1944)

Methyl Trimethylnitramine Methane, Silver Salt (Silver Pentaglyceryl Trinitramine).
$CH_3.C(CH_2NAgNO_2)_3$, mw 572.81, N 14.68%. OB to CO_2 −23.74%, sol in aq ammonia. Prepn from pentaglyceryl trinitrourethane in ammoniacal soln upon addition of Ag nitrate in acetic acid. The Ag salt detonates when heated
Refs: 1) Beil – not found 2) Blomquist, OSRD **4134** (1944)

Methyl Trimethylol Methane Trinitrate (Trimethylol methyl methane trinitrate, 1,1,1-Trimethylolethane Trinitrate, Nitropentaglycerin, or Metriol [trinitrate]).
$CH_3.C(CH_2ONO_2)_3$, mw 255.17, N 16.47%, OB to CO_2 −34.50%, colorless, oily liq, mp 9°, fr p 7.5°, d 1.46g/cc at 22/4°, RI 1.4760 at 22° (Refs 2 & 3). Prepn from methyl trimethylol methane by nitration using mixed acid (HNO_3/H_2SO_4) at 20° followed by pouring on cracked ice; yield is 81% (Refs 2 & 3). Q_c^v is 674cal/mole. Heat test at 135° is acid in 35 min; no expln in 300 min (Ref 2). Hygroscopicity at 25° shows a gain of 0.07% weight at 90% relative humidity and 0.14% at 100% RH. Impact sensitivity: FI of 74% relative to PA, positive at 16.7cm vs 35–45cm for TNT; 1kg weight negative at 66cm (Ref 2). Power as shown by ballistic mortar, is 136% of TNT, and by lead block expansion is 139% of PA. Stability at high temp is indicated by ignition at 235° with expln at 360°. Vacuum stability at 100° is 11.3cm/5g in 48 hours (Ref 2). See also under Metriol and its Derivatives in this Vol
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944) 3) Blomquist, OSRD **4134** (1944)

1,1,1-Trimethylol-2-Chlorethane Trinitrate (Pentaerythritol monochlorohydrin trinitrate).
$Cl.CH_2.C(CH_2ONO_2)_3$, mw 289.61, N 14.51%, OB to CO_2 −27.62%, mp 43–50° (Ref 3) Prepn from pentaerythritol monochlorohydrin by nitration which produces a mixt of the di- & tri-nitrate (Ref 2). Impact sensitivity using a 2kg wt at 170cm shows no explns vs 35cm for PA (Ref 3). Power from lead block expansion is 305cc vs 285cc for TNT (Ref 3)
Refs: 1) Beil – not found 2) Westfälisch-Anhalt, SS-A-G, GerP 638432 (Nov 14, 1936) & CA **31**, 1212 (1937) 3) Blatt, OSRD **2014** (1944)

2-Methyl-2,4,4-Trimethylolpentane-1,3,5-Triole Hexanitrate (Ennahexite hexanitrate).
$(O_2NOCH_2)_3CCHONO_2C(CH_2ONO_2)_2CH_3$, mw 494.29, N 17.01%, OB to CO_2 −22.70%, mp 74–75°. Prepn from nitration of the condensation product formed with methyl ethyl ketone and formaldehyde. Impact sensitivity is 50% positive using a 2 pound wt dropped 18 inches
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

2-Methyl-2,3,3-Trinitrobutane.
$(CH_3)_2C(NO_2).C(NO_2)_2.CH_3$, mw 207.17, N 20.29%, OB to CO_2 −65.65%, white prisms, mp 190°, explodes. Readily sol in organic solvents. Prepn by gently refluxing bis-trimethylethylenenitrosochloride with concd nitric acid (d 1.42g/cc) (Refs 1 & 3). Q_c^v 700.46kcal/mole (Ref 4). Impact sensitivity is less than TNT (Ref 2). Power by ballistic mortar is 106% of TNT (Ref 2)
Refs: 1) Beil **1**, 141 2) Anon, BurMines, High Expls Res Div, TR No **25** (1942) 3) Blatt, OSRD **2014** (1944) 4) A.J. Miller & H. Hunt, JPhysChem **49**, 20–1 (1945) & CA **39**, 1352 (1945)

N-Methyl-2,4,6-Trinitro-N-Nitrosoaniline. See under Tetryl

3-Methyl-2,2,3-Trinitro-Pentane (2,2,3-Trinitro-3-methylpentane). $CH_3.C(NO_2)_2.C(NO_2)(CH_3).CH_2.CH_3$, mw 221.20, N 19.00%, OB to CO_2 −83.18%, cryst needles, mp 85° (Ref 1). Prepn from 3-methyl-2-pentene reacted with ethyl nitrite & HCl to yield 3-chloro-2-nitrosopentane, which is converted to the trinitro compd with nitric acid (Ref 3). Power by ballistic mortar is 86% of TNT. Sensitivity is comparable with TNT (Ref 2)

Refs: 1) Beil **1**, 150 2) Anon, BurMines, High Expls Res Div TR No **25** (1942) 3) Blatt, OSRD **2014** (1944)

Methyl Violet Tests (Storage, 120° or 134.5° Heat Tests). Proplnt stability tests using special 0.1 or 1.0N methyl violet paper. See under German 135° Stability Test in Vol **6**, G70-L to G71-L, and Methyl Violet Paper Test (below)

Prepn of 0.1N Paper. Weigh into a casserole, 0.2500g of methyl-p-rosaniline (basic compd). Add an excess of glacial acet ac, and evap to dryness on a steam bath. This will yield about 0.3g of rosaniline acetate. Rinse into a 1ℓ volumetric flask, using a total of 300ml of distd w. Add exactly 40ml of c.p. glycerin and 0.1680g of methyl violet NE (duPont Co), or methyl violet 2B (National Aniline & Chem Co), or crystal violet. Make up to 1ℓ with 95% alc and mix well. Transfer a small quantity of the soln into a rectangular glass or stainless steel trough (about 16″x6″x10″ deep), which is located in a room free of acid fumes. Raise one end of the tray so that it will be in a tilted position. Cut Schleicher & Schull filter paper No 597 sheets, 58x58cm, into four parts. Hold one edge of the paper by means of two clips, dip it into the trough up to the upper edge, and then draw the paper slowly (in about 5 seconds) thru the soln and up and over the side of the trough in order to remove the excess liq from the paper. Hold the paper in a vertical position over the tray until the liq starts to drip, then grasp the bottom edge by use of two clips. Wave the strip gently to and fro for about 30 seconds in order to evap the alc. Fasten the strips with metal push pins to wooden blocks and allow to dry overnight in a dark room, free from acid fumes. Trim the edges and cut the paper into strips 20x70cm or 20x140cm and store in a well-stoppered bottle

After seasoning for about a week, compare the new paper with standard 0.1N methyl violet paper by dropping strips of each into a container with unstable proplnt (one which will give a surveillance test of about 30 days at 65.5°). Both papers should show the same degree of discoloration after a given time period

Prepn of 1.0N Paper. Weigh out 2.5g of basic p-rosaniline and evap to dryness (as above) with an excess of glacial acet ac. Rinse into a 1ℓ volumetric flask, using a total of 300ml of distd w. Add 40ml of c.p. glycerin, 1.68g of methyl violet, and make up to 1ℓ with 95% alc. Dip and dry the paper in the same manner as the 0.1N prepn. After the paper has been seasoned for about a week, trim the edges and cut into 20x70cm strips. Compare with standard 1.0N methyl violet paper in the German 134.5° Stability Test (see Vol **6**, G70-L) using both pyrocellulose and proplnt. In a 30 minute test the results obtained should not differ by more than ±1 minute using different lots of paper. On being exposed to nitric oxide fumes, these papers slowly turn green, followed by a salmon pink coloration

Methyl Violet Paper Test (Field Test for Proplnt Powders). This method of testing proplnts using 0.1N methyl violet paper directly in the containers in which the powder is stored, was developed at Picatinny Arsenal in 1928–29 (Refs 1 & 2), and was adopted by the Ordnance Dept to replace the "Observation Test" about 1931

[*Note:* The "Observation Test" was intended to detect the initial decompn of proplnt, and was conducted at all depots and posts where powder was stored. A 6oz sample of each lot of powder with a strip of methyl violet test paper was placed in a glass-stoppered bottle, with the paper not in contact with the powder. The test was conducted in the magazine in which the proplnt under test was stored. Bleaching of the test paper was taken as an indication that the powder had started to de-

teriorate. The test was run continuously and new samples were selected each year. Test papers which lost color gradually could remain in their bottles until they were completely bleached, but papers which showed a marked color change were replaced every two months. A report was made of any evidence of deterioration, and special stability tests were run on the lot in question (Ref 3)]

The Methyl Violet Paper Test was originally developed for the purpose of testing the stability of pyro powders in bulk storage, and was later extended to other powders. The test is particularly useful in cases where the propInt is hygroscopic (such as pyro) and decomps more rapidly, at the same temp, in the presence of moisture than when dry. If, in testing one lot of propInt stored in several containers, some of them show instability, the indication is that such containers have developed leaks and that moisture has penetrated to the powder

Although moisture affects nonhygroscopic single-base propInts very little, and leaky containers do not have the same significance with respect to hazard in storage as in the case of pyro powders, the Methyl Violet Paper Test is considered useful because the paper will undergo a color change in the event the propInt becomes unstable

Test Procedure. Suspend in each bulk powder or propInt charge container, in the atm above the powder, one strip of ¾"x5½" 0.1N methyl violet paper. To do this, clamp one end of the paper between the lid and the container. In handling the strips of test paper, great care should be taken to insure that they are not contaminated with dirt or perspiration from the hands. Examine the cover gasket, and if it is defective, replace it with a new one. Allow the containers to remain in the storage magazine at the desired temp (if the powder is intended for use in tropical countries, a temp of 50° is suitable), and examine the test paper periodically. The methyl violet test paper color is categorized as Class 1 (original violet color), Class 2 (any intermediate color between the original violet and white or pale yellow) or Class 3 (white, or beyond to a pale yellow, in which case the paper becomes brittle)

If the propInt is **single-base**, and there is no reason to suspect that it is unstable, the paper should not change color after exposure for one year. In this case, at the end of one year, the strip of test paper is removed, replaced by a new one, and the test continued

Where definite loss of color by bleaching is noted, the content and container should be inspected to determine the cause. If correctable, such as a faulty gasket, broken container, etc, the gasket is changed or the powder is transferred to another container. A new strip of test paper is inserted and the propInt replaced in storage with the container definitely marked to insure reinspection at the end of one year. If the defect cannot be corrected, as in the case of deteriorated propInt, the propInt is destroyed or otherwise disposed of

In cases where a lot of propInt has successfully passed the one-year exposure to methyl violet paper, only a 3% inspection of the exposed test strips need to be made thereafter until such inspection indicates progressive deterioration of the propInt or other nonstandard condition, at which time 100% inspection and test of the lot under suspicion will be resumed

It is considered desirable that succeeding annual inspections include at least 1/3 of the containers included in the original 3% inspection as outlined above. In this manner, such containers may be considered as a basic comparative control with reference to the balance of the lot under test

If the propInt is **double-base**, it has been observed that even the most stable propInts bleach methyl violet paper in much shorter periods than one year. Investigations conducted by P.F. Macy at Picatinny Arsenal (Ref 4) showed that diphenylamine-stabilized double-base propInts in service storage at about 30°, may be considered of satisfactory stability if they do not cause complete bleaching of 0.1N methyl violet paper in one month or less. Such propInts always show satisfactory stability when subjected to the 65.5° Surveillance Test. It was observed at the same time, that double-base propInts which had deteriorated, but were not yet hazardous, took from 11 to 24 days to bleach methyl violet paper at 30°

Later tests at Picatinny Arsenal revealed that methyl violet paper very often faded in shorter time periods than described above, even for perfectly stable powders, as detd by the 65.5°

Surveillance Test and the 134.5° Heat Test. This applied particularly to double-base proplnts, although some single-base proplnts also gave erratic results. For these reasons, work was undertaken at Picatinny Arsenal to find an indicator that would be more reliable than methyl violet. About 60 commercially available dyes were examined by S. Helf (Ref 5) in exptl indicator paper tests, of which only three were found to be superior to methyl violet: benzoazurine, trypan red and ethyl violet. Laboratory and surveillance testing showed that papers prepd with a 0.1% soln of benzoazurine did not change in color after one year when used with stable double-base proplnt, while methyl violet paper was bleached in nearly every case. The other two indicators mentioned above, trypan red and ethyl violet, were not as satisfactory as benzoazurine, although they were better than methyl violet. On the other hand, when paper strips with benzoazurine, trypan red or ethyl violet were exposed to unstable double-base proplnt, or to nitrogen oxide fumes prepd in the lab, all of the papers either bleached or faded, as did the methyl violet paper

Following are methods of prepn as well as the original colors and changes of coloration of the indicator papers:

0.1% Benzoazurine Paper. Dye soln prepd by dissolving 2g of the product, supplied by Hartman-Leddon Co, in 1900ml of w and 100ml of glycerin; Bluish-violet → Light violet → Bleached

0.1% Trypan Red Paper. Prepd as above from product supplied by the Allied Chemical & Dye Corp; Rose-red → Light violet → Bleached

0.1% Ethyl Violet Paper. Prepd as above from product supplied by National Aniline & Dye Co; Medium violet → Blue → Bleached

As of this date the use of the new test papers has not been standardized

Written by **S. M. KAYE**

Refs: 1) W.T. Ingraham, PATR **R40** (1928) 2) Ibid, PATR **R57** (1929) 3) Hayes (1938), 30 4) P.F. Macy, "Development of 0.1N Methyl Violet Paper Test for Double-Base Powders", PATR **1652** (1947) 5) S. Helf, "Development of an Indicator Test Paper for Detecting Stability of Double-Base Propellants", PATR **1782** (1950)

METRIOL AND ITS DERIVATIVES

Metriol (Pentaglycerol, 2-(Hydroxymethyl)-2-methyl-1,3-propanediol, Methyltrimethylolmethane). $H_3C.C(CH_2OH)_3$; mw 120.15; white needles from abs alc; mp 199° (sublimes without decompn). Was first prepd by Hosaeus (Ref 2) by condensing formaldehyde and propionic aldehyde in cold aq soln in the presence of lime. Metriol is v sol in w, alc and acet ac; is insol in eth. It may be nitrated to an expl trinitrate, and acetylated to a nonexpl triacetate

Refs: 1) Beil **1**, 520 2) H. Hosaeus, Ann **276**, 76 (1893)

Metriol Trinitrate (MTN,1,1,1-Trimethylolethane trinitrate, Nitropentaglycerin, Metriolo in Italian). $H_3C.C(CH_2.ONO_2)_3$; mw 255.15, N 16.47%, OB to CO_2 −34.5%; oily, slightly turbid liq, mp −3°, bp decompn beginning at 182°, d 1.47g/cc at 22°, RI 1.4752 at 25°

According to Italian sources, it was first prepd and patented by the Bombrini-Parodi-Delfino Co of Italy under the name "Metriolo". A Ger patent of 1927 (Ref 1) also describes the prepn and gives some properties. It states that the trinitrate is a viscous expl oil which remains liq at −15°, is more stable than NG, and can be worked up into powdered or gelantinous products in the same way as NG. The compound was also known in France before WWII under the name "Nitropentaglycerin" and Burlot and Thomas (Ref 2) detd its heat of combustion. The Germans learned about "Metriolo" before WWII, and, recognizing its merits as a flash and erosion-reducing agent, started to manuf it. The method employed by I.G. Farbenindustries AG was as follows (Ref 6):

In the pilot plant procedure, 50kg of finely powdered metriol was fed thru an endless screw (dosierschnecke) to a nitrator provided with cooling coils and an agitator, contg 175kg of mixed acid (65/35 nitric-sulfuric). The nitration time was about 20 minutes at 20°. The mass was allowed to settle for 15 minutes, and the oil separated from the spent acid in the same manner as in the manuf of NG. The sepd oil was washed, first with w at 40°, then with aq soda soln, also at 40°, and finally with w. The yield was about 100kg of oil contg 16.32 to 16.36% N. In Italy, yields as high as

93% of theoretical were claimed

On a lab scale, metriol is nitrated by carefully mixing it with 3.5p of 65/35 nitric-sulfuric acid maintained at 20°, stirring for 30 minutes, cooling to 5°, and pouring the reaction mixt on ice. It is extrd with eth, w-washed, and adjusted to pH 7 by shaking with a Na bicarbonate soln and again w-washed three times. It is then dried with Ca chloride, filtered, and freed of eth by bubbling with dry air until minimal rate of loss in weight is attained. The yield is 88% of the theoretical, and the product has a nitrate-N content of 16.35% (calcd 16.47%). The RI at 25° is 1.4752 (Ref 10)

MTN is practically insol in w (<0.015g/100g at 25° and <0.015g/100g at 60°); sol in alc and many other organic solvents

It is a powerful expl, as sensitive to impact as NG (BurMines drop test with 2kg wt, 4cm). Its Abel Test stability is about 20 minutes at 82°. MTN alone does not gelatinize NC unless the temp is raised to 110°, which would be dangerous, but if mixed with only 8% of the triacetate, it gelatinizes the NC at 80°

Physical and chemical properties of MTN, detd primarily at Picatinny Arsenal, are as follows:

Brisance (Sand Test). 43.7g vs 48.0g of TNT, or 91% or TNT

Explosion Temperature. 5 secs at 235°

Friction Pendulum Test. Explodes with steel and fiber shoes

Heat of Combustion. 2642cal/g at C_v and water liq, or 674kcal/mole

Heat of Formation. 422cal/g at C_v and 446 cal/g at C_p (Ref 9)

Hydrolysis, % Acid. 10 days at 22°, 0.018; 5 days at 60°, 0.115

Hygroscopicity, %. At 25°, gains 0.07 at 90% RH and 0.14% at 100% RH

Impact Sensitivity. BurMines app, 2kg wt, 4cm; PicArsn app, 20"

Power. Trauzl Test, 140% of TNT; Ballistic Mortar, 136% of TNT

Stability. In 100° Heat Test loses 2.5% wt in first 48 hours and 1.8% in second 48 hours; no expl in 100 hours. In 100° Vacuum Stability Test, evolves 1.9cc of gas per g in 40 hours; not considered very satisfactory

Volatility. At 60°, loses 24mgs/cm^2 in 1 hour

MTN was used as a flash and erosion reducing additive in proplnts (Refs 7 & 8), and as an ingredient of commercial expls

Refs: See under Metriol Triacetate (below)

Metriol Triacetate (MTA, Acetometriolo in Italian). $H_3C.C(CH_2.OO.CCH_3)_3$, mw 246.25. Was prepd by Bombrini-Parodi-Delfino Co in Italy, and then by I.G. Farbenindustrie AG in Ger by azeotropic distn of acet ac and methyltrimethylolmethane in benz (Ref 2, p 4)

The Germans found it to be a good gelatinizer for NC, but possessing no stabilizing action. The Italians found that the addition of as little as 8% MTA to Metriol Trinitrate (MTN) improved the gelatinizing properties of the latter (see under Metriol Trinitrate). Its Q_f^v is 1347cal/g, and Q_f^p is 1376cal/g (Ref 9)

The following proplnts contg both MTN and MTA were manufd in Italy (Ref 3, p 7):

M4; NC 55.0, MTN 40.5, MTA 2.0 & Centralite 2.5%

M6; NC 57.5, MTN 36.0, MTA 4.5 & Centralite 2.0%

M8; NC 59.0, MTN 33.0, MTA 5.5 & Centralite 2.5%

M10; NC 59.0, MTN 29.5, MTA 7.0, Centralite 3.5 & vaseline 1.0%

Refs: 1) E. von Herz, GerP 474173 (1927) & CA **23**, 3346 (1929) 2) E. Burlot & M. Thomas, MP **29**, 262 (1939) 3) D. Dinelli & G. Piccardo, AnnChimApplicata **29**, 523–33 (1939) & CA **34**, 6075 (1940) (Methods of analysis of proplnts contg NC, MTN & MTA, with or without Centralite) 4) A. Izzo, ChimIndAgrBiol **16**, 155–9 (1940) & CA **34**, 4905 (1940) (Properties of products of nitration of trimethanolmethylmethane from the view of their utilization in the production of expls used for military and industrial purposes) 5) Blatt, OSRD **2014** (1944) 6) O.W. Strickland, "General Summary of Explosive Plants", US Office of Technical Service, PB No 925 (1945), pp 15 & 61 7) P.F. Macy, "Basic Research Leading to the Development of Ideal Propellants. Explosive Plasticizers for Nitrocellulose", PATR **1616** (1946) 8) V. Lindner, "Foreign Propellants. Evaluation of Some German and Japanese Rocket Propellants Used in World War II", PATR **1817** (1951) 9) P. Tavernier, MP **38**, 302 & 328 (1956)

10) Anon, EngrDesHndbk, "Explosives Series. Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 206–08

Mettegang Recorder. A device, designed by Mettegang in 1904, for measuring the vel of deton of expls with an accuracy of ±10 to 15 meters per second. The apparatus consists essentially of a strong, well-turned and balanced, heavy cylinder of steel which is rotated at a high but exactly known vel. The vel of its smoked surface relative to a Pt point which almost touches it may be as much as 100m/s. The expl to be tested is loaded into a cylindrical steel cartridge from 1 to 4m in length. At a known distance apart, two thin copper wires are passed thru the expl at right angles to the axis of the cartridge. If the expl has been cast, the wires are bound tightly to its surface. Each of the wires is part of a closed circuit thru an inductance, so arranged that, when the circuit is broken, a spark passes between the Pt point and the steel drum of the chronograph. The spark makes a mark upon the smoked surface. When the expl is fired by means of a detonator at one end of the cartridge, first one and then the other of the two wires is broken by the detonating expl, and two marks are made on the rotating drum. The distance between these marks is measured with a micrometer microscope with a vernier reading to 0.01mm, making it possible to det the time interval to within $1x10^{-7}$ second when the drum vel is 100m/s. The time duration which corresponds to the movement of the surface of the rotating drum thru this distance is calcd, and this is the time which was required for the deton of the column of known length of expl which lay between the two wires. From this, the vel of deton in m/s is computed

Refs: 1) H. Mettegang, BerichteInternKongf-AngewChem, Berlin **2**, 327 (1904) 2) H. Kast, SS **8**, 90 (1913) 3) Marshall **2** (1917), 477 4) Colver (1918), 622 5) Barnett (1919), 186–7 6) H. Kast & H. Selle, SS **23**, 217 (1928) 7) C.E. Munroe & J.E. Tiffany, "Physical Testing of Explosives at the Bureau of Mines Explosives Experiment Station, Bruceton, Pa", US Bureau of Mines Bull 346 (1931), 60–63 & 126–133 8) Stettbacher, **1** (1933) 54–6 9) Davis (1943), 16 10) A. Pérez Ara (1945), 95–7

M.G.C. Abbreviation for "Military Gun Cotton", which is NC between about 13.0–13.5 N content. It is used in various proplnts

Mica. A class of silicates of a wide variety of compns, but consisting essentially of silicates of Al (sometimes partly replaced by Fe, Cr, etc) and an alkali, such as K, Na or Li. All characteristically cleave into thin sheets, which are flexible and elastic. Occurs naturally thruout the world. In its powd form, it has been used in pyrotechnic compns (Ref 1), as well as in Dynamite

Refs: 1) Davis (1943), 95 2) CondChemDict (1971), 586-L

Mica Dynamite or Mica Blasting Powder. An expl invented by G. Mowbray in the USA in 1873, and used in the latter part of the construction of the Hoosac tunnel, replacing the guhr Dynamite used in the beginning. It consisted of 48 to 60p of finely powd mica, thoroughly blended with 52 to 40p of NG. Because of the fact that NG was not absorbed by mica but adhered to the scales, thus resulting in a large exposed surface area, the resulting Dynamite was more sensitive to deton than guhr Dynamite (Ref 2). The max amt of NG that could be held by mica was 52% vs 75% for guhr

Berthelot (Refs 1, 2 & 5) detd vel of deton of mica and guhr Dynamites, and found that the former gave slightly higher values with the same NG content. He attributed this to the cryst structure of mica, which made it less deformable than the amorphous silica kieselguhr. General Abbott (Ref 2) found the expl effect of 52% mica Dynamite under w was about 83% that of guhr Dynamite contg 75% NG. According to Barnett (Ref 3), mica Dynamites were also used in Spain, where they contd about 42% NG

Refs: 1) M. Berthelot, MémPoud **4**, 18 (1891) 2) Daniel (1902), 438–39 3) Barnett (1919), 96 4) Van Gelder & Schlatter (1927), 419–20 5) Davis (1943), 193–94

Michailovsky (Mikhailovsky) Powder. A mining expl resembling tea in appearance. Contains K chlorate 50, sawdust and/or powd tanbark, bran, etc 45, and Mn dioxide 5%. It was also called "Poudre des Mineurs"
Ref: Daniel (1902), 439 & 441

Microanalysis of Explosives. See under Color Reactions and Color Reagents in Vol **3**, C405-L to C420-L, and Addnl Refs below
Addnl Refs: 1) Anon, "Military Explosives", **TM 9-1300-214** (Nov 1967), 12-1 to 12-5 (Identification procedures for initiating & non-initiating high expls & BlkPdr) 2) W. Selig, "The Semimicro Determination of Fluorine in Plastic-Bonded Explosives", Lawrence Livermore Laboratory (LLL) Rept **UCID-15074** (1967), Univ of Calif, Livermore 3) I. Wright, "The Rapid Micro Combustion Determination of Carbon, Hydrogen, and Nitrogen in High Explosives", Explosivst **16**, 176–78 (1968) 4) R. Jenkins & H.J. Gallop, "The Identification of Explosives in Trace Quantities on Objects near an Explosion", Explosivst **18**, 139–41 (1970) 5) J.C. Hoffsommer & J.M. Rosen, "Ultramicroanalysis of Explosives in Seawater", NOL-TR-**71-151** (1971), AD-730444 6) D.E. Chasan & G. Norwitz, "Qualitative Analysis of Primers, Tracers, Igniters, Incendiaries, Boosters, and Delay Compositions on a Micro Scale by Use of Infrared Spectroscopy", FrankfordArs Rept **T-71-6-1** (1971) 8) G.A. St John & M. Anbar, "Determination of Subpicogram Amounts of Chemical Agents in the Atmosphere", EdgewoodArs Contract Rept EC-CR-**74028**, SRI Proj **3122** (1974) (A method of mass spectroscopy, employing a silicone membrane and field ionization, which involves other new techniques, is presented which is sensitive to picogram amts of chemical agents in the atm) 9) H. Kramer, S. Semel & J.E. Abel, "Trace Elemental Survey Analysis of Trinitrotoluene", PATR **4767** (1975) (An evaluation of the applicability of spark source mass spectrometry and thermal neutron activation for the detn of origin-related trace elemental impurities in TNT) 10) C. Ribando & J. Haberman, "Origin-Identification of Explosives Via Their Composite Impurity Profiles; I. The Relation of the Origin of Military Grade TNT to its Mono-, Di- and Tri-nitrotoluene Isomer Impurities", PATR **4768** (1975) (Gas chromatography employed to demonstrate the feasibility of associating trace organic impurities in TNT to its origin of manuf) 11) W.J. Fisco, "A Portable Explosives Identification Kit for Field Use", JForensicSciences **20**, 141 (1975) 12) W.J. Fisco, A.F. Smetana & T.C. Castorina, "Modification and Extended Application of a Portable Explosive Identification Kit for Field Use", PATR **4796** (1975) (Modification of field kit of Ref 11 with provisions for the collection of post-explosion vapors; its application was extended to include over 100 foreign expl samples. Gas and thin layer chromatography are employed)

MICROENCAPSULATION. Microencapsulation is the enclosure of small particles or droplets of materials within micro-capsules to control their release or to protect them from premature chemical attack. It has found wide application in such products as carbon paper, extended medication and slow-release insecticides, to mention only a few (Ref 11); but it has been applied to the energetic materials field with only very limited success. Reactive pyrotechnic ingredients such as Mg have been encapsulated in resin coatings to reduce hydrogen evolution in flare grains (Refs 5 & 7), and individual grains of smokeless powder have been encapsulated in deterrent coatings to program their ignition in gun proplnt service (Ref 4); however extensive efforts to encapsulate extremely reactive proplnt materials such as nitronium perchlorate have been only partially successful (Refs 2 & 10) and have been discontinued. Similarly, attempts to encapsulate droplets of liquid monoproplnts to facilitate their controlled ignition and burning have encountered stubborn problems (Refs 6, 8 & 9) and the effort appears to have been abandoned. Thin capsule walls tend to be too permeable to protect their contents, and thick capsule walls tend to contribute too much inert material to the overall formulation. No reports have been found of attempts to apply microencapsulation to detonating expls

Micro-particles can be encapsulated in polymer films, in metal shells or in shells of their

own reaction products; and all three approaches have been explored for high energy proplnt ingredients. In the *aqueous coacervation* process, a film-forming colloid dissolved in water is pptd into a second, concd, colloid-rich, aq phase which collects on and adheres to the surface of suspended particles or droplets to form a continuous shell. The shell is hardened and cured by appropriate cooling and/or chemical treatments, after which the capsules can be filtered off and collected as a dry powder (Refs 5, 7 & 11). A few of the polymer wall materials which can be deposited by this process are gelatin, polyvinyl alcohol, methyl cellulose, gum arabic, carboxymethyl cellulose and starches. The material to be encapsulated must of course be insoluble in and unreactive with w. *Precipitation* is similar in that the capsule wall former is dissolved in a solvent and deposited onto the suspended particles or droplets – but by cooling, evapn or the addition of a miscible non-solvent (Refs 2, 4 & 11). Organic solvents are most commonly used, and encapsulating polymers include ethylcellulose, NC, polyvinylidene chloride, polystyrene, polycarbonate, polymethylmethacrylate, polyvinyl acetate and others. *Interfacial polymerization* produces a polymer such as nylon at the interface between layered solns of two precursor materials such as (in the case of a nylon) a diamine and a diacid (Refs 3 & 11). If the particle or droplet to be encapsulated is made to pass thru the interface by, say, sedimentation, it will pick up a coating of the polymer as it passes thru

Polymer films can also be deposited on solid particles by vapor phase reaction or from a melt. The best example of vapor phase reaction is the deposition of Union Carbide's "Parylene", a derivative of *p*-xylylene. In this process, di-*p*-xylylene, or more commonly a halogenated derivative of it, is vaporized in a vac and thermmally dissociated into the very reactive monomer, a diradical. The monomer is allowed to condense on the surface of the particles to be coated, where it instantaneously polymerizes to form a high molecular weight, polymeric film (Ref 10). Less reactive, vaporizable or meltable polymers can be applied by hot spraying onto agitated particulates or by deposition in a fluidized bed or in liq suspension (Ref 2). Wax is a common example of wall material applied in all three ways

Metal capsule walls are most commonly deposited onto particulates by vac evaporation of, say, Al onto an agitated bed of particles to be coated (Ref 2). Any metal which can be evaporated in a bell jar can be used. Metals can also be deposited from soln by reduction from ions. Examples are Ag and complex Ni phosphides in electroless processes

A final category of encapsulating materials consists of reaction products of the nucleus material and a reagent. For example, pellets of nitronium perchlorate have been encapsulated in shells of the less reactive amm perchlorate (AP) by exposing the pellets to ammonia gas. The fragile AP shells were usually further protected by a top-coating of Al or a polymer film (Ref 2). The most familiar example of this process is the natural one wherein Al powders (or articles) become coated with a protective coating of Al oxide thru exposure to atmospheric air

Microencapsulation is usually attempted because a proposed ingredient is too reactive or too sensitive to withstand exposure to other ingredients or to the environment. For example, the very energetic oxidizer nitronium perchlorate (NP) cannot be mixed directly into a proplnt or expl formulation because of its extreme reactivity. It is actually a solid anhydride between nitric and perchloric acids, and even traces of moisture hydrolyze the surface layers to free concd nitric and perchloric acids. Moreover, it is so reactive that it will literally expld on contact with substances such as aromatic compounds including solid naphthalene. Consequently, the only real hope of using it lies in effective encapsulation; and extensive efforts have been made to encapsulate it. Processes involving w or organic solvents are obviously inapplicable, but small pellets have been successfully coated with Parylene and with AP and Al (Refs 2 & 10). The efforts were not fully successful, though; because it never was possible to form capsule walls thick enough to protect the NP completely and at the same time thin enough not to add too much inert material to the formulation

The US Air Force has studied the encapsulation of liq monoproplnts such as alkyl nitrates in polymer films to form small spheres much like ball powder for use as gun proplnts (Refs 6, 8 & 9). Suspension coating techniques were used, and microcapsules were made with gelatin,

NC, polyvinyl alcohol and combinations thereof. A free-flowing "ball powder" containing 60–80 wt percent of liq monoproplnt was obtained and successfully fired in small arms cartridges. There were serious difficulties with permeation of the volatile liquids thru the capsule walls and with ignition of the smaller capsules

Most of the energetic materials related work on microencapsulation was done on the high-energy rocket proplnt program around 1960 to 1970 and was classified CONFIDENTIAL or SECRET at the time. Most of the work is now declassified. The refs contain several good reviews of the state of the art, both military and general

Written by **J. BROWN**

Refs: 1) J.D. Millar, "Encapsulation of Propellants And/Or Explosives", Southwest Research Institute for Air Force Systems Command, Report **ASD-TR-61-39** (30 Sept 1961), AD-327320 2) S. Witz and H. Heidsman, "Encapsulating Process Development For Reactive Propellant Ingredients", Aerojet-General Corp, Azusa, Cal, for the Air Force Materials Laboratory, Final Technical Engineering Report **ASD-TR-63-7-900** (July 1963), AD-344885 3) C.C. Petropoulos, "A Study of the Encapsulation of High Energy Substances", National Cash Register Co for the Office of Naval Research, Final Report of Contract **NOnr 2848(00)** (April 1964) 4) L. Stiefel, "Sequential Ignition of Small Arms Propellants by Means of Scheduling Coatings", Frankford Arsenal Report **R-1885** (Feb 1968), AD-832316L 5) C.K. Shaab et al, "Microencapsulation of Selected Flare Materials (U)", National Cash Register Co and Illinois Institute of Technology Research Institute for Air Force Avionics Laboratory, Technical Report **AFAL-TR-68-25** (March 1969), AD-500878 [Secret report, sections on encapsulation techniques unclassified] 6) R.K. Lund, "Encapsulated Liquid Monopropellant Ammunition Feasibility Study", Thiokol Chemical Corp for Air Force Armament Laboratory, Technical Report **AFATL-TR-69-27** (March 1969), AD-859272 7) K.A. Musselman, "Encapsulation of Magnesium to Reduce Hydrogen Generation", Naval Ammunition Depot, Crane, Indiana, Report **RDTN No 198** (25 Aug 1971), AD-900094L 8) S.V. Peterson, "Encapsulated Liquid Monopropellant Ammunition Demonstration", Thiokol Chemical Corp for Air Force Armament Laboratory, Technical Report **AFATL-TR-72-64** (March 1972), AD-893773 9) Anon, "Liquid-Solid Gun Propellant (U)", Thiokol Chemical Corp for Air Force Armament Laboratory, Technical Report **AFATL-TR-72-131** (June 1972), AD-523308L [Confidential, declassified on 31 Dec 1978] 10) L.L. Carpenter et al, "Manufacturing Methods for Oxidizer Encapsulation", Union Carbide Corp for Air Force Materials Laboratory, Technical Report **AFML-TR-68-144** (June 1968) [Declassified on 31 Dec 1974] 11) J.E. Vandegaer, Ed, "Microencapsulation – Processes and Applications", Plenum Press, NY (1974) [Proceedings of the American Chemical Society Symposium on Microencapsulation: Processes and Applications, held in Chicago, 28 Aug 1973]

Micrograin. A dust-like mixt of Zn and S used as an unrestricted burning rocket proplnt. It has a linear burning rate of 60.1 inches/sec as compared to 1.1 inches/sec for ballistite, and costs $0.20/lb vs $5–10 for ballistite. The sp impulse of micrograin is approx 50 sec, that of ballistite is 200 sec

Ref: G.S. James, Astro-Jet **1948**, No 21, 2-12 & CA **44**, 5591–92 (1950)

Microscopy. A broad definition of microscopy is the observation and measurement of optical parameters with any instrument that uses energy sources such as photons, electrons or X-rays to provide an enlarged image of an object. Energetic material parameters that have been observed and measured include quantity, size, shape and color (*Expls:* Refs 12–15, 19, 20, 25, 25a, 27, 28, 32, 48 & 62; *Proplnts:* Refs 1–7, 11, 22, 23, 27 & 40; *Pyrots:* Ref 40); qualitative identification, mp and crystal growth rate (*Expls:* Refs 13, 14, 26, 30, 34, 36, 38, 41 & 55); and combustion parameters such as burning rate, flame erosion of metals and component behavior (*Expls:* Refs 9, 10, 16, 17, 34, 35, 39, 40, 46, 47, 49 & 52; *Proplnts:* Refs 8, 37, 40 & 56; *Pyrots:* Ref 40)

The optical microscope (OM), which has

always been of use from the crude lenses of the ancient Assyrians, thru advances made in optics and OM design by Kepler, Tortona, Martin, Adams and Young, to the latest Balpan or Zeiss creations for crystal morphology, has found important application in energetic materials' research (Refs 51, 61 & 62). This importance is evidenced by work which has ranged from the crystal habits or morphology of expls (Refs 12–15, 26, 30 & 41) and proplnts (Refs 1–7 & 11), to expl and proplnt particle sizing and counting (Refs 19, 20, 27, 28, 32, 48 & 63), to metallographic investigations (Refs 8 & 16)

Many attachments and special devices have been developed to extend and implement the applicability of the OM. One of these is a controlled atmosphere microscope dry-box which offers reproducible environmental control for applications involving toxic, air, or moisture sensitive ingredients, typical of many energetic materials (Ref 33)

Procedures for OM particle sizing and counting of expls are presented in Refs 19, 20, 32, 48 & 63. A procedure for proplnts is presented by J.W. French (Ref 27), who used both OM and EM (electron microscope) to study plastisol NC curing. He found that the cure time of plastisol NC is a logarithmic function of temp, and direct functions of chemical compn and total available surface area, as well as of particle size distribution. It should be noted that extensive use of statistics is required as a time-saving means of interpreting particle size distribution data. The current state-of-the-art utilizes computer techniques to perform this function, and in addition, to obtain crystal morphology data (Ref 62)

The epochal advances in energetic material OM made in 1944 by the OSRD committee headed by A.T. Blomquist provided a cohesive guide for quantitatively identifying primer and detonator ingredients and formulations. The technique involves using the individual morphology of a composition's constituency, as well as thru the application of specific color-resulting chemical reactions. Individual energetic materials, inorganic and organic additives so identified included MF (Mercury Fulminate), LA (Lead Azide), Pb Styphnate, Pb Picrate, Pb 2-4 dinitroresorcinol, Pb 4-6 dinitroresorcinol, Pb thiocyanate, Pb nitrate, Pb chromate, Pb oxide, Red Pb, K chlorate, Sb sulfide, K nitrate, Ba nitrate, Diazadinitrophenol, Tetracene, S, Ca silicide, Si, sand, glass, Si carbide, C, gums, PETN, Tetryl, TNT, RDX, etc (Ref 13)

A work of equal magnitude, again by Blomquist (Ref 14), is directed toward the OM examination of high expls and boosters. It explains comprehensively how to identify these components using fusion analysis, optical crystallography and polymorphism. Materials so characterized include Amm nitrate, Amm picrate, Ba nitrate, Pb nitrate, DINA (Diethanol nitramine dinitrate), DNT (Dinitrotoluene), EDDN (Ethylenediaminedinitrate), HMX, PETN, RDX, TNT, TNB (Trinitrobenzene), various waxes, etc. Procedures are also included for the microscopic identification of mixts, and the particular manufg process used to form the mixt, ie, plasticized, pressed or cast. The importance of the methodology presented, aside from the universality of the technique, lies in the use of microgram samples, and in many instances, the non-destructivity of the procedures employed

OM was used in a basic NC study by S.I. Morrow of PicArsn (Ref 56). He used glass capillary tubes to observe the combustion of thin films of NC (12.6% N) at high press (He at 26–34atms) while heating at the rate of 10° per min. It was found that the NC tended to deflagrate in a manner suggestive of ignition caused by the presence of N oxides. Older NC films behaved differently from freshly prepared specimens in that pyrolytic degradation occurred at higher temps

One of the more important uses of OM is the study of crystallization growth rates. K. Cermak constructed an interference microscope with which measurements can be taken to 50° (Ref 31). This app allows for study of the decompn of the solution concentrated in close proximity to the growing crystal of material such as Amm nitrate or K chlorate. In connection with this technique, Stein and Powers (Ref 30) derived equations for growth rate data which allow for correct prediction of the effects of surface nucleation, surface truncation in thin films, and truncation by neighboring spherulites

In order to obtain higher magnification than is possible with light microscopy, by a ratio of 1000 to 1, instruments employing magnetically

deflected electron beams were devised, and were called electron microscopes (EM). For a short, historical survey of EM's, see Vol 5, E75-L to E77-L. A large amount of work has been conducted on energetic materials using two basic types of EM's, the transmission electron microscope (TEM) (Refs 17, 18, 21–25, 27, 29, 34, 35, 43, 45, 54, 58, 60 & 62), and the scanning electron microscope (SEM) (Refs 36, 37, 39, 40, 42, 43, 44, 45, 46, 47, 49, 50, 52, 53, 55, 59, 60 & 62)

A comparison of these two magnification systems is important. The internal structure of energetic materials is revealed using the broad, fixed beam of the TEM so that internal stresses can be determined (Refs 17, 42, 58 & 62). The SEM, on the other hand, examines the surfaces of materials with its moving, narrow electron beam, which is reflected (Refs 40, 43, 49 & 62). The TEM is therefore especially useful for studying the effects of specimen exposure to heating, cooling, stress, etc, *after the fact*, while the SEM is excellent for surface examinations of corrosion or combustion phenomena taking place *in situ*. TEM works because electrons passing thru matter may be absorbed or scattered by various mechanisms, but the effects of interest in TEM involve, primarily, coherent elastic scattering or diffraction. This implies that the specimen to be studied must be crystalline, and that the facts deduced from its study are correlative information about the crystal structure and specific orientation of the specimen (Refs 43 & 45). Hence, specimens must satisfy certain conditions if they are to yield satisfactory images in the TEM: (1) they must be thin enough to transmit a large fraction of the incident electrons with only minor changes in velocity and direction, and (2) they must maintain their character in vacuum, and undergo the amount of electron bombardment essential for image formation without deterioration (Refs 45 & 62). Therefore, the class of objects which can be studied directly are large (crystalline) organic molecules, finely divided matter, or thin films. This means that surfaces of etched metallographic or other compact specimens must be investigated directly by observing thin film replicas. A replica is a means of reproducing the detail of a specimen surface on an amorphous, stable film. These replicate surfaces can also be fabricated from carbon which has been vacuum deposited on the specimen. The specimen is then dissolved or polished away. A two-step carbon replica can also be made from a plastic mold or copy of the original specimen. The preparation of replicas is discussed in Refs 17, 21–25, 29 & 35

An important area of work utilizing TEM involves the study of metals and metal oxides. Explosively formed or fractured metals are of special interest using this technique (Refs 35 & 46), as are studies of metallic smoke particles (Ref 17) and metallic stress phenomena (Ref 34)

Another area of TEM application to energetic materials is the work of S.M. Kaye at PicArsn on expls and proplnts. He used TEM to establish a procedure for detg the particle size distribution of LA batches of different crystal habits from various manufacturers (Ref 25). He showed that the success or failure of ballistic testing of M-17 proplnt was related to the number and character of cracks and voids observed in the grain surface (Ref 22). In another study, Kaye found that a correlation existed between the type of surface active agent used in the manuf of M-15 proplnt and the successful dispersion of the crystalline ingredients (Ref 23). In an examination of M-8 mortar increment proplnt which had deteriorated in storage, he discovered bacterial infestation penetrating deeply into the grain structure, with resultant unacceptable ballistic performance. It was concluded that wash water used in the processing of this proplnt was contaminated (Refs 21 & 24)

As part of a basic study on M-8 proplnt, Revere (Ref 21), using TEM, discovered that proplnt stored at −20° and −40° for 12 hour periods became wrinkled and exhibited definite parallel cracking and changes in crystalline structure, which was reflected in erratic burning

Although the SEM has about one-tenth the magnification of the TEM, it offers the advantage of being able to examine a specimen surface without resorting to replication. Specimen topography is represented in such excellent detail that the image produced gives the impression of being three dimensional (Refs 17, 18, 34, 35, 40, 43, 49 & 50)

A major investigative effort using SEM at the US Naval Weapons Center was concerned with solid proplnt combustion (Refs 37, 39 & 47).

The study was divided into three categories, the deflagration of single crystals of Amm perchlorate (AP), ignition of individual Al particles, and the burning of polyurethane type proplnt containing AP, K perchlorate or HMX of varying particle sizes as oxidizers. Interpretation of SEM observations revealed that at pressures less than 2000psi, AP crystals deflagrate from a melt instead of by direct vaporization (sublimation); that the fragmentation of burning Al particles is caused by overpressurization within an Al oxide globule rather than by superheating of the globule itself. The proplnt study determined that burning rate was inversely proportional to AP and HMX particle sizes and was slightly affected by K perchlorate particle size. It was also found that the reaction mechanism is diffusion-pressure flame controlled for AP proplnts, and that K perchlorate proplnt burns via a gas phase chemical reaction of the second order. The HMX proplnts melted in such a manner prior to burning that attempts to determine reaction mechanisms from reaction site observation was not possible

Another SEM application is the work of Markham and Cox of R.A.R.D.E. (Engl), whose studies included techniques which allow for the recognition of fractured polymeric or steel fragments as having been generated by either low energy, high energy, or fatique mechanisms. They also studied the particle size distribution and morphology of Mg powder used in pyrots, as well as paint pigments used for camouflage applications. They found the SEM an excellent tool in revealing imperfections in surface coatings such as ceramic glazes or phosphor coatings applied to heat treated steel parts. Additionally, faulty electronic circuits in shell fuzes were found to be caused by the growth of Sn whiskers. Examination of composite matrix interfaces such as Ni plated carbon fibers gave insights into fracture causation, based on both inherent weaknesses in the composite constituents, as well as on fissures and voids between the materials caused by low compaction (Ref 40)

More recently, the work of Beetle and Steward (Ref 49), using SEM, has shown it well-suited for studies of steel fracture surfaces produced by expl action. Several Si-Mn steels with selected, known microstructures were formed into cylinders and explosively fragmented using Comp B. The direct identification of such microscopic fracture modes as transgranular cleavage, radial fracture, intergranular separation or ductile dimpled rupture, was shown to be considerably more dependable by SEM than by OM

Voreck of PicArsn applied SEM to the examination of detonator ingredients, which included a comparison of normal dextrinated Lead Azide (LA) which had been involved in so-called "spontaneous" explns vs "safe" LA. Although no significant differences were noted between the batches, the SEM revealed details of LA structure hitherto unobservable. In particular, 0.1 to 0.5 micron wide, onion-like, clearly defined growth rings were noted around individual seed crystals. In the course of the examination, holes some 3–6 μ in diameter were burned into individual Au coated LA particles without causing detonation of adjacent material (Ref 44)

Mapes, at PicArsn, studied thin films of RDX using SEM (Refs 36 & 55). Much of the work was performed on uncoated specimens mounted on sapphire substrates, so as to provide some index as to the degree of crystallinity and morphology of the materials, per se. The SEM used in this work had a W field oriented emission source of four stages (with avalanche amplification) together with the conventional electron triode gun. The field emission source SEM operates under a much higher (clean) vacuum than conventional SEM's without contaminating the specimens. The field emission source enables the SEM to reveal lattice imperfections of 2.0Å at high resolution (Refs 58 & 59)

Other instruments which have been devised for microstructure examination include the X-ray microscope, with greater resolving power than the EM (Ref 41), and the electron microprobe, capable of indicating subtle changes in composition over small specimen areas (Refs 57 & 62)

Written by **H. L. HERMAN**

Refs: 1) A.J. Phillips, "Characteristics of Wood Pulps and their Preparation for Nitration", PATR **19** (1931) 2) A.J. Phillips, "Study of the Suitability of Wood Pulps for the Preparation of Guncotton", PATR **24** (1931) 3) A.J. Phillips, "Study of Grains of NH Powder having a Mottled Surface", PATR **29** (1931) 4) C.S. Davis, "Special Study of Erratic Behavior of P.A. Lot

3529, 75mm F.N.H. Powder", PATR **30** (1931) 5) W.T. Ingraham, "A Study of the Varieties in the Residual Solvent of Powders in Storage under Water", PATR **63** (1931) 6) J.A. Taylor, "Investigation of Mark IV-B Adapters and Boosters of Frankford Arsenal Manufacture", PATR **90** (1931) 7) H.A. Aaronson, "Nitration of Wood Pulp from Johnson & Johnson Co"' PATR **191** (1931) 8) W.A. Gibson, "Examination of Fin for 81mm Stokes-Brandt Shell, T3", PATR **337** (1933) 9) A. Michel-Levy & H. Muraour, CR **198**, 825–6 (1934) & CA **28**, 2907 (1934) 10) A. Michel-Levy & H. Muraour, CR **198**, 1499-1501 (1934) & CA **28**, 3904 (1934) 11) D.D. Sager, "Study of the Suitability of Wood Pulps for the Preparation of Guncotton", PATR **683** (1935) 12) W.H. Rinkenbach, "Special Tests of Rocket Propellants", PATR **1197** (1942) 13) A.T. Blomquist, "The Microscopical Examination of Primer Compositions", OSRD **3757** (1944) 14) A.T. Blomquist, "Microscopic Examination of High Explosives and Boosters", OSRD **3014**, CWS Fld Lab Memo **1-3-14** (1944) 15) W.C. McCrone, "RDX (Cyclotrimethylene-trinitramine)", AnalChem **22**, 954–5 (1950) 16) E.M. Brumberg, G.A. Sautsev & T.G. Porokhova, "The Etching of Metals and Minerals for Ultra-Violet Microscopy", DoklAkadNaukSSSR **73** (6), 1165–68 (1950) 17) R. Feder, "Preliminary Uses of Electron Microscopy In Ordnance Research", FA Report **R-990** (1951) 18) Yu.M. Kushnir, "Soviet Electron Microscopes and Their Application in Research", SovetatayaElectronnaya-Mikroskopiya, Znaniye Publishing House (1952) 19) J.W. Lavitt, "A Microscopic Method for the Determination of the Particle (Crystal) Size Distribution of '2 Micron' RDX", PATR **1909** (1953) 20) J.W. Lavitt, "An Improved Microscopic Method for the Determination of the Crystal Size Distribution of '2 Micron' RDX", PATR **1957** (1953) 21) A. Revere, "Report On Electron Microscope Study of M-8 Propellant Powder", Stevens Inst Tech Report for PicArsn (1953) 22) S.M. Kaye, "An Electron Microscope Study of the Surfaces of Sectioned M-17 Propellant Grains", PATR **2177** (1955) 23) S.M. Kaye, "An Electron Microscope Study of the Surfaces of Sectioned M-15 Propellant Grains", PATR **2201** (1955) 24) S.M. Kaye, "An Electron Microscope Examination of the Surfaces of M-8 Propellant for Bacterial Contamination", PATR **2210** (1955) 25) S.M. Kaye, "An Electron Microscope Method for the Determination of the Particle Size Distribution and Particle Shape of Colloidal and Ball-Milled Lead Azide", PATR **2133** (1955) 25a) A.T. Blomquist, "Microscopic Examination of High Explosives and Boosters", OSRD Rept **NDRC-B-3014** (AD-29944) (1957) 26) W.D. Williamson, "Microscopic Studies of System RDX–TNT", JApplChem(London) **8**, 646–51 (1958) & CA **53**, 8629 (1959) 27) J.W. French, "Microscopical Investigation of Plastisol Nitrocellulose", NAVWEPS Rpt **7086**, **NOTS TP 2497** (1960) 28) B.T. Fedoroff et al, Encycl **1**, PATR **2700** (1960), A567-L to A568-R 29) D.E. Bradley, "Replica and Shadowing Techniques", Techniques of Electron Microscopy, Blackwell Scientific Publ, London (1961) 30) S. Stein & J. Powers, "The Microscopic Measurement of Crystallization Rates", **ONR TR 31** (1961) 31) K. Cermak, "Interference Microscope for the Study of Crystallization", JemnaMechanikaAOptika, 203–6 (1962) 32) Anon, "Explosives: Sampling, Inspection and Testing", USMilStd **MIL-STD-650**, 206.1 (1962) 33) J.P. Crisler & F.E. Brinckman, "A Controlled Atmosphere Microscope Drybox", NAVWEPS 8574, **TR 150** (1964) 34) E.R. Levin, "Research Conducted On Secretary of the Army Research and Study Fellowship in the Field of Transmission Electron Microscopy", **FA TR R-1706** (1964) 35) J.F. West, "Methods and Capabilities of Electron Microscope Fractography", Springfield Armory **TR 20-2411** (1966) 36) J.E. Mapes, "Crystal Growth and Preparation", PicArsn FRL Research & Eng Lgbk **761-25** (1968) 37) T.L. Boggs, J.L. Prentice, K.J. Kraeutle & J.E. Crump, "The Role of the Scanning Electron Microscope in the Study of Solid Propellant Combustion", NavWepsCentr **TP 4723** (1969) 38) D.G. Graber, F.C. Rauch & A.J. Fanelli, "Observation of Solid-Solid Polymorphic Transformation in 2,4,6-Trinitro Toluene", JPhChem **73**, (10), 3514–15 (1969) 39) J.E. Crump, J.L. Prentice & K.J. Kraeutle, "Role of Scanning Electron Microscopy in the Study of Solid Propellant Combustion. Part II–Behavior of Metal Additives", NavWepsCentr **TP-5142-PT-2** (1969) 40) J.A. Markham & A.R. Cox, "Applications

of Scanning Electron Microscopy at RARDE", RARDE Memo **53169** (1969) 41) F.G.J. May, B.W. Thorpe & W. Connick, "A Glass Transition in Trinitrotoluene", JCrystGrowth **5**, 312 (1969) 42) K.M. Bowketh & D.A. Smith, "Field-ion Microscopy", Defects In Crystalline Solids Series, **2**, North Holland Pub Co. (1970) 43) J.A. Swift, "Electron Microscopes", Barnes & Noble Publ (1970) 44) W.E. Voreck, "Photomicrographic Examination of Explosives", PATR **4093** (1970) 45) Anon, "Structural Characterization of Materials by use of Electron Microscopy and Spectroscopy", General Electric Co (1971) 46) Anon, "The National Fragmentation of Steel Cylinders with Tempered Martensite", Defence Stds Labs (Australia) (1972) 47) R.L. Derr & T.L. Boggs, "Role of Scanning Electron Microscopy in the Study of Solid Propellant Combustion. Part III. The Surface Structure and Profile Characteristics of Burning Composite Solid Propellants", NavWeps-Centr **TP 5142-Part 3** (1971) 48) B.T. Fedoroff & O.E. Sheffield, Encycl **5**, PATR **2700** (1972), D1281-L–84-R 49) J.C. Beetle & W.B. Steward, "A Fractographic Investigation of Explosively Fragmented Silicon-Manganese Steels By Scanning Electron Microscopy", **FA-M72-11-1** (1972) 50) J.W.S. Hearle, J.T. Sparrow & P.M. Cross, "The Use of the Scanning Electron Microscope", Pergamon Press (1972) 51) Anon, "Microscopes", SciProdCat **602-45** (1972) 52) K.F. Lukens & J.V. Rinnovatose, "Metallurgical Studies of Erosion in Aluminum Alloys", **FA-M72-14-1** (1972) 53) J.N. Maycock, "Lattice Defects in Metastable Solids (Azides)", Martin Marietta Corp Res Inst for Advanced Studies (1972) 54) B.T. Fedoroff & O.E. Sheffield, Encycl **5**, PATR **2700** (1972), E75-L to E77-L 55) J.E. Mapes, PicArsn FRL Res & Engr Lgbk **761-146** (1973) 56) S.I. Morrow, "Microscopical Combustion Studies of Nitrocellulose Thin Films in Pressurized Capillary Tubes", Microscope **22**, 229–241 (1973) 57) Anon, "Element Analysis of Microareas By Electron Energy Analyzer", JEOL News **12e** (1), 18–22 (1974) 58) Anon, "100KV Field Emission Electron Microscope", JEOL News **12e** (1), 23–28 (1974) 59) Anon, "JFSM-30 Field Emission Scanning Microscope", JEOL News **12e** (1), 29–31 (1974) 60) T. Yamamoto & H. Nishiyama, "Imaging of Crystalline Substances in Scanning Transmission Electron Microscopy", JEOL News **12e** (2), 19–22 (1974) 61) Anon, "Microscopes", ThomSci-AppCatalog **857-69** (1974) 62) W.N. Wharn, K.S.H. Alaby, S.J. Morris & F.I. Scott, Jr, "Microscopy Pollution Analysis", International Sci Communications Inc, AmLabSeries **1** (3) (1974), 1–161 63) B.T. Fedoroff & O.E. Sheffield, Encycl **6**, PATR **2700** (1974), F152

Miedziankit. A type of chlorate expls manufd in Ger and Poland prior to WWII. They typically contd K or Na chlorate 88–91 and liq hydrocarbons (with flash p not below 30°) 12–9% (Ref 1); K chlorate 90 and petroleum 10%; or K chlorate 87, petroleum distillate 10 and beechwood flour 3%. Their history, props and prepn are detailed in Ref 2

Refs: 1) Naoûm, Expls (1927), 131 2) M. Winter, Kali **22**, 161–4, 181–4, 201–5, 226–9 (1928) & CA **22**, 4249 (1928) 3) Marshall **3**, 112 (1932) 4) A. Pérez Ara (1945), 207 5) Stettbacher (1948), 91

Mikhailovskii Mining Explosive. Russ expl mixt patented at the end of the 19th century contg K chlorate 50, sawdust (or pulverized spent tan bark, or bran) 45, and Mn dioxide 5%

Refs: 1) Daniel (1902), 439 2) B.T. Fedoroff et al, "Dictionary of Russian Ammunition and Weapons", PATR **2145** (1955), p Rus 11-R

Military Biology and Biological Agents. See under Chemical, Biological and Radiological (CBR) Warfare in Vol **2**, C171-R

Military Blasting Explosives and Military Demolition Explosives. See under Demolition Explosives, Vol **3**, D56-R to D61-L

Military Blasting Gelatines. Expls used in Austria between 1878 and 1892 contg 96p of blasting gelatin (NG 90, Collodion Cotton 10%) and 4p of camphor. A similar expl was used in Russia during WWI for filling trench mortar rounds. It contd NG 90, Collodion Cotton 7 and cam-

phor 3%. Blasting gelatin expls were also used by Italian pioneer troops and cavalry in WWI
Refs: 1) Anon, SS **9**, 414 (1914) 2) Naoûm, NG (1928), 310

Military Specification. A procurement specification promulgated by the military agencies and used for the procurement of military supplies and equipment. Typical contents include ingredients, formulae, tests, precautions, and acceptance marking information. The USA Dept of Defense Index of Specifications, Standards and related standardization documents is comprised of two separate parts: Part I – an alphabetic listing, Part II – a numeric listing, and Part II Appendix, contg a cumulative listing of canceled documents published triennially. The primary distribution agency is: Commanding Officer, Naval Publications and Forms Center, 5801 Tabor Ave, Philadelphia, Pa 19120, USA
Refs: 1) OrdTechTerm (1962), 192-R 2) G. Cohn, Ed, Expls&Pyrots **6** (3), March 1973

Military Standard (Mil Std). An authoritative USA Dept of Defense publication setting forth uniform procedures, definitions and standards for mandatory use thruout the Depts of the Army, the Navy, and the Air Force. See *Military Specification* for distribution source
Ref: OrdTechTerm (1962), 192-R

Millbank Explosives. Mining expls contg K chlorate. Typical formulations contain K chlorate 66.96, amorph P 3.75 and charcoal 29.29%; K chlorate 64.30, K ferrocyanide 32.20 and charcoal 3.50%
Ref: Daniel (1902), 439

Miller Explosive. Consisted of two mixts, each of them relatively inert, but becoming an expl when mixed. They contd Na nitrate 35, K chlorate 35 and starch 2ps, K dichromate 3, sulfur 13 and charcoal 12ps
Ref: Daniel (1902), 439

Mills Grenade. A pineapple-shaped fragmentation grenade, originating in Engl during WWI and adopted in the USA. The grenade used in WWII was a modified form, the Mark II. It has a cast iron body, serrated on the surface. It is loaded with TNT or other HE and has a time fuze with a delay element, a priming cap and a striker. When the grenade is to be thrown, the safety pin is removed and this causes the striker pin (held by a spring) to hit and ignite the primer compn and the delay element. After a lapse of 4–5 seconds, a detonator initiates the bursting charge, and the serrated grenade body splits into about 40 pieces on exploding
Refs: 1) Newman (1943), 62 2) Ohart (1946), 356

Mindeleff Explosive (Terrorite). Consisted of NG with various amts of methanol. It was used in Mexico for charging projectiles, but was found to be unsatisfactory
Ref: Daniel (1902), 440 & 765

Mines (Military). Originally mine warfare consisted of tunneling beneath impenetrable enemy positions and placing expls there to destroy them. This was known as *sapping* and dates back far in military history. Mine warfare did not become prominent, however, until WWI, when late in 1914 on the Ypres front, the Germans placed charges in tunnels dug under the British lines, which they fired at the opening of their attack. This had the effect the Germans expected. When their first assault wave reached the British position, the Germans found the British defenses so badly shocked by the explosions that they were able to pass thru without difficulty

Mine warfare as we know it today, however, began when the Germans produced or improvised land mines from artillery shells as a countermeasure against the newly introduced British armored tanks. These were detond electrically when the tanks reached the mined area. At the same time the Allies also developed an antitank mine of artillery shells that detond under the weight of a tank. These German and Allied improvisations, though crude, were very effective

During WWII, as mine warfare was carried on widely by both sides, land mines were developed to a very high degree. They came to include a variety of antitank, antivehicle, dual purpose, and antipersonnel mines with a variety of fuzes.

Mine cases, at first made largely of steel, were later made from all sorts of nonmetallic materials. Today, many of the metallic and nonmetallic bodied mines are equipped with improved contact fuzes and influence fuzes that do not require direct contact with the target, and are thus difficult if not almost impossible to detect and disarm

Land mines are placed on land or just beneath the surface, to inflict damage on either personnel or equipment. They are of the trap type, being initiated by unsuspected action of the enemy. If they are for the purpose of destroying vehicles, trucks, and tanks, they are called *Antitank Mines*, and if they are directed against personnel they are called *Antipersonnel Mines. Beach Defense Mines* are laid just under the water to defend beaches against landing craft. Since all mines, but particularly antipersonnel mines, can be hidden in a great variety of places and can be actuated in a variety of ways, some are called *Booby Traps,* because the "boob" or unsuspecting soldier may sit on something, pick something up, step on something, or trip over a wire, any one of which actions may actuate the mine

Antitank mines consist of an HE charge, usually 3 to 22 lbs, in a metallic or nonmetallic casing fitted with a primary detong fuze, and usually secondary, antiremoval fuzes. Ordinarily, antitank mines require a press of 300 to 400 lbs to actuate them

Antipersonnel mines consist of a small amt of HE, generally less than 1 lb, in a metallic or nonmetallic container fitted with a detong fuze arranged for actuation by press or release of press by pull on a trip wire, or by release of tension (cutting) of a taut trip wire. Two types are available, the blast type, which explodes in place, and the bounding type *(bouncing Betty),* which projects a fragmenting body into the air that, upon deton, scatters fragments over a wide area

Naval mines contain a large amt of HE, and are deployed under w for destroying passing enemy vessels. General types include *Ground, Moored, Magnetic* and *Drifting* mines. Ground mines possess considerable negative buoyancy and are intended to rest on the bottom. For this reason they are suitable for use in relatively shallow w only. Moored mines, in positively buoyant mine cases, are held at a predetermined depth below the surface by a cable or chain mooring attached to an anchor that rests on the bottom. Magnetic mines are intended to be detonated when the hull of a passing vessel causes a change in the magnetic field at the mine. Drifting mines are adjusted to float, unanchored, on or just below the surface of the w. A special type of drifting mine is the *oscillating mine,* which rises and falls gently as it continuously seeks its point of balance

Aerial mines are designed to be dropped from an aircraft, especially into w, hence, aerial minelaying, aerial mining, etc

Although land mine warfare has been effectively used in recent conflicts, mines have not been used to their greatest potential advantage because of their limited versatility, being time consuming to emplace, and generally useable only in defensive situations on land controlled by friendly forces. The standard US **M15** anti-tank mine weighs 30 lbs with 20 lbs of high expl. It requires the manual insertion of the fuze just prior to use, and until the recent availability of a towed mine planter, could only be laboriously emplaced by hand. Another disadvantage in using standard mines like the **M15** is that they frequently pose as much of a threat to the mobility of friendly as well as enemy forces. What was needed was a family of lightweight, effective, and rapidly emplaced mines which could be used in areas not under friendly control. In addition, to permit flexibility in their use, these mines should be capable of deactivation at a predetermined time after emplacement

The **XM56** mine system, aerially emplaced and scatterable, was developed in the 1960's as a response to these needs (Refs 14 & 15). The **XM56** subsystem consists of an aircraft dispenser and the appropriate aircraft controls, as well as the mines themselves. It was designed to be carried aboard the **UH-1H** helicopter which has a payload of 160 mines – 80 in each of two dispensers. The mine itself consists of an aluminum body in the shape of a half cylinder about 10 inches long and 4½ inches in diam. It weighs about 6 lbs and carries a little over 3 lbs of expls. The **XM56** minefield will clear itself a predetd time after emplacement by means of a self-destruct mechanism. The need for lengthy clearing procedures are thus eliminated

Written by **S.M. KAYE**

Refs: 1) Newman (1943), 203, 218, 226 & 267 2) Ohart (1946), 9, 135, 363–70 3) Anon, "Land Mines", **TM 9-1940** (May 1956) 4) OrdTechTerm

(1962), 193L–194L 5) Anon, "Foreign Mine Warfare Equipment", **TM 5-280** (April 1963) 6) Anon, "Mines, Land: Identification; Care; Handling and Use", **TM 9-1345-200** (June 1964) 7) Collier's Encycl, "Naval Mines", **17**, 231–235 (1965) 8) Anon, "Mine, Antipersonnel, PWP, Pop Up, SM54", **TM 3-1345-205-10** (Sept 1968) 9) Anon, "Mine, Special Purpose, Claymore", **TM 9-1385-212** (Dec 1968) 10) Anon, "Mine, Antipersonnel, M26", **TM 9-1345-202-12** (Nov 1970) 11) Anon, "Mines, Antipersonnel (Practice), XM35", **TM 9-1345-12/1B** (Nov 1970) 12) Anon, "Mines, Antitank (HE, Heavy), M15", **TM 9-1375-200/2** (June 1971) 13) Encycl Britannica, "Land Mines, Naval Mines", **15**, 494–98 (1973) 14) Anon, "New Dimension Added to US Mine Warfare", AMC News **2**, No 9 (July 1974) 15) A.R. Nunes-Vais, National Defense, **LIX**, No 327 (Nov–Dec 1974), 240–42

Mine Clearing Equipment. Devices used to actuate land mines without damage to personnel or equipment. Expl devices are typified by a group of linear shaped prefabricated structural sections, filled with composition expls, with a nose section and a towing and pushing attachment, designed for assembly into a device to be propelled by any standard tank. It is designed to breach a path thru a mine field upon the deton, by fire from the pushing tank's machine guns, of the linear shaped charges (Ref 1). Earlier designs were termed *snake, demolition* (Ref 3)

Mechanical devices include the Brit *Scorpion*, the US Mine Exploder **T1E3** (Ref 1) and a Russ tank-mounted mine clearing roller (Ref 3). The *Scorpion* consisted of a horizontal drum, rotating (by means of a drive connected to the tank engine) between two long beams attached to the front of a medium tank. Several long, thin bars were attached to the drum, with a length of chain attached to the end of each bar. As the drum rotated, the chains whipped the ground, initiating any concealed tank mines. The US **T1E3** Exploder consisted of a series of armor-plate steel discs, 8 ft in diameter, mounted loosely on a horizontal shaft, which was attached to two beams extending in front of a tank. These discs were quite heavy (30 tons), and rolled along the ground before the tank, exploding all mines over which they passed. Recent Russ models of rollers and flails clear two wide tracks, each about 2 meters wide, for the passage of tanks and other vehicles (Ref 3)

Refs: 1) G.M. Barnes, "Weapons of World War II", D. Van Nostrand Co, NYC (1947), 96–97 2) Anon, "Land Mines", **TM 9-1940** (May 1956), 107–109 3) OrdTechTerm (1962), 193-R 4) Anon, "Foreign Mine Warfare Equipment", **TM 5-280** (April 1963), 962–3

Mine Detector. Devices, usually electrical or magnetic, used to locate metallic mines. Man portable units consist of a search coil housed in a detector head assembly, a search handle, control box, oscillator amplifier, batteries, headphone and tuner. They operate on either induction or heat frequency principles. In the latter, the tone in the earphones changes in pitch rather than in volume; a buzzing sound occurs only when the search coil is held over a metallic object (Ref 2). A jeep-mounted mine detector which automatically stops the vehicle when it locates a land mine is described in Ref 1

Refs: 1) M.L. Worley, Jr, "A Digest of New Developments in Army Weapons, Tactics, Organization and Equipment", The Military Service Publishing Co, Harrisburg, Pa (1958), 164 2) Anon, "Foreign Mine Warfare Equipment", **TM 5-280** (April 1963), 921–950

Mine, Poudres de. BkPdrs manufd in Fr beginning in 1900 for use in mines. Their shape was either angular or round, and they were divided into three classes: strong (forte), ordinary (ordinaire) and slow (lente). K nitrate content ranged from 72.62% for "forte" to 40% for "lente". A special "lente" pdr contd K nitrate 65, sulfur 15, charcoal 10 and sawdust 10%

Ref: Daniel (1902), 440

Minélites. Expls developed in Fr and found to be satisfactory by the Commission des Substances Explosives. Their compn and props are given below

Minélite	A	B	C
K chlorate	90	90	89
Heavy Petroleum Oil	3	–	–
Paraffin	7	7	5
Vaseline	–	3	4
Tar (pitch)	–	–	2
Density, g/cc	1.92	1.90	1.84
Power by Trauzl Test (PA=100)	74	72	74
Vel of Deton (max), msec	3355	3180	3125

Their expl props resembled expl ONo 4; K chlorate 90, paraffin 10, previously manufd in Fr. Minelite B, under the designation ONo 6, was used by the Fr during WWI for filling grenades and land mines. A similar expl, contg 90% Na chlorate instead of K chlorate, was used in grenades and trench mortar bombs (Refs 3 & 4)
Refs: 1) H. Dautriche, MP **16**, 211–2 & 224–9 (1911–1912) 2) Marshall **1**, 382 (1917) 3) Davis (1943), 360–63 4) A. Pérez Ara (1945), 210

Mineral Acid Esters as Gelatinizers for Nitrocellulose. L. Médard studied the gelatinizing ability of typical mineral acid esters with NC of 11, 12 and 13% N content:
Trimethyl Borate, $(CH_3)_3BO_3$, did not gel any of the NC's; *Trimethyl Phosphate,* $(CH_3)_3PO_3$, gelatinized all three NC's rapidly and completely; *Dimethyl Sulfate,* $(CH_3)_2SO_4$, gelatinized 11 and 12% N NC's rapidly and completely, the 13% N NC incompletely; *Dimethyl Sulfite,* $(CH_3)_2SO_3$, gelatinized all three NC's rapidly and completely; *Butyl Nitrite,* $(C_4H_9)NO_2$, did not gel any of the NC's; *Propyl Nitrite,* $(C_3H_7)NO_2$, did not gel any of the NC's; *Ethyl Nitrate* $(C_2H_5)NO_3$, did not gel any of the NC's, but its mixt with 20% of 95% alc gelatinized the 11 and 12% N NC's rapidly and completely; there was no effect on the 13% N NC. NG, run for comparison purposes, acted very slowly on the 12 and 13% NC's, and did not affect the 11% N NC. At 100°, however, NG completely gelatinized all three NC's in about 4 hours
Ref: L. Médard, MP **29**, 10–11 (1939) & CA **34**, 1486 (1940)

Minerite. A Belg safety expl which has the same compn as the Ger expl, Kohlencarbonit (qv)
Ref: Marshall **1**, 376 (1917)

Miner's Friend. A lignin Dynamite, formerly manufd in the USA by the Hecla Powder Co. It contd varying amts of NG together with lignin and Na nitrate
Refs: 1) Daniel (1902), 440 2) Thorpe **2**, 439 (1918) 3) Van Gelder & Schlatter (1927), 659

Miner's Safety Explosive (Explosif de Sûreté Mineurs). The name under which "ammonites" were originally known
Ref: Daniel (1902), 441

Miner's Safety Fuse (Meches de Sûreté). See Bickford Safety Fuse

Miner's Safety Fuse Matches (Allumeurs de Sûreté). See under Igniters for Fuse

Miner's Squib (Pétard de Mineurs). One of the primitive devices which was invented by Daddow in Engl in 1874 for igniting blasting expls. It consists of a tapered paper tube, about 7 inches long, filled with fine gunpowd. One end of the tube is filled with chemicals, such as milled gunpowd mixed with either sulfur or sulfur and charcoal , so as to form a sort of slow match. A little gunpowd is added at the end in order to facilitate ign of the slow match. When used, the squib is inserted with the slow match outward in a hole made in a charge of BkPdr blasting expl. When the match is lit, the fire burns slowly, allowing the miner time to reach a place of safety. As soon as the fire reaches the BkPdr core of the squib, it burns fiercely and then suddenly explodes, igniting the blasting expl. Instead of the paper tube, quills filled with fine BkPdr joined to a slow match, can be used

Hunter (Ref 1, p 379) proposed, in 1882, a squib which resembled that of Daddow, except that the tube contg the BkPdr was varnished on the outside

According to Marshall (Ref 2), there were also devices called **German Spills**, which resembled Daddow's squib, but no description of them is given

It should be noted that all of these devices are dangerous and not very reliable. Their use, being against the regulations of most countries, can only be justified when no other devices are available

Refs: 1) Daniel (1902), 379, 441 & 611 2) Marshall **2**, 539 (1917) 3) Barnett (1919), 173–74

Minex. One of the variations of **DBX** (Depth Bomb Explosive). It consists of TNT 40, RDX 5–15, AN 35–25 & Al pdr 20%. It is a gray solid with a cast d of 1.68g/cc and a mp of 80–90°, which permits cast loading. Its props are similar to that of DBX (Ref 2)

Refs: 1) All&EnExpls (1946), 130 2) Encycl **3** (1966), D19-L

Miniature-Cartridge Test. For quantitatively evaluating the relative initiating efficiency of detonators. The test is based on the principle that the ability of a detonator to initiate an insensitive expl is the best criterion of its initiating efficiency. The insensitive expl used for this purpose is a mixt of 70–80 TNT and 30–20% Fe_2O_3. The degree of deton of the mixt is detd by means of a modification of the Sand Test (qv). A 5g charge of the mixt is packed to a const diam around the detonator in a paper cartridge, and the assembly is detond in the center of 1000g of standard Ottawa sand in a steel bomb 3 inches in diam. The crushed sand which passes thru a No 30 sieve is a measure of the energy of the deton, less a correction for the detonator in Fe_2O_3

Ref: R.L. Grant & J.E. Tiffany, IEC AnalEd **17**, 13–19 (1945) & CA **39**, 1053–5 (1945)

Miniature Conductive Mix Detonator. Since conductive mix detonators would have no bridge wire, which is a delicate and expensive step in the manuf of bridge wire detonators, it has been proposed that conductive mix detonators would provide an attractive alternative to bridge wire units from standpoints of economics and reliability. A typical DuPont conductive mix detonator is 0.14 inch in diam by 0.292 inch in length, uses pin and cup for electric contacts, and contains a DuPont conductive mix, LA and an output charge of HMX. It is designed to fire from a 2.2 microfarad capacitor charged to 15V. Output is sufficient to initiate pressed Tetryl over an 0.045 inch air gap thru an 0.008 inch thick barrier of mild steel

Ref: Explosives Products Division, E.I. DuPont de Nemours & Co, Wilmington, Delaware & G. Cohn, Ed, Expls&Pyrots **6** (6), (1973)

Mining Explosives. See under COMMERCIAL OR INDUSTRIAL EXPLOSIVES in Vol **3**, pp C434-R to 406-L, and BLASTING EXPLOSIVES in Vol **2**, pp B202-L to 211-R in this Encycl

Minite. A Belg permissable expl of the "Carbonit" type, NG 25, K nitrate 35, flour 39.5, Na carbonate 0.5%. Charge limit is 750g, equiv to 405g of Brit Standard Gelignite. According to Gody (Ref 2) it is called Minite d'Arendonck. According to Daniel (Ref 1) one of the minites was a Dynamite contg NH_4 sulfate

Refs: 1) Daniel (1902), 441 2) Gody, Explosifs (1907), 714 3) Marshall **1**, 376 (1917) 4) Barnett (1919), 140

Minol (Ammonal, Alumatol, Burrowite). Minols are explosive mixtures containing aluminum, ammonium nitrate (AN) or a mixt of AN and potassium nitrate (KN), and TNT. The Ammonals (see Vol **1**, A287-L to A293-R), forerunners of the Minols, were developed prior to and during WWI because of a scarcity of TNT. At that time they were not highly regarded because of a nonrealization of the effectiveness of aluminized expls, coupled with the high cost and nonavailability of Al. Ammonals were used as shell fillers for their fragmentation effect (Ref 8), but were later found to be inferior to Minol II (see below) with respect to blast and shock effects, and less brisant than Composition B (see Vol **3**, C477-R to C484-L)

During WWII, the plentiful supply of TNT

in the USA rendered the use of Ammonals unnecessary, and the development of expls having great blast effects rather than brisance led to the use of Tritonal by the US and of Minols by the United Kingdom (UK). The UK used the following three Minol formulations during WWII (Refs 8 & 21):

	Composition, %		
Ingredient	Minol I	Minol II	Minol III
TNT	48	40	42
Ammonium Nitrate	42	40	38
Aluminum	10	20	20

These Minols were prepd by adding appropriate quantities of dry AN and Al powder to molten TNT at 90° under agitation. Minol II could be prepd by adding 25 parts of Al to 100 parts of 50/50 Amatol, or the calculated amounts of ingredients to other Amatols previously prepd

Minols are gray in color, have densities ranging between 1.62 and 1.74g/cc, and are cast loaded. They resemble Torpex in explosive properties, but are less brisant. They exhibit dimensional instability when exposed to thermal cycling during long term storage

In 1945, all bombs, depth charges and mines were loaded with Minols in the UK (Ref 21). Undesirable gassing and spewing, as well as expansion of the Minols were encountered on mixing or after loading into ordnance. Limited exptl work indicated that the Al-water reaction could contribute significantly to spewing and would be markedly enhanced by impurities in the Al. These undesirable phenomena were observed coincident with the adoption of Minol II, having double the amount of Al powder and with the introduction of a lower grade of Al (Ref 31). The Al reactivity was reduced thru the use of a "biscuit" technique (addition of chunks of solid expl to the melt to reduce the temp), and better control of the pouring temps (Ref 21). In manuf of Minol II, the Al particle size range first used in the UK was "120 mesh to dust". This was later changed to a coarser "36 mesh to dust" fraction in order to obtain increased production, remove dust hazards and decrease the chemical reactivity of the Al (Ref 21)

During the Vietnam conflict, the USA utilized Minol II in general purpose (GP) bombs, and encountered a milder form of spewing which was termed *oozing*. The cause of this occurrence was never determined, although the hygroscopicity of AN and volume changes associated with its polymorphic transitions were considered contributing factors (Refs 17, 23, 26, 29 & 47; also see under Ammonium Nitrate in Vol 1, A311)

Recent studies (Ref 46a) indicated that water did indeed enhance the gassing of Minol at temps above 75°, but that this gassing represented less than 0.1% of decompn in the mixt, and would be a small volume of gas relative to the mass of expl in a munition. At the present time, therefore, the cause(s) of spewing or oozing are still not known

The excessive growth of Minol II in the field during storage was also a problem in Vietnam. It has been speculated that such growth could have been caused by gas producing reactions between AN and Al, AN and TNT or Al and water (Ref 45), but it is considered by many that the observed growth was the result of volume changes resulting from the polymorphic phase transition between form III (gamma) and form IV (beta) AN (Refs 1, 3, 4, 5, 9, 10, 11, 12, 14, 16, 17, 18 & 19). It was also found that Minol II grows more when low set-point, continuous process TNT is used, and when CP grade AN is employed in the mix (Ref 40). The greatest chemical and mechanical stability over the ambient temp to 100° range was obtained when dry, "Product A", large-grained AN was employed (Ref 36)

At elevated temps (<90°), Minol II reacts with inert sealing compound and asphalt-based coatings used in bomb cavities. Asphalts contg free S, unsaturated compds, V and Cu are particularly reactive with Minol II (Ref 35). A new coating, a polypropylene base hot melt was found suitable as a replacement cavity liner for the 750lb M117A1 GP bomb (Ref 41). This new liner material is basically a mixt of amorphous polypropylene wax and rosin. It is completely compatible with Minol II, and can be used in place of the hot melt asphaltic compd presently used. Anothe liner material, primer paint, has been reported to reduce growth and exudation when used as an interior coating in bomb casings (Ref 40)

The particle density and bulk density of AN particulates (prills, granules, pellets) are reflected in the density of the cast Minol II prepd. The highest Minol II density is attained thru use of

grained AN which has the highest particle and bulk density (Ref 48)

AN particle shape, size distribution and density have a significant effect on the mixing and loading characteristics of molten Minol II. The product made with grained AN was best with respect to ease of mixing, smooth consistency, uniform viscosity, pourability and cast density (Ref 48)

Unlike grained AN, which is virtually uncoated, prills and other forms of AN, as marketed commercially, are coated with substantial and varying amounts of clay, talc, diatomaceous earth, or a mixt of one of these with various organic additives, used to inhibit or retard "caking". Not all of these coating agents are compatible with the Minol ingredients, and each coating material must be checked prior to use to determine that it is compatible (Ref 48)

In addition, manufacturers have attempted to phase-stabilize AN by adding small amounts of boric acid, diammonium phosphate and amm sulfate prior to crystn. It was hoped that this stabilization of AN against change from one solid phase to another, with accompanying change in volume, might minimize the Minol II growth problem (Ref 48). Recent studies have shown that both coated and uncoated, phase-stabilized, high density AN can be used in Minol II. However, Minol II charges made with grained AN have the highest detonation velocity compared to charges made with other forms of AN (Ref 48)

It is well known that AN slowly evolves ammonia on storage, particularly in the presence of moisture. In the presence of Al, this evolution is markedly greater. The evolution of ammonia is particularly undesirable in mixts such as Minol II, inasmuch as TNT has been reported to form a readily ignitable compound when treated with concd aq ammonia (Ref 28). Unfortunately, there has been no detailed study of the TNT–NH_3 reaction, and there is no evidence that this reaction can occur in solid Minol

Originally, the Al used in Minol II was in the form of a fine powder. It was shown later that such a high degree of sub-division was unnecessary, and that good performance could also be achieved with Al filings, shavings and flakes. The latter form is particularly advantageous in that the smaller total surface area of Al present in the mixt minimizes its reactivity in Minol and enhances the chemical stability of the compn (Ref 28)

Minol II expands more and exudes less than TNT or Tritonal under similar temp cycling conditions (Ref 40). The exudation of inert sealer in connection with bomb fills has been a problem since 1945, when an inert sealer pad was adopted as a safeguard against impact initiation. The exudation products appeared to be a mixt of wax sealer and black asphalt, and contained no expl. The use an inert, compressible material in place of the inert wax in GP bomb tail sections, along with better sealing, has been successful in overcoming such exudation (Ref 32)

It has been reported that dry Minol II is stable and unreactive when cycled between ambient temp and 100°, and if prepd with dry AN, does not show a phase transition under 50°. However, when AN is used which is not thoroughly dry, Minol II will exhibit a reversible phase transition beginning at 32°, producing volume changes of about 3.8%. These volume changes could cause microcrystalline cracks and pores which could reduce detonation velocity and mechanical strength (Ref 36)

In addition to the above chemical reactivity and dimensional stability problems, Minol II exhibits borderline initiatability at –65°F with small boosters, but initiates reliably at low temps with standard larger boosters (Ref 43)

In an effort to overcome the dimensional stability problem, recent work has been directed toward substituting a solid soln of K nitrate (KN) in AN (AN–KN or KN–AN form III) for the AN in Minol II. Charges containing 40% TNT, 40% AN–KN and 20% Al (designated Minol IV) did show better dimensional stability during temp cycling than either TNT or 67/33 TNT/Al (Ref 45). The 90/10 AN–KN samples were readily prepared in the laboratory and in prilling towers using existing AN technology

The use of 90/10 AN–KN in place of AN in Minol greatly delays the onset of charge growth and minimizes this growth (Ref 45). However, it has been found that growth still does occur, and charges subjected to very many thermal cycles will ultimately begin to crack, as does Minol containing AN. Raising the KN concn to 20% in AN–KN provides a Minol with no detectable growth or cracking after months of cycling, but such a Minol has not been qualified for service use

Table 1 details the physical, chemical and explosive properties of Minols II and IV

Table 1
Properties of Minol II and Minol IV

Property	Minol II	Minol IV	Refs
Loading density (cast), g/cc	1.62–1.68	1.793	37, 49
Air Blast (relative to TNT)			
Peak pressure	115	–	19
Impulse	116	–	19
Energy	133	–	19
Brisance by sand test, grams	40.5 (86% of TNT)	–	37
Booster Sensitivity			
Pressed density, g/cc	1.74	–	20
Wt of Tetryl pellet, grams	100	–	20
Max inches for 50% detonation	1.46	–	20
Brisance by Plate Dent			
Unconfined	66% of TNT	–	4
Compressive Strength, lb/sq in at density, g/cc	1910–2070 1.68	–	15
Cook-off (large scale)	Less sensitive than H-6 or Comp B	–	43
Detonation Velocity, m/sec	5900	5900–6000	5, 49
Electrostatic Sensitivity, 20/20 no fires at 0.25 joules	Passed	Passed	49
Explosion Temperature, 5 second	435°	–	35
Flammability Index	100	–	35
Fragmentation Velocity	100% of TNT	–	37
Friction Sensitivity, 20/20 no fires at 250 lb force	Passed	Passed	49
Growth and Exudation on thermal cycling between –54° and +60° for 30 cycles	Charge completely disintegrates	9.92%, no measurable exudation	49
Heat of Combustion, cal/g	3160	–	10
Heat of Explosion, cal/g	1620	–	10
Impact Sensitivity			
PA App with 2kg wt, inches sample wt 17 mg	13	–	37
BurMines App, cm sample wt 20 mg	35	–	37
Qualification tests, cm	73	55	49
Large Scale Gap Sensitivity, cards	140	107	49
Power,			
by Ballistic Mortar	143% of TNT	–	13
by Trauzl Test	165% of TNT	–	15

(continued)

Table 1 – Properties of Minol II and Minol IV (continuation)

Property	Minol II	Minol IV	Refs
Rifle Bullet Sensitivity, affected, percent	48	–	8
Self Heating	–	No temp exotherms from ambient to 170°	49
Specific Heat			
density, g/cc	1.74	–	35
at –5°, cal/g/°C	0.30	–	
Thermal Conductivity			
density, g/cc	1.74	–	15
cal/sec/cm/°C	16.5×10^{-4}	–	
Vacuum Stability Test			
cc gas in 40 hrs at 120° from 5.0g sample	2.1	–	37
cc gas/g sample in 48 hrs at 100°	0.00	0.05	49
Young's Modulus			
density, g/cc	1.66	–	15
E', dynes/sq cm	5.03×10^{10}	–	
E, psi	0.73×10^{6}		

Uses. Minols have historically been used in four types of ordnance, a) underwater (mines, torpedoes and depth charges) where the confinement of water offsets some of the loss of detonation velocity, b) "blockbuster" bombs in which a sustained and powerful impulse is more destructive than a high peak press, c) concrete fragmentation bombs where the high impulse will impart a satisfactory fragment velocity but will not pulverize the concrete they contact on impact, and d) in general purpose (GP) bombs

Analytical. The quantitative analysis of Minol II is given in US Military Specification **MIL-M-14745** (MU), Amendment 1 (15 June 1972) (Minol-2 Composition), which also lists the following requirements:

Ammonium Nitrate, % (Spec MIL-A-50460)	40 ± 3
Aluminum Powder, % (Spec MIL-A-51L)	20 ± 3
TNT, % (Spec MIL-T-248)	40 ± 3
Moisture, %	0.15, max
Specific gravity	1.65g/cc, min
Workmanship	Shall be free from all foreign material

The quantitative analysis procedure involves benz extr of TNT, water extr of AN, and taking of the Al content as insol residue. Moisture content is detd by the Karl Fischer method described in ASTM Method E203-62, except that 8 to 10g samples are added to methanol. Specific gravity is detd by water displacement, and workmanship by visual examination

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60/40", ARDE Report **67/44**, AC 6506 (May 1944) 26) Anon, "Studies of the Preparation, Stabilization and Testing of Explosives", NDRC Div 8 ERL Interim Report (May 15–June 15, 1944) 27) Anon, "Bombs, 500 lb M.C. Mk IV Filled RDX/TNT 60/40, Minol 2, Torpex 2. Fragmentation Trails at Rest", ARDE Report **76/44**, AC 6612 (June 1944) 28) Anon, "Bombs, H.C. 4000 lb Mk IV. Static Detonation Trials of Minol with Al Content Varying from 0–28 Percent", ARDE Report **68/44** (July 1944) 29) J.L. Copp & A.R. Ubbelohde, "Energy Release in Detonation of Aluminized Explosives. Part I. Effect of Confinement and Charge Diameter on the Detonation Velocity of Minol 2", ARDE Report **616/44** (July 1944) 30) Anon, "Studies of the Preparation, Stabilization and Testing of Explosives. Aluminized Explosives", NDRC Div 8 ERL Interim Report (August 15–September 15, 1944) 31) Anon, "Minol Mixtures of High Aluminum Content. Improved Blast Performance of Minol Containing 28% Aluminum", ARDE Report **118/44** (Sept 1944) 32) Anon, "Studies of the Preparation, Stabilization and Testing of Explosives. Aluminized Explosives", Interim Report (Sept 15–Oct 15, 1944) 33) W.A. Dukes & D.W.G. Style, "Formation of Gas in Minol and Its Inhibition", Advisory Council Scientific Research & Tech Develt, Sub-Committee HE.II., **AC 7109/HE.II.263** (Oct 1944) 34) Anon, "Minol and Torpex", OSRD Report No **4243**, Final Report (Oct 1944) 35) Anon, "Bombs, Aircraft, H.C. 4000 lb and M.C. 500 lb Filling with Minol Containing 28 Per Cent Aluminum", ARDE Report **118/44** (Nov 1944) 36) R.A. Thomas, "Bomb Explosions, 30 May 1944, ROF Hereford", Brit Accident Report No **F. 274** (Nov 1944) 37) W.A. Dukes & D.W.G. Style, "The Influence of Thermal Treatment on the Activity of Aluminized Dusts", Advisory Council Scientific Research & Technical Develt Sub-Committee HE.II., **AC 7555/HE.II.284** (Dec 1944) 38) P.A. Briscoe & C.F.N. Tipper, "The Determination of Moisture in Aluminised Explosives", Bristol Research Report No **150** (Feb 1945) 39) Anon, "The Boostering of High Explosive Bombs", **BRL-555** (June 1945) 40) Anon, "Bombs, H.E., Aircraft, for use in the Tropics. Survey of the Serviceability of Current H.E. Fillings", BritOrdnBoardProc **31460** (June 1945) 41) Anon, "High Explosives and Bombs, Aircraft. Serviceability of Current and Proposed H.E. Fillings for Use in the Tropics", BritOrdnBoardProc **31794** (August 1945) 42) Anon, "High Explosives. Torpex, Sensitivity to S.A. Fire. Results of Comparative Trials with Various Types of Explosives Attacked by 20mm Projectiles", BritOrdnBoardProc **31986** (August 1945) 43) W.P. Biddleman, "Measurements of Fragment Velocity of 4000 lb L.C. Bombs and 1800kg S.C. German Bombs", **BRL-MR-390** (August 1945) 44) Anon, "Bombs H.C. 4000 lb; Blast Performance of Minol 2 with Al of Grist 36/Dust", ARDE Report **91/45** (Sept 1945) 45) Anon, "Explosives, H.E. Effect of Addition of Aluminum on High Explosives", BritOrdnBoardProc **32373** (Oct 1945) 46) Anon, "Bombs, Aircraft, and High Explosives. Minol 2 as Filling for Aircraft Bombs. Relaxation of Grist Size of Aluminum Powder (4000 lb Bombs)", BritOrdnBoardProc **32477** (Oct 1945) 47) Anon, "The Gas Evolution from Minol", NDRC Div 8 ERL, OSRD Report No **5595** (Nov 1945) 48) Anon, "High Explosives and Bombs, Aircraft. Serviceability of H.E. Fillings Stored in the Tropics and in Countries Where High Temperatures and/or High Humidities are Experienced", BritOrdnBoardProc **33265** (April 1946) 49) Anon, "Bombs, Aircraft. H.C. 4000 lb Mark 8 (with Aluminum Case). Report of Rough Usage Trials of Bombs Filled with Minol 2", BritOrdnBoardProc **33292** (April 1946) 50) Anon, "High Explosives. Effect of Addition of Aluminum to High Explosives", BritOrdnBoardProc **33683** (July 1946) 51) W.R. Tomlinson, Jr & L.H. Eriksen, "Stability Tests of Aluminized Explosives", PATR **1635** (Oct 1946) 52) Anon, "Effects of Impact and Explosion", OSRD, NDRC, SummaryTechRept-Divn 2, Vol I (1946) 53) Anon, "The Preparation and Testing of Explosives", OSRD, NDRC, SummaryTechReptDivn 8, Vol I (1946) 54) E. Cheylan, "Aluminum Behavior towards Ammonium Nitrate, with or without TNT", MP **30**, 139–41 (1948) 55) A. LeRoux, "Water Resistant Explosives of Type N", MP **33**, 265–82 (1951) & CA **47**, 10227 (1953) 56) Anon, "Explosives, General. Aluminized Explosives in Underwater Stores", BritOrdnBoardProc E **346** (July 1951) 57) Anon,

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Minolite Antigrisouteuse. A Belg coal mine expl considered safe for use at charge wts up to 650g. It contains AN 72, Na nitrate 23, TNT 3 and TN-Naphthalene 2%

Refs: 1) Anon, SS **3**, 337 (1908) 2) Marshall **1**, 390 (1917) 3) A. Pérez Ara (1945), 243

Minolites. Expls manufd by Cornet & Verviers in Belg since 1897. One of the later compns cont AN 87, Na nitrate 3, DNNaphthalene 3, TNNaphthalene 5, sawdust and rosin 2%, and has a calcd temp of expl of 1916°

Ref: Daniel (1902), 441

Minuteman. US intercontinental ballistic missile series (see Ballistic Missile in Vol **2**, B6). They are three-stage missiles with solid proplnt motors designed as simplified and low cost weapons for launching from silo sites. The first production model was assembled in April 1962, and since then 1000 Minuteman missiles, in three versions, have become operational. A new version (Minuteman 3) with multiple warheads has also been developed. **LGM-30A** (Minuteman 1) is 53ft, 9 inches long, weighs about 60000 lbs and delivers a megaton warhead over 6000 miles at a speed of about Mach 22, utilizing an inertial guidance system. The warhead is armed only after the missile is airborne. **LGM-30B** is a little longer, heavier and more precise than the **LGM-30A.** These were subsequently phased out by the **LGM-30F** (Minuteman 2), which is 50ft, 10 inches long, weighs 70000 lbs and has a 7900 mile range. Instead of the swivelling quadruple

nozzles of the two earlier types, it has a liq-injection single nozzle system. The Minuteman 2 has a two-megaton warhead, and became operational in 1966. A Minuteman 3 with MIRV (qv) multiple warheads is currently being produced, and is reported to carry three 0.2 megaton warheads

Refs: 1) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 130
2) Encycl Britannica **19**, 403–24 (1973)

MIRV. Acronym for Multiple Independently-Targetted Re-Entry Vehicle. A single missile can dispense several warheads, each of which is separately guided to its target. MIRV warheads were developed with the intent of improving **ICBM** cost-effectiveness. USA MIRV's include the **Minuteman 3** and the **Poseidon**

Ref: E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 131–32

Mischdynamit. A typical nongelatinous Dyn contg NG 40, Na nitrate 45, wood meal 12, carbonate & moisture 3%

Ref: Beyling & Drekopf (1936), 89

Misch Metal. An alloy of rare earths of the following approx compn: Ce 49, La 25.6, Nd 16.0, Pr 4.6, Sm 2.0, Tb 1.0, Y 1.0 & Fe 0.8%. The powd alloy was patented as an ingredient of delay compns used in delay elements for electric blasting caps. Other ingredients included Mg, Al, Ni & Zr homogeneously mixed with a fuel such as Si and Pb_3O_4 as oxidant (Ref 1). Misch metal, ground under xylene in small ball mills and incorporated into bridgewire sensitive ignition mixts as well as in some delay formulas, was still in use in Ger in WWII (Ref 2)

Refs: 1) H.M. Kerr & C.R. Hall, USP 2560452 (1951) & CA **46**, 1259 (1952) 2) Ellern (1968), 34–35

Missile (Guided, Non-Ballistic). An unmanned and disposable vehicle which is guided to, rather than aimed at its target. They differ in this principle from *Ballistic Missiles* (see Vol **2** of Encycl, B6), which are guided during powered flight in the upward part of their trajectory, and become free falling bodies subject to the laws of ballistics, in the latter stages of their flight toward targets

Non-ballistic missiles are usually classified as: **Air-to-Air** (AAM), used as aircraft-to-aircraft weapons to supplement or replace guns; **Air-to-Surface** (ASM), a larger category, which includes stand-off missiles, antiradiation missiles such as **Shrike**, as well as ordinary ASM's; **Surface-to-Air** (SAM), are anti-aircraft missiles ranging from the man-portable *Redeye* to the long-range *Bomarc*, and include anti-missile missiles such as *Sprint*, *Spartan* and *Galosh*; **Surface-to-Air**, includes non-ballistic nuclear bombardment missiles such as *Mace B*, as well as the separately listed ballistic family; also includes small non-nuclear anti-tank missiles and naval missiles such as the Rus *Styx*, and **Anti-Submarine**, typified by *Asroc*, *Subroc* and *Ikara* (Refs 4, 5, 8 & 9)

Infra-red homing is used in many air-to-air and some anti-aircraft types such as *Sidewinder*, *Red Top* and *Redeye*. Since it relies on optical radiation, this form of guidance is short range and dependent on reasonably clear skies

Semi-active radar homing units consist of a narrow-beam tracking radar receiver which "locks on" the target, and a computer which generates flight-correction signals for the servo-controls. In semi-active systems, the target is "illuminated" by a radar transmitter on board the launching ship or aircraft, or, in the case of surface-to-air missiles such as the *Hawk*, on the ground

Active radar homing, where the missile has a complete transmitter-receiver set, is a method of guidance suitable only for rather large missiles. Unlike infra-red homing, it is useable in all weathers and at night. This type of guidance can be used only against targets which have a clear radar image when opposed to their backgrounds, such as aircraft or ships (Refs 4, 8 & 9)

Radio-command is generally used in air-to-ground systems, where the target is invisible to radar because it blends into the ground image. In the simplest form, the operator observes visually both target and missile, and directs the latter by joy-stick controls transmitted to the missile by radio or along a wire link *(Fr AS.20/AS.30* & US *Bulpup)*. Many ground-to-

ground anti-tank missiles use a variation of this system, where the signals are transmitted from the pilot to the missile by a thin wire uncoiled from the missile in flight. More sophisticated radio-command methods employ remote observation by TV, as used in the US *Walleye*, or infrared assisted tracking of the missile, as in the US *Tow*. Radio command systems which do not rely on visual observation are employed in longer-range anti-aircraft and anti-shipping missiles, and in ballistic missile defense. In these, the missile is flown by remote control on the basis of data provided by radar tracking both target and missile. Radar is also employed in two other guidance methods: beam-riding, where the missile "rides" or tracks a pencil point beam directed at the target (Brit *Seaslug*), and comparative radar-mapping (US *Mace* & *Matador*). In the latter, a high definition air-to-ground radar maps the ground over which the missile is flying, and compares the ground image with a recorded image stored in the memory of its computer. The computer compares the two images and, if the ground image picked up deviates from that stored in its memory, it actuates servo-controls to make suitable adjustments in its flight (Refs 7, 8 & 9)

Early missiles, from the Ger V-2 to the first generation of nuclear delivery vehicles (such as the US *Atlas*) were generally powered by liq-fueled rocket motors. The liquids used were highly unstable and could not be stored inside the missile, requiring lengthy fueling before launch. Storable-liq fuels were introduced in the next generation of missiles (US *Titan II* & Rus *SS-9*), and are still used on many missiles including most Rus ICBM's. Most missiles today are propelled by solid fuel motors, which are generally more reliable and economical than liq-fueled ones. Since most missiles require a powerful initial thrust for lift-off and a substantially weaker sustaining thrust, different "stages" are generally used, a powerful "booster" and a longer acting but less powerful "sustainer". More recently, dual-thrust rocket motors have been evolved; these are single-unit motors which can modify the thrust to fit different phases of flight (Ref 9)

Missile payload varies from nuclear, through HE fitted with proximity fuzes, to chemical warheads. Electronic countermeasures equipment is an increasingly important part of missile payloads, mainly intended to deceive or confuse enemy radar surveillance and tracking (Ref 8)

Also see Vol **6**, G178-L under Guided Missiles

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Refs: 1) A. Ball, "Ballistic and Guided Missiles", Frederick Maller, Ltd, London (1960) 2) H. Jacobs & E.E. Whitney, "Missile & Space Projects Guide", Plenum, NY (1962) 3) N.A. Parson, "Missiles and the Revolution in Warfare", Harvard Univ Press, Cambridge (1962) 4) R. Shapiro, "ABC's of Missile Guidance", H.W. Sams, Indianapolis (1962) 5) A.T. Cartier, "Missile Technology Abbreviations and Acronyms", Hayden Book Co, NY (1965) 6) Collier's Encycl **20**, 120–130 (1965) 7) McGraw-Hill Encycl of Science & Technology **8**, 599–602 (1971) 8) E. Luttwak; "A Dictionary of Modern War", Harper & Row, NY (1971), 39 & 132–34 9) Encycl Britannica **19**, 403–24 (1973)

Mist and Spray Explosions. See FAE & FAX (Fuel-Air-Explosives) in Vol **6**, F3-L–F4-R

Mittasch Stability Test for Nitrocellulose. A test based on the measurement of press developed on decompn of NC. The app may be considered a very complicated modification of devices originated by Abel (Ref 4, p 241) and Hess (Refs 1 & 4). Abel heated NC samples in vac and detd the press increase. Hess believed that on heating NC in a closed vessel contg air, connected to a Hg manometer, it would be possible to achieve conditions more closely resembling those in storage in closed magazines. Neither of these methods found any practical application

Mittasch, recognizing the fact that decompn of NC in Hess' app was abnormally high because the gases under press excercised an autocatalytic action, constructed an app in which NC, heated to 70° under atm press, was connected to a manometer. Thus, any vol changes because of gas formation were automatically registered. As Mittasch's app was very complicated and costly, it did not find practical application except in Engl, where it was used in modified form for

testing "cordites". This modification is described in detail by Kast & Metz (Ref 4, p 313)
Refs: 1) J. Hess, MiltArtuGeniew **10**, 360 (1879) 2) J. Mittasch, ZAngChem **16**, 929 (1903) 3) Reilly (1938), 87 4) Kast-Metz (1944), 241 & 313

Mixed Acids. See under Nitration in this Vol

MJ Powder. An experimental double-base proplnt developed during WWII contg NC 48.0, NG 31.0, K nitrate 17.5, carbon blk 2.5 & et centralite 1.0%
Ref: F.H. Westheimer, OSRD **4758** (1945), 10

M.N. An old US proplnt, invented by Maxim-Nordenfelt, contg NC gelatinized by et acet. It was also manufd in Italy as "N57"
Ref: Daniel (1902), 442

MNO (N,N′-Dinitrodimethyloxamide), $C_4H_6N_4O_6$; mw 206.14, N 27.20%, OB to CO_2 −38.8%, mp 123°, d 1.52 g/cc. Can be prepd by treating dimethyloxamide with HNO_3 or mixed acid (Ref 1). Pb block expansion is 110% PA or 110–115% TNT; BalMort is 116% TNT; deton vel is 5050m/sec at d 1.0 g/cc, 7050m/sec at d 1.5g/cc (Refs 3 & 9). Impact sensitivity is approx 0.9 TNT; Q_c 508.4, Q_c^v 511.9cal/mole (Refs 4, 5 & 6). Storage at 100° for 30 days produces no red fumes (Ref 9) and 6 month storage at 65° causes no decrease in stability (Ref 8). MNO is stable to hot concd HCl; with alkali furnishes salts of methylnitramine; with w develops acidity. At 25° it gains 0.03% at 90%, and 0.2% at 100% rel humidity (Ref 7)

$$\begin{array}{l} CON(NO_2)CH_3 \\ | \\ CON(NO_2)CH_3 \end{array}$$

MNO has been evaluated as being between Tetryl and TNT in performance, but of considerably lower stability because of a hydrolytic action with w (Ref 5). It is reported to form a eutectic with PETN, having the compn MNO 30, PETN 70%, which is liq at 100° and which, cast, passes a rifle-bullet test (Ref 3). A detailed study of the expl properties of MNO is given by MacDougall (Ref 5). MNO and analagous dialkyldinitrooxamides are claimed to be less sensitive and as powerful as PA (Ref 2)

Also see under Dimethyloxamide and Derivatives in Vol **5** (1972), D1359-R to D1361-R
Refs: 1) Beil **4**, 86 2) Westfälisch-Anhalt Sprengs -A -G, GerP 203190 & 291830 (1921) & CA **15**, 1997 (1921) 3) Dynamit-A-G, GerP 499403 (1930) & CA **24**, 4160 (1930) 4) R. Schmidt, SS **29**, 262 (1934) 5) D.P. MacDougall, OSRD **560** (1942) 6) G.P. Kistiakowsky, OSRD **702** (1942) 7) R. McGill, OSRD **830** (1942) 8) Anon, OSRD **1947** (1943) 9) A.H. Blatt, OSRD **2014** (1944)

Moddite (Modite). A variety of "Cordite" manufd in the form of strips by Eley Brothers of Engl for use as sporting rifle proplnt. It contd NC (about 35% sol in eth-alc) 56.8, NG 38.7, mineral jelly 4.3 & vol matter 0.2%
Refs: 1) Marshall **1**, 308 (1917) 2) Barnett (1919), 79

Model Designations. In order to identify a particular ammunition design in the USA, a model designation is assigned at the time the model is classified as an adopted type. This model designation becomes an essential part of the standard nomenclature and is included in the marking on the item

Prior to WWI, the number of the year in which the design was adopted preceded by an "M" was used as the model designation; for example, M1906. From WWI until July 1, 1925, it was the practice to assign mark numbers. The word "Mark", abbreviated "Mk", was followed by a roman numeral; for example, Shell, HE, Mk III. The first modification of a model was indicated by the addition of MI to the mark number, the second by MII, etc. The present system of model designation consists of the letter "M" followed by an Arabic numeral, for example, M1. Modifications are indicated by adding the letter A and the appropriate Arabic numeral. Thus, M1A1 indicates the first modification of an item for which the original model designation was M1. Wherever a B suffix appears in a model designation, it indicates an item of alternative design, material or manuf. AT or XM model designation signifies that the item is

under development. An E with an Arabic numeral signifies a modification thereof. Ammunition developed by other services use other systems, eg, Mk-Mod system for US Navy materiel
Refs: 1) Anon, "Ammunition Inspection Guide", **TM 9-1904** (1944), 5–6 2) Anon, "Artillery Ammunition", **TM 9-1300-203** (1967), 1–13

Modernization Engineering Project for US Army Ammunition Plants. The US Army Munitions Command (MUCOM), in 1970, had 27 ammo production facilities located throughout the US to support the Government's military ammo needs for standard-type ammo for the military services. These plants were Government-Owned Contractor-Operated (GOCO), and were engaged in the manuf of proplnts and expls, metal parts and small arms ammo, and the load, assembly and pack (LAP) of ammo. The purpose of the ammo plants complex was to provide reliable ammo production capability which would match established mobilization objectives in a timely and economical manner. The majority of the GOCO plants were built in the early 1940's, were operated in WWII, were activated during the Korean conflict, and were used to support the Governmant's requirements in the hostilities in Southeast Asia. These plants, in many instances, were built on an emergency basis, and had been operated far beyond their designed capabilities and life expectancy. Little had been done to modernize them. Early in 1968, MUCOM detd that an accelerated and revised modernization program was required for approx 22 of the production plants to overcome evident shortcomings and deficiencies. MUCOM modernization committees were formed to cover Propellants and Explosives (P&E), LAP, Metal Parts (MPTS), and Small Arms (SA) GOCO plants. These committees provided guidance regarding the technology priorities and the overall time phases of modernization plans for each MUCOM GOCO facility, and identified those areas where additional technological advances were required

On June 30, 1969, MUCOM awarded a contract to Kaiser Engineers, in association with A.T. Kearny & Co, Inc, management consultants and industrial engineers, and Stetter Associates, Inc, industrial equipment consultants, to perform a comprehensive modernization engineering study of the GOCO ammo production plants during a one-year period. The project was developed under two separate but coordinated tasks: (1) Establishment of modernization master plan, and (2) Project modernization control. The objectives of the first task was to establish a modernization program for the GOCO ammo plants which would enable production of the then current and mobilization requirements for ammo in the most efficient, economic and expeditious manner utilizing the latest proven state-of-the-art in manufg processes. Under the second task, the objectives were to develop an integrated modernization master plan for the GOCO plant complex, establish a Master Facilities Data Bank with procedures for maintenance, data insertion and retrieval, and determine the feasibility of establishing an economic model and a priority system to facilitate management decisions on modernization

The contract effort required a modernization plan report by ammo category and by GOCO plant. The ammo category report was to contain modernization planning considerations (including an assessment of current and advanced technology), and the recommended modernization master plan for all the GOCO plant production facilities with capabilities to produce items in the particular ammo category. Separate ammo category report volumes were to provide for LAP, P&E, MPTS & SA. Plant reports would treat the modernization planning applicable to a particular plant, reflecting the conclusions reached in ammo category-wide planning. Individual plant reports were to cover each GOCO plant designated by MUCOM for consideration

A summary volume (Ref 1) provides a concise summary of the results of the entire project including the complete recommended modernization master plan subdivided by plant and by ammo category. Refs 2 to 4, with appendices, supply modernization master plans by ammo category together with the detailed advanced technology studies and other applicable background material. Refs 5 thru 25 present the modernization master plan for a GOCO plant with applicable analyses and background material. An appendix bound with each report includes P-15 summary sheets

and economic analyses for recommended production facility projects. Refs 26 to 32, bound separately in seven parts, report on the results of the LAP model line studies on specific end items. Refs 33 & 34 contain material on integration of the modenization master plan, feasibility study for economic model, and priority system

Written by **S. M. KAYE**

Refs: 1) Anon, "Modernization Engineering Report for US Army Ammunition Plants", Vol **1** (Summary), Contract No DAAA 21-69-C-0788, Report No **70-28-RE**, USA Munitions Command, Dover, NJ (Aug 1970) 2) Ibid, Vol **2**, "Ammunition Category Report; Load, Assemble and Pack", Appendix C (separately bound) 3) Ibid, Vol **3**, "Ammunition Category Report; Propellants and Explosives", Appendix C (separately bound) 4) Ibid, Vol **4**, "Ammunition Category Report; Metal Parts and Small Arms Ammunition" 5) Ibid, Vol **5**, "Badger Army Ammunition Plant" 6) Ibid, Vol **6**, "Burlington Army Ammunition Plant" 7) Ibid, Vol **7**, "Cornhusker Army Ammunition Plant" 8) Ibid, Vol **8**, "Holston Army Ammunition Plant" 9) Ibid, Vol **9**, "Indiana Army Ammunition Plant" 10) Ibid, Vol **10**, "Iowa Army Ammunition Plant" 11) Ibid, Vol **11**, "Joliet Army Ammunition Plant" 12) Ibid, Vol **12**, "Kansas Army Ammunition Plant" 13) Ibid, Vol **13**, "Lake City Army Ammunition Plant" 14) Ibid, Vol **14**, "Lone Star Army Ammunition Plant" 15) Ibid, Vol **15**, "Longhorn Army Ammunition Plant" 16) Ibid, Vol **16**, "Louisiana Army Ammunition Plant" 17) Ibid, Vol **17**, "Milan Army Ammunition Plant" 18) Ibid, Vol **18**, "Radford Army Ammunition Plant" 19) Ibid, Vol **19**, "Ravenna Army Ammunition Plant" 20) Ibid, Vol **20**, "Riverbank Army Ammunition Plant" 21) Ibid, Vol **21**, "Scranton Army Ammunition Plant" 22) Ibid, Vol **22**, "St Louis Army Ammunition Plant" 23) Ibid, Vol **23**, "Sunflower Army Ammunition Plant" 24) Ibid, Vol **24**, "Twin Cities Army Ammunition Plant" 25) Ibid, Vol **25**, "Volunteer Army Ammunition Plant" 26) Ibid, Vol **26-1**, "LAP Model Line C-750, 750 pound HE Bomb" 27) Ibid, Vol **26-2**, "LAP Model Line I-175, 175mm HE Projectile" 28) Ibid, Vol **26-3**, "LAP Model Line Ind SEW and Ind-155, 155mm Bag Manufacturing and Propelling Charge Loading" 29) Ibid, Vol **26-4**, "LAP Model Line LS-81, 81mm Mortar Cartridge" 30) Ibid, Vol **26-5**, "LAP Model Line M-40X, 40mm Cartridge and M67 Grenade" 31) Ibid, Vol **26-6**, "LAP Model Line J-CBU, CBU 24/49" 32) Ibid, Vol **26-7**, "LAP Model Line K-1000, 105mm, HE/RAP" 33) Ibid, Vol **27**, "Feasibility Study for an Economic Model" 34) Ibid, Vol **28**, "Integrated Master Plan and Priority System; Feasibility Study"

Modified TNT. After WWI, a considerable quantity of Trojan grenade powd that had been spoiled by moisture, was available for use. It consisted of nitrostarch, Na nitrate, Amm nitrate, and a small quantity of oils. In order to utilize the powd, an equal amt of TNT was added, and the resulting mixt designated "modified TNT" was found to be an efficient expl. It was used as a commercial blasting expl

Ref: C.E. Munroe & S.P. Howell, Report of Investigation, Bur of Mines (June 1920) & CA **14**, 2708 (1920)

Mohaupt Effect. The effect of a metal liner introduced in a shaped charge to increase penetration. Generally incorporated in high expl antitank (HEAT) ammo. See Munroe-Neumann Effect, Vol 4, 444-R

Refs: 1) J.J. O'Connor, Ordn **37**, 171 (1952) 2) OrdTechTerm (1962), 197-L

Moisson Number (Nombre de Moisson in Fr). The Fr ballistician M.L. Gabeaud (Ref 1) claimed that the so-called *Nombre de Mach* (Mach number) should be called the *Nombre de Moisson* because it was the Fr Gen Moisson who first proposed the equation in 1883, four years before Mach. Gabeaud also stated that the Rus ballistician Gen Mayevski, in his work "Traité de Balistique Extérieure", Gauthiers-Villars, Paris (1872), gave a somewhat similar equation for the detn of the resistance of air at the vel of sound, for round and elongated projectiles

Refs: 1) M.L. Gabeaud, MAF **21**, 857 (1947) 2) M.M. Garnier, MAF **25**, 693 (1951)

Moisture. The effect of moisture on expls, proplnts and pyrots can be deleterious in terms of reliability, efficiency and safety. This unwanted ingrenient can add uncertainty and possible hazard in the manuf, storage and eventual use of ammo. Moisture adds to the costs of ammo in many ways. These include less effective material being available per unit volume, with concomitant increases in malfunction rate, curtailed shelf life because of structural failures occasioned by moisture-generated chem reaction products; and the cost of many investigations undertaken to understand and prevent effects (*Expls:* Refs 6, 8, 11, 12, 15, 17, 21, 26, 28, 31, 34, 35, 39, 40, 41, 43, 44, 46, 48, 52 & 54; *Proplnts:* Refs 9, 13, 16, 19, 21, 23, 27, 29, 37 & 53; *Pyrots:* Refs 5, 7, 10, 14, 18, 20, 23, 24, 28, 30 & 38)

Moisture exists in energetic materials primarily because of the procedures used in their manuf. Since many of these materials are hygr, they absorb moisture from the atm on site when they are prepd. In addition, w may be added for either safety considerations or as an economical solv in prodn procedures. Examples of these moisture sources include shell loading operations, which are performed using steam-heated facilities and cold w cooling jackets. The latter are used in many stages of expl and proplnt manuf. They condense atmospheric moisture onto their cold surfaces, some of which enters the mixt being processed, resulting typically in delayed expl gelation (Ref 34), undependable deton phenomena (Refs 26, 46, 48 & 54), or ballistic uncertainties with proplnts (Refs 13 & 27). Moisture can also permeate energetic materials during storage of ammo contg them (Refs 16, 19, 37, 50, 53 & 59)

Illustrations of the deleterious effects of moisture on the manuf, storage and performance of individual classes of energetic materials will now be considered

Effect of Moisture on Explosives: Expls are the only energetic materials which can exist in useable form as a w slurry. These materials do not meet Mil specifications, however, they are commercially available and are used as gels in mining operations (Refs 35, 36, 43 & 44)

The immediate effect of large amts of moisture on conventional Mil (and commercial) dry expls is to prevent deton. In Engl, to safely store many expls, the use of w wet materials is advocated. Of course, a drying process must be used to make the expl useable and efficient. In this connection, to accurately determine the amt of w required to prevent the accidental deton of expls, the Lidestone Cartridge Case Test was evolved (Ref 54). Presented below are results from this work, the data being obtained from plots of %w added to the dry expl vs the base wt of the expl plus added w, on attempting deton of the mixt. The plotted data resulted in sigmoid-shaped curves which clearly define the minimum w content necessary for non-deton

Table 1
Minimum % of Water Required for Non-Detonation When Subjected to Contact Impulse from a Detonator

Explosive	% water
PETN	165
RDX	60
Tetryl, Gr I, cryst	60
1,3,5 Trinitrobenzene	55
RDX/TNT 80/20	48
Strontium picrate	31
2,4,6 Trinitrobenzoic acid	28
Picric Acid	26
TNT, cryst	20
Ammonium picrate	8
Gunpowder, meaied	7
Nitroguanidine	6
2,4 Dinitrophenol	4
Sodium 2,4 dinitrophenate	0

The work of Avrami et al on the impact sensy of Lead Azide-water (LA-w) mixts contg various expls and drying agents, conducted with the standard PicArsn impact test app, is of interest. It was found that under confined conditions, LA mixts contg up to 28% w are more sensitive than dry LA mixts, while in unconfined tests, the reverse is evident (Refs 39, 40 & 41). This study, as a corollary to the Lidestone test work, is indicative of the uncertainties inherent in expl initiation when w is present

Small amts of moisture can also affect expl performance. As little as 0.5% can cause unpredictable deton initiation and randomly variable deton vels, which could defeat the efficient use of an expl in, for example, a shaped charge application (Ref 26). See also Vol **4**, D347-L & D356-R

On long term storage, moisture can cause undesirable chem reactions such as the formation of nitric acid, which can react with such metals as Al, Mg, Fe, Cu, etc, to yield H_2. The H_2, in turn, in redox reactions with both metals and org chemicals present can form shock sensitive compds (Refs 6, 11, 12, 15, 17 & 26). In addition, H_2 is extremely sensitive to spark initiation, and can cause premature detons when ammo is being handled, is in-tube during launch, or is being steam-cleaned for reloading purposes. A parallel reaction involves the release of NH_3, which can combine with metals such as Cu in the presence of nitrates to form such extremely shock sensitive compds as tetramino cupric nitrate (Ref 17). To obviate these effects, desiccants such as silica gel may be added to the extent of 0.5% (Ref 12)

Moisture can also result in undesirable dimensional changes occurring in AN–K nitrate based expls, caused by changing crystal habit on thermal cycling. The physical stresses produced may cause stress failures of their containers (Refs 26 & 32)

Effect of Moisture on Propellants. The effects of the addition of 0.1% moisture on the performance of small arms proplnt is shown below (Ref 13):

Table 2
Effects of Addition of 0.1% Moisture to Small Arms Propellant

	Additional Charge (%) Required to Maintain Constant Velocity		Change in Velocity (%) for Constant Charge Weight		Change in Pressure (%) for Constant Charge Weight	
Cartridge	Single Base	Double Base	Single Base	Double Base	Single Base	Double Base
Cal .50 AP	1.06	0.85	–0.70	–0.70	–3.00	–3.00
Cal .30 Ball	0.64	–	–0.60	–	–1.60	–
Cal .30 AP	0.56	0.56	–0.55	–0.50	–1.60	–1.75
Cal .45 Ball	1.00	–	–0.55	–	–1.00	–

The magnitude of these effects is such that relative humidity control in proplnt production and loading areas is mandatory in order to achieve predictable and dependable ammo performance. It should be noted that not only are ballistic parameters adversely affected by moisture, but the frequency of misfires, hangfires, etc, because of ignition difficulties, may also increase (Ref 27)

The deterioration of proplnt charge increment bags because of moisture has been reported (Refs 16, 19 & 53). Since each bag contains a charge necessary to obtain a finite range for a finite proj, moisture-caused deterioration of the bag with associated proplnt degradation can defeat the increment's purpose and produce an unpredictable, erratic round

The effect of moisture on felted combustible cartridge cases includes ignition delay, and out-of-phase or low peak pressures, all contributing to round inaccuracy (Ref 37). Temp cycling of this item contg an excess of moisture in the casing matrix will lead to case embrittlement, cracking and eventual case rupture. This effect has led to the development of protective coatings and seals (Refs 19, 23 & 37)

Small arms ammo can be so severely affected by moisture that a special indicating lacquer was developed for 20mm rounds which changes color from grey to black on w exposure (Ref 59)

Effect of Moisture on Pyrotechnics: Pyrot formulations usually contain finely powdered metal fuels such as Mg, Al, Fe, Cu, etc, all of which can react with moisture to yield H_2. This effect has been dubbed "gassing" in pyrot circles, and is the major problem associated with the storage of hermetically sealed ammo of this class. The pyrot charges so affected become deton sensitive, and are generally unreliable as to burning rate and illumination. An associated effect of "gassing" is the deformation and rupture of ammo casings, making the items nonserviceable. Many programs have been initiated to circumvent these effects, and have included the use of dichromate, resin and wax coatings for the metal particles. The inclusion of drying

agents in pyrot formulations, careful pre-drying of ingredients and post-processing drying of loaded items, as well as hermetic sealing of end-item casings have been attempted (Refs 5, 7, 10, 14, 18, 20, 23, 24, 30 & 38)

The salts of Na, Ba and Sr, used as oxidants and to impart appropriate flame colors, are w soluble. Excessive moisture content (over 0.5%) is deleterious in terms of light intensity, color saturation and burning duration. BlkPdr, a widely used ignition source and flame transfer agent, absorbs moisture and deteriorates rapidly. Many instances of pyrot "no-fire" incidents have been found to be the result of such deterioration (Refs 10, 18, 21 & 38)

Moisture, Analytical Procedures. Various quantitative procedures have been developed ranging from simple oven drying thru sophisticated instrumental methods (*Expls:* Refs 31, 33, 42, 47, 52, 56, 57, 60 & 62; *Proplnts:* Refs 25, 28, 29, 49, 51 & 55; *Pyrots:* 30 & 38)

Many procedures have already been described in this Encycl, and are listed below:

Encycl **5**, D1620-L to D1622-R (Moisture by Distillation Method); Ibid, D1622-R to D1628-L (Moisture by Karl Fischer Method); Encycl **6**, E158-L to E160-R (Water by Karl Fischer Method); Ibid, E162-R to E164-R (Ethanol, Ether and Water Determinations in Single Base Propellants by Gas Chromatographic Method); Ibid, E164-R to E169-R (Total Volatiles and Moisture Using the Vacuum Oven Method); Ibid, E170 (Electrolytic Hygrometer Method); Ibid, E171-L to E172-L (Moisture Determination in Propellants and Explosives by Distillation Method); Ibid, E172-L to E173-L (Moisture Determination in Propellants and Explosives by the Karl Fischer Method)

Encycl **6**, E173-L details a literature method for detg w in NC and proplnts thru the use of dry K carbonate pumice to absorb w in a gravimetric procedure. Encycl **6**, E176-R describes a differential d measurement of the solvents used in proplnt manuf for the detn of alc, eth & w (Ref 2). Other older gravimetric methods are given in Refs 1, 3 & 4

A modern version of the oven heating method is the Mytron FAB-1 moisture tester, in use at Waltham Abbey, Sussex, Engl, for detg moisture in proplnts (Ref 55). It consists of a hot air oven containing a motor driven turntable with numbered spaces for 10 circular flat Al dishes. Below the oven compartment is a simple beam balance, so arranged that when the beam is moved from rest onto its knife edges, the rotation of the turntable is stopped and the wt of the dish immediately above the balance is recorded on a scale that shows the % moisture lost (a 10g sample being specified). The range of the balance is 0 to 22% moisture

Ref 58 discusses the application of electronic instrumentation to moisture measurement. Procedures amenable to use for energetic materials include:

Capacitive Sensors. This device usually consists of a capacitor which is formed either from two concentric cylinders or from a pair of parallel plates. The solid sample to be analyzed for moisture content is passed between these plates. Since w has a large dielectric constant, the w content of the sample causes a significant change in the dielectric constant of the solid, which is measured using bridge or frequency techniques. To obtain the % of moisture directly, a calibration curve is first constructed which relates % moisture in the solid to capacitance. A drawback inherent in this method is the dependence of the dielectric constant on factors other than moisture content, such as density, particle size and packing. Ref 61 describes a Capacitance Moisture Analyzer (CMA) capable of providing moisture analyses of LA with a precision of ± 0.17% in samples containing a max of 0.5% w

Neutron Measurements. The interaction of neutrons has been used on a laboratory basis to measure low concentrations of moisture in powd expls and other energetic materials. The approach is based on the phenomena that fast neutrons, on passing thru materials of high scattering and stopping power, are slowed down to slow or thermal energies. The fractional loss in energy when a neutron collides with an atom is greatest for the H atom. Thus, by passing a beam of fast neutrons thru a series of samples of the same material, but with varying moisture contents, a relationship is observed between moisture content and measured thermal neutron intensity. Using a small radioisotope fast neutron source and a lithium iodide thermal neutron detector, this neutron

moderation technique was applied to the measurement of moisture content in AN, K nitrate, BlkPdr, K perchlorate and NC in the range from 0.01 to 10 wt % (Refs 42 & 57). For additional details see Encycl **8** under Nuclear Applications

Nuclear Magnetic Resonance. This transient NMR technique, developed by the Southwest Research Institute, permits moisture in BlkPdr to be measured without weighing by sampling the amplitude of the free induction magnetic decay at two points in time. Amplitude measurements of the BlkPdr signal shape enables one to obtain signals linearly related to the solid material (the dry wt of the sample) and liq (w) signals respectively. Moisture levels in the range 0.2 to 1.0% can be measured with an accuracy of ± 5.5%. The accuracy with which a measurement can be repeated is 1.0% of the quantity measured (Ref 47)

Infrared Spectroscopy. A device known as OMA, an acronym for Optical Moisture Analyzer, has been used to determine moisture content in non-metallic cartridge cases and certain fine-grained proplnts (Ref 51). The operating principle of the OMA depends on the utilization of discrete portions of the electromagnetic spectrum. The "near" infra-red region, between 0.7–2.5 microns permits the use of relatively simple optical systems and includes a strong w-absorbent band at 1.93 microns so that moisture content may be determined by measuring the attenuation, at this wavelength, of an infra-red beam reflected from the surface of a sample. A reference beam (at a wavelength unaffected by moisture) is used to compensate for variations in reflectance and dispersion at the sample surface. Since both beams are responsive to these factors, the difference in attenuation represents the effect of moisture only

For this instrument to be applicable, a sample material must satisfy the following requirements: Its surface must be reflective enough to activate the PbS detector; it must be thermally non-conductive so that the infra-red energy will be reflected rather than transmitted; it must have a moisture content at the surface that is representative of the total moisture; and, it must not be so thin that incident radiation either passes thru the sample or is reflected by a backing material or a sample container

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Refs: 1) G.N. Huntly & J.H. Coste, JSCI **32**, 62–67 (1913) 2) M. Marqueyrol & E. Goutal, MP **19**, 368–80 (1922) & CA **17**, 3656 (1923) 3) W. Fermajin, SS **26**, 370 (1931) & CA **26**, 1124 (1932) 4) F. Becker & P. Dittmar, SS **29**, 327–31 & 371–75 (1934) 5) H.J. Eppig, "Caking of Photoflash Powder", PATR **1346** (1943) 6) L.H. Eriksen, "Action of Explosives on Metals Used in Ammunition", PATR **1388** (1944) 7) D. Hart, "Coating Agents for Magnesium and Magnesium Alloy", PATR **1403** (1944) 8) K.S. Warren, "Study of the Action of Lead Azide on Copper", PATR **1152** (1942) 9) R.D. Sheeline, "Develop Flashless Powder for 90mm Gun M1", PATR **1204** (1942) 10) D. Hart, "Investigation of the Stability of Igniter Composition 'K' and Red Tracer Composition", PATR **1303** (1943) 11) L.H. Eriksen, "Action of Explosives on Metals Used in Ammunition", PATR **1325** (1943) 12) K.S. Warren, "Study of the Effect of Moisture On 80-20 Tritonal", PATR **1560** (1945) 13) Anon, "Moisture Content Effect on Ballistic Performance of Propellants", OrdProofManual **7-26** (1945), 27, 29–31 14) H.J. Eppig, "Stability of Pyrotechnic Compositions Employed in the AN-M53 to M58 Aircraft Signals", PATR **1588** (1946) 15) L.H. Eriksen, "Surveillance of PETN and Pentolite Stored in Contact with Steel Strips", PATR **1598** (1946) 16) V. Lindner, "Deterioration of Propelling Charges; Determination of Effect of Rayons, Silk, and Cotton Cloth on Storage at 65°C with NH Smokeless Cannon Powder", PATR **1626** (1946) 17) W.R. Tomlinson, "Stability Tests of Aluminized Explosives", PATR **1635** (1946) 18) D. Hart, "Investigation of Stability of Igniter Composition 'K' and Red Tracer Composition", PATR **1645** (1947) 19) V. Lindner, "Deterioration of Propelling Charges; Examination of 155mm Gun Propelling Charges Received From the Canal Zone and Noumea, New Caledonia", PATR **1646** (1947) 20) H.J. Eppig, "Effects of Moisture on the Stability of Pyrotechnic Compositions", PATR **1661** (1947) 21) S. Livingston, "Long Range Research On Improved Igniter Type Powder. Develop Non-Hygroscopic Igniter Powder", PATR **1802** (1951) 22) Anon, "Test Method OD1A45-Karl Fischer", MIL-T-20326 (1951) 23) S.H. Liff, "Fuze Sealants", PATR **1899** (1952) 24) G. Weingarten & C.

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Moisture Instrumentation", Buyers Guide Issue, Instruments & Control Systems (1973) 59) B.W. Brodman & M.J. Ennis, "Moisture Indicating Lacquer for 20mm Ammunition", Frankford Ars MR **M-73-20-1** (1973) 60) Anon, "Explosive Composition A-5", US Mil Spec **MIL-E-14970B** (1974) 61) A.A. Nativo, "Instrumental Moisture Analysis of Initiating Explosives for Use in the Modernized Detonator Backline", PATR **4727** (1974)

Molasses (Treacle). There are several types of molasses, differing as to method of prepn and source; whether from beet root or cane sugar. In the beet sugar industry, molasses represents the final mother liquor, obtained after concn of the beet juice and crystn of white and brown sugars. Such molasses cont about 50% sucrose, with only traces of reducing sugars. In the cane sugar industries, molasses is a syrupy mother liquor left after the sugar has been removed by concn, crystn and centrifugation. If only one crop of crysts is removed, the molasses is known as "first molasses"; if two crops, as "second molasses", etc. The final mother liquor, from which no more sugar can be extrd by usual factory practice, is called "blackstrap" and cont about 30% sucrose and 20% reducing sugars (Refs 2, 3)

Korbonits(Ref 1), commenting on a spontaneous ignition in a molasses tank, recommended that excessive foaming be avoided. He stated that molasses should be poured slowly into tanks, stirring must be done slowly, and manholes should be left open until the molasses is cooled

Molasses in nitrated form has also been used in some expls (see below)

Refs: 1) A. Korbonits, Mezögazdaság és Ipar **3**, No 9, 25–28 (1949) & CA **46**, 283 (1952) 2) Kirk & Othmer **13**, 613–33 (1967) 3) CondChemDict (1971), 591-L

Nitrated Molasses. The nitration of molasses produces liq and solid nitrates of variable N content and expl props. They were used as constituents of Keil's expls and in Murtineddu Powder (qv)

Ref: Daniel (1902), 562–3

Molex Explosives. According to Hopper (Ref 2), Molex no's 2 & 3 are physical mixts of AN 52–84, K perchlorate 0–20, DNT oil 7–12, baked cork 1–10, Al powd 5–7 & Ca carbonate 1%. They exhibited satisfactory sensitivity to impact, friction, flame & initiation, and had excellent stability. Philips (Ref 4) reported on tests of Molex "B" and "BB", manufd by the National Explosives Co. They are described as physical mixts of AN 80.77–85.06, flake Al 6.02–6.10, DNT oil 4.32–5.84, activated cork 2.55–4.47, Ca stearate 1.10–1.99 and Ca carbonate 0.83–0.95%. They were shown to be stable, to have fairly high brisance, but to be sufficiently sensitive to expl in the rifle bullet impact test. Byers (Refs 1 & 3) describes blasting expls similar in compn

Refs: 1) L.S. Byers, USP 2079105 (1937) & CA **31**,4500(1937) 2) J.D. Hopper, PATR **938**, "Test of Explosive 'Molex' ", (1938) 3) L.S. Byers, USP 2136205 (1939) & CA **33**, 1500 (1939) 4) A.J. Phillips, "Tests of Molex Explosive 'B' and 'BB' ", PATR **1094** (1941)

Monachit. A Ger blasting expl also known as Vigorit. Monachit **I** cont AN 81, trinitroxylene (TNX) 13, K nitrate 5, and flour 1%. Monachit **II** cont AN 64, TNX 12, K nitrate plus Na nitrate 3, K chloride 19, charcoal 1, collodion cotton 1%. Monachit **II** has a limit charge of more than 500g. Its vel of deton at d 1.20 g/cc is about 4800m/sec, while at d 1.56g/cc it falls to 1780m/sec

Refs: 1) H. Kast, SS **8**, 136 (1913) 2) Marshall **1**, 392 (1917) 3) Marshall, Dict (1920), 63

Monakay Explosive. Dyn consisting of NG absorbed by a mixt, in equal wts, of Na nitrate, ashes, carbon blk, earth and borax, to which was added 12.5% kerosene

Ref: Daniel (1902), 442

Monarkite. Brit permitted mining expl contg typically NG 12.0, AN 4.97, Na chloride 24.5, Na nitrate 7.5, starch 4.0, mineral jelly 2.0, and collodion cotton 0.3%. Its charge limit is 26oz, and power by BalPend is 2.61 inches

Refs: 1) Marshall **1**, 396 (1917) 2) Marshall, Dict (1920), 63

Monoacyl Glycerol Nitrates. Formed by reacting in the liq phase at temps as high as 120°, a mixt of glycide nitrate and an aliphatic carboxylic acid of the benzene series such as benzoic acid, with $FeCl_3$ as catalyst. They were recommended as additives for NG, or like expls, to lower their freezing points
Ref: H. Jacobi & W. Flemming, USP 2302324 (1942) & CA **37**, 2014 (1943)

Monobels. Brit permitted mining expls made by Nobel's Explosives Co (Refs 1, 2 & 3):

Table 1

Monobel No	1	A1	A2
NG, %	8.5	10	10
AN, %	68	60	59
Woodmeal, %	8.5	10	10
Na chloride, %	15	–	–
K chloride, %	–	20	20
Mg carbonate, %	–	–	1
Limit charge, oz	10	28	22
Power (swing of BalPend), inches	2.81	2.78	2.44

The duPont Co manufd under this name, low velocity permissible expls in six grades, AA, A, B, C, D and E, based upon velocity and cartridge count. As a rule, these grades are used in operations where coarse coal is desired (Refs 4 & 5)
Refs: 1) Marshall **1**, 396 (1917) & **3**, 120 (1932) 2) Marshall, Dict (1920), 64 3) Davis (1943), 342 & 351 4) Blasters' Hdb (1950), 67 5) Cook (1958), 10

Mono-Oil. (Commercial mono nitro toluene). Mixt of about 62% ortho-, 34% para-, and 4% meta-nitrotoluenes. Yel oil with pungent odor; d 1.16g/cc; distills between 220–240°. It is used in low-freezing Dynamites, as a plasticizer for NC, and in blasting expls in combination with chlorates or nitrates. Such plastic expls have the desirable property of completely filling the bore hole by using only a light press. The oily nitro compound also serves as a protection against dampness, and it has the advantage of being an active ingredient in comparison with paraffins and greases which have previously been used as plasticizers
Ref: Bebie (1943), 103–4

Monopropellant. The common name for any single, stable fluid which cont an ozidizing agent and combustible material that can undergo an exothermic reaction to release heat for conversion to propulsive thrust in a typical rocket thrust-chamber assembly. It requires no auxiliary oxidizer for the release of its thermochemical energy, although it may require a solid or liq catalyst. The solid catalyst can be satd pellets previously soaked in a liq catalyst. Although the use of a liq catalyst to break down the monoproplnt actually constitutes a second working fluid, it has not become the practice to name these systems as biproplnt rocket power plants because the catalyst does not cont either the oxid or the fuel (Ref 4)

A partial list of monoproplnts that have been tested and applied to the production of rocket thrust includes concd high strength hydrogen peroxide (85% or above), ethylene oxide, ethyl nitrate, methyl nitrate, hydrazine, propane, nitromethane, and n-propyl nitrate (Refs 2 & 6)

The burning of a monoproplnt resembles the burning of a fuel in an internal combstn engine because of the formation of fine droplets, their vaporization and their burning, although no air is introduced as in a carburetor. Also, since the combstn chamber is a straight tube, there is no specific sepn between the droplets and the final gaseous combstn products. As a result, during equil burning, liq is being injected as a spray at one end of the chamber, vaporized further down the tube, ignited and completely decompd just prior to entering the exhaust nozzle. Because the flow rates are high and there is a considerable amt of turbulence, sharp definition of the various reactions is not possible. Nevertheless, there is a specific area which can be characterized as the "flame front". The liq and gaseous phase chemical reactions, and the interaction between such physical reactions as droplet formation, evapn, and diffusion, prevent the selection of any one process as the rate-controlling one. Experience has shown that each monoproplnt requires a specific type of injector and a specific chamber length for a given mass flow rate in order to ef-

fect complete decompn of the proplnt (Ref 3)

Liq monoproplnts are inherently unstable and consequently behave in an unpredictable manner. One of a number of reasons why this class of proplnts is not used more frequently is that they have a tendency to change over from an actual burning rate to a deton velocity. When this occurs in the inlet lines, the deton is transmitted back to the proplnt tank with disastrous results (Ref 3)

The term monoproplnt has also been applied to solids, where a solid monoproplnt is defined as a single physical phase comprising both oxidizing and fuel elements. These include many chemicals used as Mil high explosives, as the thermochemistry of proplnts is essentially the same as that for HE's. The difference between combstn and deton of a cryst monoproplnt is merely a difference in reaction rate (Ref 1). Except for primary expls which can deton on burning, these chemicals will burn quietly when ignited. They will deton only under the influence of a mechanical shock of severity far greater than can be found in a rocket chamber. The physical and ballistic props of **NGu, RDX, HMX, PETN, Amm nitrate,** and **Amm perchlorate** are detailed in Ref 5

Refs: 1) L. Wöhler & F.J. Roth, SS **29**, 9 (1934) 2) E. Burgess, "Guided Weapons", Macmillan (1957), 50–57 3) F.A. Warren, "Rocket Propellants", Reinhold (1958), 101–2 4) J.W. Herrick & E. Burgess, "Rocket Encyclopedia Illustrated", Acro Publishers, Inc, Los Angeles, Calif (1959), 276 5) Anon, EngrDesHdbk, "Solid Propellants, Part One", **AMCP 706-175** (Sept 1964), 42–44 6) Urbański **3** (1967), 291–321

Monotriethyl Lead Azoaminotetrazole. See Azoaminotetrazole, listed under Tetrazoles

Montan Wax (Lignite wax). White, hard earth wax; crude product, dark brown, mp 80–90°. Obtained by countercurrent extrn of lignite. Sol in CCl_4, benz & chlf; insol in w. It is combustible & nontoxic. Has been used extensively in Ger for coating particles of expls such as PETN & RDX, in order to reduce their sensitivity to impact and friction

Ref: CondChemDict (1971), 595-R

Montravel. In 1889 proposed treating the ingredients used in the prepn of BlkPdr with nitrobenzene. This procedure resulted in the formation of a thin coating on the grains which served as waterproofing

Ref: Daniel (1902), 443

Moorite Propellant. A series of rocket proplnts submitted to PicArsn for evaluation in 1949. They consisted of an oxidizer (such as K perchlorate) 70, and a cured rubber hydrocarbon plus accelerators, 30%. Although the examined samples proved to possess desirable props for rocket proplnt use, their thermal stability was poor and their press exponent undesirably high. It was concluded that further work was required on the method of prepn to eliminate these defects

Ref: C.S. Davis & J.E. Rainier, "Evaluation of Moorite Propellant", PATR **1748** (1949)

Morse's Powder (or Explosive). Inexpensive expl mixts, invented by C.A. Morse in 1880, consisting of NG and resin (colophony, copal, shellac, sandarac), with or without the addition of a nitrate or chlorate. The ingredients were disd in a common solvent, such as methanol, grained as the solvent distd off. Typical examples are: 1) NG 25, rosin 75% (mixed with 50p methanol); 2) NG 10, rosin 22, K nitrate 68% (mixed with 20p methanol)

Refs: 1) Daniel (1902), 443 2) Van Gelder & Schlatter (1927), 658

Mortars. See under Cannon, Vol **2**, C27-R–C28-L. Addnl updated references are given below

Refs: 1) Anon, "Field Maintenance: 60-mm Mortars M2 and M19", **TM 9-3071-1** (Jan 1958) 2) Anon, "Organizational Maintenance: M577 Mortar, 107-mm, Self Propelled", **TM 9-2300-224-20** (Dec 1961) 3) Collier's Encycl **2** (1965), 716–737 4) Anon, "Operation of and Organizational Maintenance Manual: Mortar 4.2 Inch and Mortar, Sub-Caliber, 60mm, M31", **TM 9-1015-215-12** (Jul 1966) 5) Anon, "Operation and Organizational Maintenance Manual: Mortar, 81-mm, M29A1 and M29", **TM 9-1015-200-12** (Apr 1971) 6) Encycl-

Britannica **2** (1973), 531–47 7) R.T. Pretty & D.H.R. Archer, "Jane's Weapon Systems 1973–74", McGraw Hill, NY (1973), 395–450 (Mortars in use by Finland, Fr, Ger, Switz, Br, USA, USSR & Yugoslavia) 8) F.W.A. Hobart, Edit, "Jane's Infantry Weapons", Franklin Watts Inc, NY (1975), 640-L to 727-R (Mortars & mortar ammo in use by China, Cz-Sl, Finland, Ger, Israel, Spain, Switz, Engl, USSR, USA & Yugoslavia)

Mortar, Ballistic. See Ballistic Mortar Test, Vol **2**, B6-R

Mortier and Sandon. Patented in 1897 the following cannon powd: K nitrate 65, trinitrocresol 25, charcoal 9 & stearic acid 1%
Ref: Daniel (1902), 443

Moss. Proposed as an absorbent for NG in Dyn
Ref: C.O. Black & W.A. Moore, USP 1713816 (1921) & CA **23**, 3576 (1929)

Motorite. An expl mixt, consisting of NG 70 and guncotton 30%, which was proposed in the USA for use as a fuel for the propulsion of torpedoes and torpedo boats
Ref: H. Maxim, CA **3**, 375 (1909)

Motors Activated by Explosives (Moteurs à explosifs). Huyghens, in 1678, first proposed construction of a motor in which the explns of BlkPdr were to be utilized for motive force. A similar concept was proposed in 1680 by Hautefeuille, and the first motor of this type was actually constructed later by Papin. Other motors were built in the 18th and 19th centuries, notably those of Gras, Renoir, Hureau de Villeneuve and Penaud, Wolf and Pietzcker, Hawkins, von Ruckterschell, etc. However, none of these could compete economically with steam engines existing at the time, even though they were lighter than steam engines of corresponding horsepower
Ref: Daniel (1902), 444

Mowbray, G.M. (1814–1891). Brit-American chemist who arrived from Engl about 1855, and was one of the first to manuf NG. His product was used in the construction of the Hoosac tunnel. He later did valuable work in the development of Zylonite (qv) and also exptd with proplnt powd
Refs: 1) Daniel (1902), 445 2) Van Gelder & Schlatter (1927), 375

MOX Explosives. Expl mixts contg a HE plus powd metal and an oxidizing agent. They were developed beginning in 1950 by National Northern, technical division of the National Fireworks Ordnance Corp, West Hanover, Mass, USA, and were used in small cal antiaircraft projectiles (Refs 1, 2, 3, 4, 5, 7 & 11). MOX formulations and more important props are given below (Ref 12):

Table 1
MOX FORMULATIONS AND PROPERTIES

Composition, %	MOX				
	1	2B	3B	4B	6B
NH_4ClO_4	35.0	35.0	–	–	–
KNO_3	–	–	18.0	–	–
$Ba(NO_3)_2$	–	–	–	18.0	–
Al, atomized	26.2	52.4	50.0	50.0	49.2
CuO	–	–	–	–	19.7
Mg, atomized	26.2	–	–	–	–
Other ingredients *	9.7	9.7	32.0	32.0	29.6
Ca stearate	1.9	1.9	2.0[a]	2.0[a]	–
Graphite, artificial	1.0	1.0	1.0[a]	1.0[a]	1.5
OB to CO_2, %	–44	–49	–52	–53	–50
OB to CO, %	–37	–43	–43	–43	–42
Q_c, cal/g	4087	4484	4331	4392	4293
Q_e, cal/g	2087	1472	980	709	750
Gas vol, cc/g	212	221	232	208	204
Activation energy, kcal/mole	12.5	7.6	–	–	–
PicArsn Impact Test, inches	13	12	17	18	19
Expln temp, 5 sec, °C	285	375	540	610	510
Sand Test Value	10.6	11.5	33.2	33.6	10.8
100° Heat Test:					
% Loss, 1st 48 hrs	0.10	0.27	0.35	0.22	0.00
% Loss, 2nd 48 hrs	0.01	0.12	0.13	0.12	0.00
Explosion in 100 hrs	None	None	None	None	None

* (MOX-1) Tetryl
(MOX-2B) 5.8% RDX & 3.9% TNT coated on NH_4ClO_4
(MOX-3B) 29.1% RDX, 0.9% wax & 2.0% TNT
(MOX-4B) same as 3B
(MOX-6B) 28.7% RDX coated, 0.9% wax

[a] Percent added

Blast measurements made with MOX-2B are given relative to TNT in Ref 12:

Table 2

	Bare Charge in Air		Cased Charge in Air**	
	EW*	EV*	EW	EV
Peak Pressure	1.02	1.34	1.09	1.44
Impulse	1.08	1.41	1.16	1.53
Density, g/cc	1.96	1.96	1.98	1.98

* EW, equiv wt as compared to TNT
* EV, equiv vol as compared to TNT
** strong, paper base phenolic case

Preparation of MOX Explosives

The various ingredients used in the prepn of MOX expls are coated separately as follows: *Dichromated Atomized Aluminum.* 75g of chemically pure grade Na dichromate is dissolved in 1500ml of w at 100° under mechanical agitation. 600g of atom Al powd is added gradually (2–3 mins) and stirring is continued for 0.5 hr. The dichromated material is filtd, washed with w (15–20 times) until the washings show only a sl cloudiness with Ag nitrate. The w

wet prod is then dried at 50°, hand-rolled to reduce any agglomerates, and blended before use

Wax-Coated RDX. 18g of molten Be Square Special Wax (manufacturers' 180° to 185°F grade amber) is added to 582g of finely divided RDX (w pptd from acet soln) in a w slurry under mechanical agitation. The temp of the wax-RDX slurry is maintained above the mp of the wax (about 90°), and the stirring is contd for 0.5 hr. After cooling to 50°, the wax-coated RDX is recovered by filtrn and air dried. The RDX thus coated and presumed to be 3% waxed RDX or a 97/3 RDX/wax mixt, is hand rolled to crush agglomerates and hand blended before use

TNT-Coated Barium Nitrate. 30g of TNT in alc soln is added to 270g of Ba nitrate in an alc slurry under agitation. The temp of the mixt is maintained at 80° and stirring is contd until most of the alc is evapd. The coated material is spread in a thin layer and air dried overnight. The Ba nitrate thus coated with 10% TNT is reduced to an intimate mixt by hand rolling and blending before use

TNT-Coated Potassium Nitrate. Prepd by the same procedure used for coating Ba nitrate

RDX/TNT Coated Ammonium Perchlorate. The Amm perchlorate is coated by dissolving the appropriate wts of RDX & TNT in hot alc. After adding the Amm perchlorate, the slurry is stirred until most of the solv is evapd. The treated material is spread on a tray to dry overnight. Agglomerates formed during the process are crushed by hand rolling and blending the mixt before use

TNT Coated RDX. 60g of molten TNT are added to a w slurry of 540g of finely divided RDX (w ppt from acet soln) under mechanical agitation. The temp of the TNT-RDX slurry is maintained at about 90° and stirring is contd for 0.5 hr. After cooling to about 50°, the TNT-coated RDX is recovered by filtrn. The RDX thus treated, and presumed to be 10% coated or a 90/10 RDX/TNT mixt, is further blended by hand after rolling to crush any aggregates formed during the process

The MOX expl mixts are prepd by blending the appropriate wts of the dry ingredients in a twin-shell blender for at least 30 mins

Written by **S. M. KAYE**

Refs: 1) A.O. Mirarchi & A.T. Wilson, "Development of MOX Explosives for Improved 20mm Ammunition", Navy Contract NOrd-10975, Task 1, National Fireworks Ordnance Corp, First Yearly Summary (Aug 1950–Aug 1951) 2) A.T. Wilson, "Development of MOX Explosives: Various Oxidants in MOX", First Progress Report NFOC-6, Navy Contract NOrd-12382, National Fireworks Ordnance Corp (Dec 1952) 3) A.O. Mirarchi, "Properties of Explosives: Theory of the MOX Explosion", First Progress Report NFOC-10, Navy Contract NOrd-11393, National Fireworks Ordnance Corp (Dec 1952) 4) A.O. Mirarchi, "Properties of Explosives: MOX Explosives in Various Atmospheres", First Progress Report **NFOC-9**, Navy Contract NOrd-11393, National Fireworks Ordnance Corp (1952) 5) A.T. Wilson, "Development of MOX Explosives: Composition Variations", First Progress Report **NFOC-7**, Navy Contract NOrd-12382, National Fireworks Ordnance Corp (1952) 6) S.M. Adelman, P.B. Tweed & J.D. Hopper, "Study of Loading of MOX-2B Into 20mm Shell and Acceptance Tests of Cartridges Containing Projectiles Filled with this Explosive", PATR **1935** (11 May 1953) 7) A.T. Wilson, "Development of MOX Explosives: Various Oxidants in MOX", Second Progress Report **NFOC-14**, Navy Contract NOrd-13684, National Fireworks Corp (Oct 1953) 8) V. Lindner & S.M. Adelman, "Investigation of the Effects of Composition Variations on the Properties of the MOX-Type Explosives", PATR **1969** (26 Oct 1953) 9) O.E Sheffield, "Properties of MOX-Type Explosive Mixtures", PATR **2205** (Oct 1955) 10) P.Z. Kalanski, "Air Blast Evaluation of MOX-2B Cased and Bare Charges", NAVORD **3755** (5 Apr 1956) 11) A.W. O'Brien, Jr, C.W. Plummer, R.P. Woodburn & V. Philipchuk, "Detonation Velocity Determinations and Fragment Velocity Determinations of Varied Explosive Systems and Conditions", National Northern Corp Final Summary Report NNC-F-13, Contract DAI-19-020-501-ORD-(P)-58 (Feb 1958) 12) Anon, EngDesHdbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (Jan 1971), 213-225

MSX. Code name for 1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane. Described in Vol **1**, A53-L

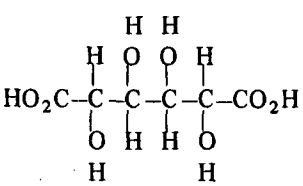
MS-80 Blasting Agents. Dow Chemical Co. products consisting of soft, silvery gels contg AN and Al particles. Five different strengths are available, ranging from 1.4 to 6.0 times the blasting power of AN-fuel oil expls. Their blasting power is detd by the Al content, which ranges from 5 to 30% by wt. Although they contain no TNT, NG or other HE sensitizer, Dow claims that they outperform slurries contg Al plus TNT
Ref: Anon, C&EN **42**, 29–30 (April 27, 1964)

MTTC. A Fr expl contg PA 55, TNT 35 and TN-m-cresol 10%, melting below 100°, used for cast loading of HE projectiles. DNPh can be substituted for TN-m-cresol (Ref 4)
Refs: 1) Pascal (1930), 214–17 2) Vennin, Burlot & Lécorché (1932), 457 3) Davis (1943), 166 4) Bebie (1943), 104

MTX. A Fr expl used during WWI consisting of PA, TNT and TN-m-xylene. Pascal (Ref 1) gives its compn as PA 30, TNT 20 and TN-m-xylene 45%, while Vennin, Burlot & Lécorché (Ref 2) state the ratio as 55/35/10
Refs: 1) Pascal (1930), 213 2) Vennin, Burlot & Lécorché (1932), 457

MUCIC ACID AND DERIVATIVES

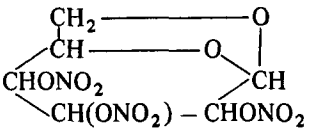
Mucic Acid (Galactaric acid, Galactosaccharic acid, Tetrahydroxyadipic acid, Saccharolactic acid, Schleimsaure (Ger).



mw 210.14, OB to CO_2 –68.53%, white prisms, dec about 255° when heated rapidly, 210° when heated slowly. Sol in 300p cold w, 60p boiling w, alkalies; practically insol in alc & eth. Prepn from oxidation of lactose with dil nitric acid on heating (Ref 1)
Refs: 1) Beil **3**, 581, (201), [380] & {1122} 2) Merck Index (1968), 478-R

Diazomucic Acid. $N_3.CO.(CHOH)_4.CO.N_3$, mw 260.20, N 32.31%, OB to CO_2 –61.49%, microcryst, very sol in w. Prepd from mucic acid hydrazid and nitrous acid. It explodes on heating
Ref: Beil **3**, 585 & (202)

Mucic Acid Trinitrate (Galactan Trinitrate).



mw 297.16, N 14.14%, OB to CO_2 –24.20%, cryst. Prepn from d-galactose and mixed acid (nitric/sulfuric). Brisance by sand test; 0.4g (13.45% N) crushes 42g of sand. Impact sensitivity is the same as Tetryl. The material is very unstable; however, this may be because of impurities
Refs: 1) Beil, not found 2) Blatt, OSRD **2014** (1944)

Silver Mucic Acid Diamide. $HO_2C.NAg.CHCHOH.OCH.CHOH.AgN.CO_2H$, mw 435.90, N 6.43%, OB to CO_2 –33.04%, gelatinous ppt. Prepn from diazomucic acid by heating in w and reacting the product in NaOH soln with Ag nitrate. The compound explds on heating
Ref: Beil **3**, (202)

Mudcapping. Rocks and boulders buried either partially or completely underground can be successfully removed by operations such as *"blockholing"* or *"snake-holing"* (qv). If, however, the boulder or rock is at ground level or only slightly imbedded, it may be broken up by positioning a fused expl charge (usually 1–3 lbs per cubic yard of boulder) atop the boulder, plastering it over with mud and firing. The mud covering, usually 3–4 inches thick, should be free from stones, as the blast would propel them as projectiles
Refs: 1) Meyer (1943), 398 2) Blasters' Hdbk (1950), 317 & 361 3) C.E. Gregory, "Explosives For North American Engineers", Trans Tech Publications, Cleveland, Ohio (1973), 236

Müllerites. Smokeless NC shot-gun powds

manufd by Müller et Cie in Belg, contg no inorganic salts
Refs: 1) Daniel (1902), 446 2) Barnett (1919), 87 3) Marshall, Dict (1920), 64

Multiperforated Propellant Grains. See Cannon Propellant or Cannon Powder in Vol **2**, C30–31, & Grains of Smokeless Proplnts in Vol **6**, G123

Mundell or Pertuisset Powder. Compn proposed by de Fleuron in 1867 to be used in lieu of BkPdr. It consisted of K chlorate 63.49, sulfur 31.74, BkPdr 4.14 & animal charcoal 0.63%
Ref: Daniel (1902), 447 & 610

Munroe, Charles Edward (1849–1938). Leader in the development of expls in the USA. Inventor of the first American smokeless powder, *Indurite* (qv), and discoverer of the **Munroe Effect** (See Detonation, Munroe-Neumann Effect (Or Shaped Charge Effect) in Vol **4**, D442-R to D454-L). Professor of chemistry at the US Naval Academy, Annapolis, Md, 1874–1886; chemist at the Naval Torpedo Station and Naval War College, Newport, RI, 1886–1892; professor of chemistry at George Washington University, 1892–1917; and chief expls chemist of the US Bureau of Mines, 1919–1933. Author and co-author of numerous publications on expls
Refs: 1) H.W. Wiley, IEC **15**, 648–9 (1923) 2) Anon, JACS News Ed **16**, 647 (1938) 3) C.A. Browne, JACS **61**, 731 (1939) 4) Davis (1943), 18–20

Muraour, Henri (1881–1954). Fr scientist, a specialist in expls (Ingénieur général des poudres) and ballistics. Published more than 200 papers from WWI thru 1952 (Ref 2) on expls, proplnts, combstn of proplnts, expl phenomena, antiflash agents, purification of TNT, theory of expl reactions, etc, as well as a widely read book (Ref 1)
Refs: 1) H. Muraour, "Poudres et Explosifs", Presses Universitaires de France, Paris (1947) 2) Anon, MAF **24**, 586–608 (1950) & CA **46**, 7329 (1952) 3) Anon, MAF **28**, No 108 (1954) (Obituary)

The following references detail Muraour's more important publications: 1) H. Muraour & G. Aunis, CR **192**, 418–21 (1931) & CA **25**, 2569 (1931) (Variations in $\int$Pdt with loading d for poudres B contg either vaseline or centralite) 2) H. Muraour & G. Aunis, CR **193**, 1082–4 (1931) & CA **26**, 1124 (1932) (Continuation of work in Ref 1) 3) H. Muraour & G. Aunis, CR **194**, 1927–9 (1932) & CA **27**, 190 (1933) (Influence of proplnt temp on variation of $\int$Pdt at different loading d's) 4) H. Muraour & G. Aunis, CR **196**, 478–80 (1933) & CA **27**, 2301 (1933) (Laws of combstn of mixts of slow & fast burning proplnts are the same as for the slow burning proplnt alone, ie, if $\int$Pdt is plotted vs time, the values fall on the same straight line in both cases) 5) H. Muraour, BullFr **9**, 511–16 (1942) & CA **37**, 6526 (1943) (Rate of combstn of colloidal proplnts as a function of the press & temp of emitted gases) 6) H. Muraour, Chim&Ind(Paris) **47**, 602–606 (1942) & CA **40**, 2985 (1946) (Study of the validity of the relation V=a+Pdt in combstn of proplnts) 7) H. Muraour, Chim&Ind(Paris) **48**, 11–13 (1942) & CA **38**, 4446 (1944) (Investigation of the change of $\int$Pdt with d of charge) 8) H. Muraour, Chim&Ind(Paris) **49**, 253–4 (1943) & CA **39**, 3161 (1945) (Influence of the variable "time" in the combstn of colloidal proplnts in a closed vessel) 9) H. Muraour, Chim&Ind(Paris) **49**, 254–5 (1943) & CA **39**, 3161 (1945) (Influence of geometric form of proplnt grains on the total effect of pseudo-radiation) 10) H. Muraour, Chim&Ind(Paris) **50**, 105–08 & 168–72 (1943) & CA **39**, 3161 (1945) & **40**, 2986 (1946) (Relation between expl temp of a proplnt and its vel of combstn; experimental results) 11) H. Muraour & G. Aunis, CR **220**, 198–9 (1945) & CA **40**, 5252 (1946) (Variation in the rate of combstn of colloidal proplnts as a function of temp) 12) H. Muraour & G. Aunis, CR **225**, 381–3 (1947) & CA **42**, 2431 (1948) (Modification of a previously presented formula for the relation between the expl temp of a colloidal proplnt and its combstn vel; the new formula reads: $V=0.13+0.54(T_B')$ / 1000, where V is burning rate and T_B' is the temp reached after NO has completely disappeared) 13) H. Muraour & G. Aunis, MAF **22**, 133–70 (1948) & CA **44**, 8659 (1950) (The press and covolume

of colloidal proplnts) 14) H. Muraour, G. Aunis & J. Domart, MAF **22**, 517–93 (1948) & CA **44**, 8659 (Detn of the quickness of combstn of colloidal proplnts in a bomb) 15) H. Muraour & G. Aunis, CR **228**, 818–20 (1949) & CA **43**, 5189 (1949) (Study of the laws of combstn of colloidal proplnts; remarks on the equation V=a+bP) 16) H. Muraour & G. Aunis, CR **229**, 173–5 (1949) & CA **43**, 8681 (1949) (Relation between the potential and vel of combstn of colloidal proplnts) 17) H. Muraour, Chim&Ind(Paris) **62**, 22–25 (1949) & CA **44**, 329 (1950) (Exptl detn of vel of combstn of proplnts) 18) H. Muraour & G. Aunis, CR **229**, 749–51 (1949) & CA **44**, 3257 (1950) (Relation between expl temp of a colloidal proplnt and its rate of combstn) 19) H. Muraour & G. Aunis, MAF **23**, 859–66 (1949) & CA **45**, 1769 (1951) (Study of the quickness of colloidal proplnts) 20) H. Muraour & J. Fauveau, Chim&Ind(Paris) **65**, 53–5 (1951) & CA **45**, 7353 (1951) (The combstn of colloidal proplnt in N_2 at pressures from 100–10000kg/sq cm) 21) H. Muraour & G. Aunis, Chim&Ind(Paris) **67**, 920–6 (1952) & CA **46**, 10623 (1952) (The relation between the expl temp of a proplnt and its burning rate; exptl verification on Fr & foreign proplnts)

Murtineddu Powder. A mixt patented in 1856 contg K or Na nitrates, sulfur, sawdust, dried horse dung, Na chloride and nitrated molasses
Ref: Daniel (1902), 447

Mustard Gas (Yperite, 2,2′-Dichlorodiethyl sulfide). $C_4H_8Cl_2S$, mw 158.9, oily liq, bp 215–17°, d 1.28g/cc. A toxic agent first employed by Ger during WWI at Ypres in 1917. Its variants are still deployed for military use. Mustard and its modern derivatives are almost colorless but have a faint garlic or mustard smell if impure. It penetrates normal clothing, causing severe burns, and it inflames the eyes and irritates the lungs. Short exposure to an atm concn of one p in 100000 causes acute vomiting and fever. The effect is delayed so that an effective dose can be absorbed before the agent is detected. Modern derivatives, **T**, **Q** and **HN-3**, are lethal in smaller doses. **Q** causes incapacitating blisters after 3mgs are absorbed. No adequate treatment exists, and mustard is the most severe blistering agent in existence
Refs: 1) Hackh's (1944), 554-L 2) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 136-R

Muzzle. The end of the barrel of a gun from which the bullet or projectile emerges
Ref: OrdTechTerm (1962), 199-R

Muzzle Brake. (Freins de bouche in Fr, Mündungsbremse in Ger). A cylindrical device with flanged or baffled surfaces which is attached to the muzzle of a gun, usually by threads, to offset a long or complete recoil of the gun when fired. The expanding proplnt gases strike the baffles, thus pushing the gun barrel forward. This action can shorten the actual recoil distance, or it may relieve an overloaded recoil system. The latter would occur when a conventional gun was deliberately overloaded to increase the projectile velocity
Refs: 1) A. Rateau, MAF **11**, 5–34 (1932) (Théorie des freins de bouche) 2) F.H. Simpson, "Study of the Effect of Muzzle Brake Design on the Recoil of Guns", OSRD **4389** or PBL 51008 (1944) 3) G.B. Jarrett, "Achtung Panzer", The Story of German Tanks in WWII, Great Oaks, RD 1, Aberdeen, Md (1948), Appendix 3 4) OrdTechTerm (1962), 51-R

Muzzle Flash or Muzzle Flame. Flame that appears at the muzzle of a gun when a projectile leaves the barrel. See Flash Reducing (or Antiflash) Agents, Flash Reduction in Ger Projectiles, and Flash Reduction in Ger Proplnts, Vol **6**, F96-L to F99-L
Ref: OrdTechTerm (1962), 200-L

Muzzle Velocity (MV, Initial Velocity). The velocity at which a projectile leaves the muzzle of a gun, expressed either in m/sec or ft/sec. The moment the projectile emerges from the bore, its velocity starts to decrease because of air resistance. For this reason, the muzzle velocity is considered as the max velocity of a

projectile. Strictly speaking, however, this is not true, because the projectile might be slightly accelerated after emergence from the bore by expanding propInt gases immediately after friction between the projectile and the bore has ceased. As it is very difficult to detn the velocity close to the muzzle, the usual practice is to measure it a short distance from the muzzle, eg, 78 ft, and then either to correct back to the muzzle for the retardation in flight (as is done for artillery ammo), or to take it as such (usually done for small arms ammo)

Muzzle velocities may either be calcd by means of equations, such as that of LeDuc (Ref 1, p 74) or detd experimentally thru use of chronographs (Refs 4 & 5)

Refs: 1) Hayes (1938), 74–80, 84 2) Ohart (1946), 4, 5, 70, 72, 182 & 190 3) G.M. Barnes, "Weapons of World War II", VanNostrand, NY (1947), 43, 51, 63, 66, 68, 114, 118, 124, 125, 128, 134, 140, 146, 164, 168, 170, 178, 182 & 184 4) Encycl **2** (1962), B5-R to B6-L (Ballistic Measuring Methods and Ballistic Tests) 5) Encycl **3** (1966), C304-R to C319-L (Chronographs)

MVT. Abbr for Methyl Vinyl Tetrazoles, described under **Tetrazoles**

Myrite. An expl contg a mixt of nitrogen dioxide and carbon bisulfide. Its sensitivity to mechanical influences, brisance, rate of deton, and other expl characteristics were detd at PicArsn in 1940. In view of the fact that it is specially sensitive to rifle bullet impact, and has a rate of deton and brisance considerably lower than TNT, it was concluded that Myrite is not suitable for use as a military expl

Ref: C.J. Bain, "Investigation of the Explosive 'Myrite' ", PATR **1030** (1940)

Myrobalan. The dried fruits of certain Indian and Chinese trees, contg about 30% tannin. After extrg the tannin, the powd material was used as an ingredient of some commercial expls

Refs: 1) Hackh's (1944), 555-L 2) Cond-ChemDict (1950), 455

Myrobalan Explosive. Commercial blasting expl contg myrobalan 36, K nitrate 28 & Amm perchlorate 36%

Ref: D. Kilburn, FrP 389905 (1908) & CA **4**, 2733 (1910)

Myrol. A Ger liq expl consisting of a soln of methyl nitrate in methanol or other solvents. The term Myrol was also used to designate straight methyl nitrate. The material prepd prior to WWII, by cautiously adding methanol to a mixt of nitric and sulfuric acids, proved to be impure, unstable in storage and very sensitive to heat and shock. During WWII, Walter et al (Ref 2), developed a continuous method of manuf of methyl nitrate from methanol and dil nitric acid, which gave a pure and much more stable product than that prepd previously. A detailed description of the method of prepn is given in Ref 2, pp 9–10. Pure methyl nitrate proved to be an expl more powerful than NG, with a brisance exceeding any other HE known, and with a sensitivity to shock comparable to that of PETN. Pure methyl nitrate is a clear mobile liq with a bp of about 63°, and is insol in w

Inasmuch as methyl nitrate is very sensitive to mechanical action, it was found much safer to use it in methanol soln. Such solns, called Myrol, may be obtained directly in the methyl nitrate manufg process, since all that is necessary is to use an excess of methanol. One of the most suitable solns proved to be an azeotropic mixt consisting of about 75% methyl nitrate and 25% methanol. This mixt has a bp of 57.5°. *Myrols contg at least 25% methanol will not evaporate to leave 100% methyl nitrate*

Römer (Ref 1) calls Myrol a mixt contg 73% methyl nitrate and 27% technical methanol contg 4% w. Tschinkel (Ref 3) states that Myrol consisted of 80 wt % methyl nitrate and 20 wt % methanol

Following are some props of methyl nitrate–methanol mixts: vel of deton ranging from 2400–4900 to 7500–8200m/sec, gas vol about 873ℓ/kg, Q_e 1640–1700kcal/kg, power and brisance – comparable to those of NG, sensitivity to shock – comparable to that of DNB, and toxicity – comparable to that of aliphatic

nitrates, such as NG and PETN. Like NG, Myrol causes headaches and pulse excitation, but they disappear more rapidly than with NG. Caffein or coffee proved most successful in decreasing pulse excitation

Refs: 1) G. Römer, "Report on Explosives", PBL Rept **85160** (1945) 2) H. Walter et al, "German Development in High Explosives", PB Rept **78271** (1947) 3) B.T. Fedoroff et al, "Dictionary of Explosives, Ammunition and Weapons (German Section)", PATR **2510** (1958), 113–114

Myrol Explosives. Methyl nitrate (qv) and its mixts with methanol, benz, NB, etc found extensive application by Ger in WWII as ingredients of numerous liq, plastic and solid proplnts and expls. Some of these mixts were known as Ersatzsprengstoffe (substitute expls)

In the case of liq expls and proplnts, Myrol (methyl nitrate plus methanol) was used either by itself or in mixts with liqs such as benz, MNB, etc. For use as a plastic expl or proplnt, Myrol was treated with small quantities of NC to form a soft jelly. As a solid expl or proplnt, it was treated with 25–30% NC to form a hard jelly, or was mixed with the usual sol ingredients of dynamites, such as kieselguhr, sawdust, inorganic nitrates, lignin, etc

Because of the fact that Myrol is a volatile liq, all mixts contg it had to be kept in air-tight containers

Several Myrol manufg plants were constructed in Ger during the latter part of WWII, and total capacity was as great as 20000 metric tons per month. The largest of these plants was the Christianstadt Fabrik of Dynamit A-G, with a capacity of 400 tons per month

Myrol expls were used for the following purposes: (1) Liq Myrol mixts were used as rocket proplnts, as charges for bangalore torpedoes, land mines, bombs, special fuzes, and for clearing trenches, foxholes, etc; (2) Plastic Myrol mixts were used as military demolition charges and mining expls; (3) Solid Myrol expls were used as bursting charges in land mines, the 50-kg projector mine, hand grenades, V-1 and V-2 rocket warheads, the bursting charge of Panzerfaust (anti-tank shaped charge), boosters, etc

More detailed information on Myrol Expls and their uses can be found in the refs

Refs: 1) G. Römer, "Report on Explosives", PBL Rept **85160** (1945) 2) H. Walter et al, "German Development in High Explosives", PB Rept **78271** (1947) 3) J.G. Tschinkel, C&EN **32**, 2586 (1954) (Propellants for Rocket & Space Ships) 4) B.T. Fedoroff et al, "Dictionary of Explosives, Ammunition and Weapons (German Section)", PATR **2510** (1958), 114–16

V14 P219

N

"N" (Explosifs de Mine). Several types of older Fr mining expls: **No 1a** (couche), AN 95.5 & TNN 4.5%; **No 1b** (roche), AN 91.5 & TNN 8.5%; **No 1c**, AN 87.4 & DNN 12.6%; **No 1d**, AN 82.4, DNN 12.6 & Ba nitrate 5%; **No 2**, AN 80 & MNN 20%
Ref: Daniel (1902), 448

N^{15}, Reactions with. The course of the reaction between diazomethane and hydrazoic acid was studied using N^{15}-labeled reactants. It was also found that labeled methyl azide could be reliably analyzed by decompn with HI, and that unambiguously N^{15}-labeled methyl azide could be made by treating methylurea with $HN^{15}O_2$ and decompg the product with KOH to CH_2NN^{15} (Ref 2). Another study noted that in the course of the diazotization of benzhydrazide and 2,4-dinitrophenylhydrazine with $HN^{15}O_2$, only azides of the structure $R-N=N=N^{15}$ were formed (Ref 1)
Refs: 1) K. Clusius & K.Schwarzenbach, Helv **41**, 1413–16 (1958) & CA **53**, 4112 (1959) 2) K. Clusius & F. Endtinger, Helv **41**, 1823–30 (1958) & CA **53**, 5121 (1959)

N57. An older Italian proplnt used in 57mm guns. Its compn was similar to that of the American Maxim-Nordenfeldt powder (see in this Vol, p M46-R
Ref; Daniel (1902), 448

NACO (Navy Cool). A type of proplnt developed by the US Naval Ordnance Station, Indian Head, Md. It burns at temps 300° cooler than standard proplnts, thereby reducing gun-barrel wear by more than 50 percent (Ref 3). A typical formulation contains NC (12.00% N) 87.30, K sulfate 3.30, basic Pb carbonate 1.19, butyl stearate 4.16, ethyl centralite 1.03 & total volatiles 3.02% (Refs 1 & 2)
Refs: 1) J.A. Krystofik, "Ballistic Test of NACO Propellants 1X-320, 332, 332A, 332B, 332C and 1X-337 in the 3″/70 Caliber Gun", Naval Proving Ground Rept **1565** (April 1958) 2) N.H. Carpenter, "Development of a NACO (Navy Cool) Propellant for the 5″/54 Caliber Gun", Naval Proving Ground Rept **1611** (August 1958) 3) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 319

Nahsen Dynamites. Contained creosote to lower the freezing point of the mixt. A typical formulation contained creosote 41.5, NG 25.0, K nitrate 18.0, rye flour 9.0, collodion cotton 1.0 & Na bicarbonate 5.5%
Ref: Daniel (1902), 449

Nahsen Explosives. Several commercial expls of the carbonite type were patented in 1899 by Spregnstoffwerke Dr R. Nahsen & Co of Hamburg, Ger. One was named "Phoenix Powder" and contained NG 29.5, K nitrate 32.0, wood meal 38.0 & collodion cotton 0.5%
Refs: 1) Daniel (1902), 449 2) Marshall, Dict (1920), 74 3) Giua, Trattato **6** (1959), 385

Nail Test. A simple, inexpensive test for comparing the performance of detonators, developed at the Explosives Experimental Station of the US bureau of Mines by C. Hall (Refs 1 & 2). The test depends on the angle formed by a standard iron nail when a detonator is fired in close proximity to it, and gives a rough indication of the side blow of the detonator. Tests of this type should be used only for comparing constancy of manufacture in a single type of detonator. Its use in comparing detonators of different constructions can be grossly misleading
Refs: 1) C. Hall & S.P. Howell, USBurMines-Bull **59** (1913), 25–6 2) C.E. Munroe & J.E. Tiffany, USBurMinesBull **346** (1931), 113–14 3) S. Fordham, "High Explosives and Propellants", Pergamon Press, NY (1966), 114

Nansenit. A Russian pre-WWI mining expl containing AN 68, K nitrate 4, DNT 7, Na chloride 15 & vegetable oil 6%
Ref: Anon, SS **12**, 409 (1917)

Naoúm, Phokion (1875–1951). German scientist specializing in expls. He was associated for over 40 years with Dynamit A-G vorm Alfred

Nobel & Co, at Schlebusch-Manfort, and published works on NG, Nitrosugar, Dinitroglycol, coal mine expls, etc. He was also the author of books dealing with expls, such as: 'Scheiss-und Sprengstoffe", T. Steinkopf, Dresden & Leipsig (1927) and "Nitroglycerin und Nitroglycerinsprengstoffe", J. Springer, Berlin (1924). The latter work was translated into English by E.M. Symmes ("Nitroglycerin and Nitroglycerin Explosives") and published by Williams & Wilkins Co, Baltimore, Md, in 1928

Ref: A. Berthmann, AngChem **63**, 249–50 (1951)

Napalm (Thickened Fuel). An acronym for NAphthenic acid and PALMetate, the former being a petroleum product, while the latter is extracted from palm oils. Napalm was developed by Dr Louis F. Fieser of Harvard University and a group of colleagues in 1941–42 under the sponsorship of the National Defense Research Committee. Although a patent was filed in 1943, because of national security imlications, issuance of the patent was delayed until 1952 (Ref 3). Dr Fieser and his group began the search for a gasoline thickening agent for use as a flamethrower fuel shortly before Pearl Harbor. Their early work concerned the possible use of rubber mixed with gasoline, however, with rubber supplies cut off by the Japanese, the scientists had to seek some other means. Their research led to Napalm which consisted basically of the Al soaps of coconut fatty acids, Al naphthenate, and unsaturated fatty acids (Ref 4). The term Napalm has, over the years, been used to denote the total thickened fuel

Napalm has been used as an incendiary filler for air-to-ground bombing as well as a fuel for flamethrowers. The jellied composition, the extremely high temp produced on ignition, and its low cost make Napalm an ideal weapon against "soft" targets such as humans and most kinds of primative dwellings. It is also extremely effective against armored vehicles, because their armor operates as a heat conductor which broils the crew inside. Since it flows as a liq it can also be used against concrete bunkers and similar fortifications, although most modern fortifications have overhanging lips above the firing slits intended to prevent the fluid from flowing inside. Napalm is not suitable for use against "hard" structures such as bridges. An operational problem with Napalm is that its density is low so that tanks filled with it are bulky in relation to their weight, and this reduces the speed of carrying aircraft. The intense heat produced by Napalm can "kill" armored vehicles even if only a near-miss is scored, so that it is far superior to an explosive bomb for this mission (Ref 8)

Langstroth and Hart (Ref 1) detd the heat capacities of gasoline, Napalm, and various Napalm-gasoline gels by the method of mixts using an adiabatic calorimeter in the range of -50° to 50°. The specific heat in cal per g per degree at temp T° within this range is given by: $S_T = 0.479-0.00054C + 0.00092T$ where C denotes the Napalm concn by wt

There are presently three common fuel thickeners used by the US Armed Forces. These are M4 thickener (Standard A); M1 thickener (Standard B); and M2 thickener (Air Force Standard A)

M4 Thickener: It is a fine, white powder which is a by-product of petroleum. Chemically, it is a diacid Al soap of isooctanoic acid. As a general comparison with M1 thickener (the original Napalm), only one-half as much M4 thickener is needed to obtain thickened fuel of the same consistency, an unpeptized gel can be obtained at lower temps, and the aging time is shorter. It is much less susceptible to moisture in the air, and has a higher density than the other thickeners, which gives it a decided logistic advantage. Fuels prepd with M4 thickener are superior in flamethrower firing performance with respect to range, burning, and target effects as compared with fuels prepd with other available thickeners (Ref 6, p 41; Ref 7, p 8)

M1 Thickener: It is a coarse, granular material ranging in color from light tan to brown. Chemically, it is a coprecipitated Al soap of naphthenic, oleic and palmitic acids in the approx ratio of 1:1:2. The three main disadvantages accruing from the properties of M1 thickener are (1) it is a critical wartime material since it is made from coconuts; (2) it is extremely hygroscopic, and the presence of water decreases its ability to form a stable thickened fuel. In addition, the relatively large

particles of the thickener permit circulation of air into the bulk of the material, causing extensive absorption of moisture. Thus, a partially used container of M1 thickener should be discarded; (3) M1 thickener is too coarse to be used in continuous flow mixers, and can only be used for hand mixing or small field mixing unit operations (Ref 7, p 8)

When M1 thickener is stirred into gasoline at a temp ranging from 16° to 29°, it swells until the entire volume of gasoline becomes a more or less homogeneous gel. The gel may vary in consistency from a pourable fluid to a rubbery material, depending upon the proportion of thickener added. This type of gel, if allowed to set undisturbed, assumes a semirigid jellylike form. If the gel is shaken violently, stirred vigorously, or squirted thru a small opening under pressure, it becomes almost liq again, but resumes a jellylike form upon standing. The percentage of M1 thickener used ranges from 2 to 12% (Ref 6, p 41)

M2 Thickener: It is pulverized M1 thickener with an antimoisture substance (attasorb clay) added in the ratio of 1p attasorb clay to 19p M1 thickener. It readily absorbs moisture from the air, but not to the extent of M1 thickener, because less air circulates thru the pulverized particles; the attasorb clay further lowers moisture absorption. A container may be resealed after part of the M2 thickener has been used provided it has had minimum exposure to air. Since M2 thickener is composed mainly of M1 thickener, it retains most of the characteristics of M1, including the disadvantages of being manufd from critical material, absorption of water from the air, and sensitivity to moisture. As a general comparison with M1 thickener, only two-thirds as much M2 thickener is needed to obtain thickened fuel of the same consistency (Ref 7, p 9)

Peptizers are used to hasten the gelling of gasoline and thickener in cold weather. They are used, however, only when very low temps make mixing time excessively long and heating the gasoline is not possible, since they cause the mixt to break down after a short period of time (less than 48 hrs). Cresylic acid is used when preparing thickener fuel using M1 or M2 thickener and gasoline at temps below 60°F. When preparing thickened fuel using M4 thickener and gasoline at temps below 40°F, 2-ethylhexanoic acid is used. Unpeptized gels can be obtained with M4 thickener when gasoline temps are as low as 0°F, but mixing time is very long (Ref 7, p 9)

In most cases, incendiary munitions containing thickened fuel are equipped with white P igniters to insure ignition because the bursting charge may or may not cause ignition. Since ignition of white P is prevented by water, a Na igniter is used in munitions to be dropped over water. Thickened fuel in portable flamethrowers is ignited by a red P-tipped metal match which scratches an igniting mixt (Ref 6, p 42)

See also under Flame Throwers – Liquids and Gels in Vol **6**, F57-L ff

Written by **S. M. KAYE**

Refs: 1) G.O. Langstroth & K.H. Hart, CanJResearch **27A**, 151–5 (1949) & CA **43**, 8140 (1949) 2) Anon, ChemEngrg (Nov 1951), 162–3 [Description of new Napalm plant where operation is continuous and automatically controlled] 3) L.F. Fieser et al, USP 2606107 (1952) 4) Anon, C&EN **37** (Oct 8, 1952) 5) Anon, C&EN **32**, 2690 (July 5, 1954) [Structure of Napalm and manufg problems] 6) Anon, "Military Chemistry and Chemical Agents", **TM 3-215** (1963) 7) Anon, "Flame Fuels", **TM 3-366** (1965) 8) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 137-L

Naphthas. Flammable liquids, consisting mainly of hydrocarbons of the C_nH_{2n+2} series, obtained by distillation of petroleum, oil shale, coal tar or wood, bp range 95 to 220°. The principle varieties of naphthas are (a) *Light or Cleaner's Naphtha:* white, vol petroleum distillate used as a cleaning fluid, bp range 95 to 150°; (b) *Heavy Naphtha:* deep amber to dark red liq consisting of xylene and higher homologs, d 0.885–0.970 g/cc, bp range 160 to 220°, flash p 100°F. Has been used in Sprengel type expls as a fuel

Refs: 1) CondChemDict (1971), 602 2) Hackh's (1972), 444

Naphthas, Hydroformed. Produced by the Standard Oil Development Co (Ref 1) by passing

vapors of certain petroleum fractions together with H_2 over a catalyst composed of the oxides and/or sulfides of metals of group VI of the periodic table, in the presence of promotors. The reaction takes place above 20 atms press and above 482°, with suitable H_2 partial press and contact time necessary to obtain destructive hydrogenation without the formation of polymerized material. The resulting hydroformed naphthas may be halogenated, sulfonated or nitrated

Nitrated Hydroformed Naphthas. The nitration of hydroformed naphthas with mixed nitric-sulfuric acid contg a small amt of w (Ref 2) produced materials which may be used either in expls or as intermediates in the dye industry. It is also possible to reduce the nitrocompounds to amines which can be used as flash reducing agents in proplnts

Refs: 1) Standard Oil Development Co, BritP 477015 (1937) & CA **32**, 3951 (1938) 2) Standard Oil Development Co, BritP 477014 (1937) & CA **32**, 3964 (1938)

Solvent Naphtha (160° benzol). A mixt of small percentages of benzene and toluene with xylene and higher homologs from coal tar. In crude form, a dark straw-colored liq, bp about 160° (80%), d 0.862–0.892g/cc, flash p about 78°F. When refined, a w-white liq, bp about 160° (90%), d 0.862–0.872g/cc, flash p about 78°F. May be obtained from coal tar by fractional distillation. When nitrated, used in Dynamites (Ref 5)

Nitrated Solvent Naphtha (N.S.N.). As nitration of crude solvent naphtha by the usual one-stage method results in yields that are too low, because of oxidation, E. Blecher et al (Ref 3) proposed nitrating only the refined material, and in two stages. The two-stage method is described in Colver, pp 255 & 686–87 (Ref 4). The product consists chiefly of 2,4,6-Trinitromesitylene (see under Mesitylene and Derivatives in this Vol), and 3,5,6-trinitropseudocumene, with small quantities of the nitrated products of xylene, ethylbenzene, etc

N.S.N. may be either solid or liq (oil); both forms are highly expl and have been used in commercial, and to a certain extent, in military expls. Typical examples follow: (1) Explosive patented by Schultz & Gehr (Ref 1): AN 76, N.S.N. 10, K nitrate 10, K perchlorate 2 & resin 2%; (2) Explosives patented by Distler, Blecher and Lopez (Refs 2 & 3): (a) AN 88 & N.S.N. 12%. It is insensitive to shock or percussion and does not explode when heated to 200° or when ignited in an open flame, but detonates with considerable brisance when strongly initiated. The brisance may be reduced by substituting either K nitrate or Amm perchlorate for part of the AN. (b) AN 85, N.S.N. 12 & Pb or Ba dioxides 3%. This mixt is more brisant than (a). (c) AN 85, N.S.N. 12, Pb or Ba dioxides 1% & finely pulverized Cu 2%; an extremely brisant expl. (d) Brisant expls were prepd by mixing solid or liq N.S.N. with PA in all proportions. (e) Gelantinous, dough-like expls can be prepd by dissolving 6p of collodion cotton in 94p of oily N.S.N., preheated to 100°. (f) By incorporating, with warming, 30–40% of AN plus flour into the above mixt (e), a solid mass is obtained which may be pulverized and used in lieu of Dynamites

Refs: 1) G. Schultz & F. Gehr, USP 894707 (1906) 2) C. Distler, E. Blecher & C. Lopez, FrP 380996 (1907) 3) E. Blecher, C. Lopez & C. Distler, USP 898144 (1908) 4) Colver (1918), 255 & 686–88 5) CondChemDict (1971), 603

NAPHTHALENE AND DERIVATIVES

Naphthalene (Tar Camphor), Naphthalin (Ger), Naphthalène (Fr), Naftalene (Sp), Naftalina (It), Naftal (Russ); $C_{10}H_8$, mw 128.16, mp 80.2°, bp 217.98°; d_4 at 100° 0.9628g/cc, RI at 100° 1.5821 (Ref 4), Q_c 5151.23kJ/mole, Q_f 18.57 ± .25kcal/mole (Ref 10); CA Registry No 92-24-0. Colorless, volatile flakes from EtOH with a strong coal-tar odor; may be obtained from coal gas, from the fraction of coal tar boiling betw 170 and 230°, or from petroleum. The naphthene fraction is aromatized, fractionated to give an alkyl-naphthalene cut, and the latter dealkylated to naphthalene. In 1965, ca 3/8 of the naphthalene produced in the USA was made this way, the remainder being obtained from coal tar (Ref 11); 321 isolations and prepns of naphthalene are reported in Ref 5. It is sl sol in w (0.003g/100ml at 25°); sol in EtOH (915g/100ml at 19.5°); and very sol in hot EtOH, eth, C tetrachloride, C disulfide, and bz (Refs 1 & 13). It is

purified by repeated sublns followed by recrystn from EtOH or bz. A procedure for the accurate detn of purity by a differential heat loss ap is described in Ref 6. It can be identified as the picrate, mp 149° (Ref 9); or the 2,4,7-trinitrofluorenone complex, mp 151.2–4.0° (Ref 3). It can be detd in petroleum prods by IR (Ref 8), and quanty in mixts with tetralin and decalin by gas chromatography (Ref 7). It is toxic in "large doses" (Ref 12) and has a rating of 2 in Sax for skin contact and inhalation toxicity. The flammability is moderate, and it reacts with strong oxidizers (Ref 14). Its ign temp in air and O_2 are 587° and 560° resp; the temp limits of infly of air satd with naphthalene vapor at 746–8mm are 77.8° and 121.8° resp; and the flamy limits in air are 0.88 and 5.9% by vol (Ref 2)

Uses. Naphthalene and its derivatives find uses as starting materials for the prepn of dyestuffs, pharmaceuticals, pest control agents, and expls (Ref 11). It is one ingredient in the expl "Dahmenite A" (see Vol **3**, D1-R)

Refs: 1) Beil **5**, 531, (257), [432] & {1549} 2) G.W. Jones & G.S. Scott, "Limits of Inflammability and Ignition Temperatures of Naphthalene", BM Rept Investigations 3881 (1946) & CA **40**, 5919 (1946) 3) M. Orchin et al, JACS **69**, 1226 (1947) 4) G. Egloff, "Physical Constants of Hydrocarbons, Vol **4**, Polynuclear Hydrocarbons", ACS Monograph Series 78, Reinhold, NY (1947), 77 5) J.E. Faraday, "Encyclopedia of Hydrocarbon Compounds, Vol **5**, $C_{10}H_6$ to $C_{10}H_{14}$", Chemical Publishing Co, NY (1949), 10005 6) I.M. Bernstein, JPhCollChem **55**, 1231 (1951) 7) R.M. Soemantri, ProefschrTechHogeschoolDelft **1958** & CA **56**, 18672c (1961) 8) D.E. Nicholson & S.H. Hastings, AnalChem **32**, 298 (1960) 9) Shriner, Fuson & Curtin (1965), 358 10) D.J. Coleman & G. Pilcher, TrFaradSoc **62**, 824 (1966) & CA **64**, 14072b (1966) 11) Kirk & Othmer **13**, (1967), 682 12) Merck (1968), 712 13) ChemRubHdb (1974–75), C-375 14) Sax (1975), 948

Azidonaphthalenes, Naphthyl Azides

Monoazidonaphthalenes, $C_{10}H_7N_3$, mw 169.18, N 24.84%

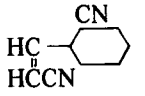
1-Azidonaphthalene (Alpha-naphthyl azide). A pale yel oil which solidifies at 12° to lustrous yellow prisms, decomps at 110° with N evolution (Refs 1 & 3), d at 24.9° 1.1731g/cc (Ref 4); it can be steam distd (Ref 2); CA Registry No 6921-40-4. It is prepd by the action of hydrazoic acid (Ref 3), or hydroxylamine sulfate (Ref 4) on 1-naphthalenediazonium salts. It decomps in boiling Ac_2O to give 20% 2-amino-1-naphthol and 28.5% 2-naphthylamine (Ref 6). When frozen on a cold surface at liq N temp and photolyzed with a Hg arc lamp, it forms 1-naphthyl nitrene (R-N:) which dimerizes to 1,1′-azonaphthalene upon warming (Ref 7). The photosensitized decompn is studied in Ref 8, with kinetic and mechanism data given

2-Azidonaphthalene (Beta-naphthyl azide). Lustrous yel needles, mp 33° (Refs 2 & 3), prepd by the action of hydroxylamine (yield 50%), hydrazine (yield 20%), or Na azide on 2-naphthalenediazonium sulfate (Ref 3); or by the action of hydroxylamine sulfate on 2-naphthalene diazonium sulfate in sulfuric acid/glac acet ac (Ref 5)

Refs: 1) Beil **5**, 565, (265), [459] & {1614} 2) Beil **5**, 565, (265) & {1614} 3) M.O. Forster & H.E. Fierz, JCS **91**, 1945 (1907) 4) J.C. Philip, JCS **93**, 919 (1908) 5) H.H. Hodgson & W.H.H. Norris, JCS **1949**, 762 6) R.K. Smalley & H. Suschitzky, JCS **1963**, 5571 7) A. Reiser et al, TrFaradSoc **62**, 3162 (1966) 8) L.J. Leyshon & A. Reiser, JCSFaradTr **68** 2, 1918 (1972)

Diazidonaphthalenes, $C_{10}H_6N_6$, mw 210.20, N 39.99%. Four isomers have been described in the literature. All are high expls and are sens to shock, light, and heat

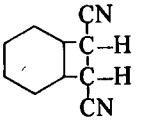
1,2-Diazidonaphthalene. Crysts from petr eth (bp 60–90°), mp 108°; prepd in four steps starting with 1-nitro-2-naphthylamine (Ref 3). It decomps in boiling decalin to evolve N and form



The mechanism of this reaction is discussed in Ref 3

1,8-Diazidonaphthalene. Pale yel crysts, mp 95–100° with decompn; prepd by the bis-diazotation of 1,8-diaminonaphthalene followed by treatment with Na azide (Ref 5). It has been patented as a photosens ingredient in a photocopying process (Ref 6)

2,3-Diazidonaphthalene. Needles from petr eth (bp 40–60°), mp 63–4°; prepd in five steps starting with 3-amino-2-naphthoic acid. Its pyrolysis in a Pyrex tube at 400° gave



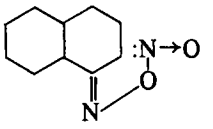
(Ref 7)

2,7-Diazidonaphthalene. Almost colorl leaflets from petr eth, mp 98°, turns red on exposure to light; prepd by the action of Na azide on 2,7-naphthalenebis(diazonium sulfate) (Refs 1 & 2). It has been patented as a cross-linking agent for polypropylene and polybutadiene (Ref 4)
Refs: 1) Beil **5**, (265) 2) G.T. Morgan & F.M. Micklethweit, JCS **97**, 2558 (1910) 3) J.H. Hall & E. Patterson, JACS **89**, 5856 (1967) 4) D.S. Breslow & A.F. Marcantonio, USP 3297674 (1967) & CA **66**, 56182r (1967) 5) R.W. Hoffman et al, JCS(C) **1969**, 769 6) B. Singh, GerOffen 2118585 (1971) & CA **74**, 40289b (1972) 7) M.E. Peek et al, JCS-PerkinTr(I) **1974**, 1260

Azidonitronaphthalenes

Monoazidomononitronaphthalenes, $C_{10}H_6N_4O_2$, mw 214.18, N 26.16%, OB to CO_2 −158%. Eight isomers are in the literature

1-Azido-2-nitronaphthalene (2-Nitro-1-naphthyl azide). Long yel needles from aq acet, mp 103–4° with decompn (Refs 1 & 4); CA Registry No 16714-21-9. Prepd by the action of Na azide on 2-nitro-1-naphthalenediazonium sulfate with urea in glac acet ac (Ref 4). It decomps at 150° with N evolution, and in toluene at 110° to give a 90% yield of



(Ref 5)

1-Azido-4-nitronaphthalene (4-Nitro-1-naphthyl azide). Yel needles from hot EtOH, mp 99°; CA Registry No 6549-18-4. Its prepn is the same as above, using the 4-nitrodiazonium salt (Refs 1 & 4)

1-Azido-5-nitronaphthalene (5-Nitro-1-naphthyl azide). Yel needles from hot abs EtOH, mp 121°; prepn the same as above using the 5-nitrodiazonium salt; decomps rapidly at 130° with N evolution (Refs 2 & 4)

1-Azido-8-nitronaphthalene (8-Nitro-1-naphthyl azide). Yel prisms from hot acet, mp 130–1° with decompn, darkens on exposure to light; prepn the same as above using the 8-nitrodiazonium salt (Refs 1 & 4)

2-Azido-1-nitronaphthalene (1-Nitro-2-naphthyl azide). Yel needles from acet, mp 116–17° with vigorous decompn; CA Registry No 16714-28-6. Prepd by the nitration of 2-naphthyl azide with nitric acid (d 1.42g/cc), or by the action of hydrazoic acid on 1-nitro-2-naphthalenediazonium sulfate (Refs 3 & 4). It gives the same product on pyrolysis in toluene as 1-azido-2-nitronaphthalene (Ref 5)

2-Azido-3-nitronaphthalene (3-Nitro-2-naphthyl azide). Cream needles, mp 101° with decompn; prepn same as above with the 3-nitro-2-diazonium salt. It decomps on heating to give tars, but no furoxan (Ref 6)

2-Azido-5-nitronaphthalene (5-Nitro-2-naphthyl azide). Brown-yel needles from acet, mp 133.5°; prepn same as above with the 5-nitro-2-diazonium salt; stable in hot et acet and hot glac acet ac (Ref 4)

2-Azido-8-nitronaphthalene (8-Nitro-2-naphthyl azide). Yel prisms from aq acet, mp 108°; prepn same as above from the 8-nitro-2-diazonium salt (Refs 3 & 4)

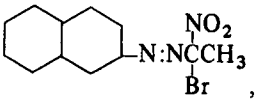
Refs: 1) Beil **5**, 565 2) Beil **5**, 565, [459] 3) Beil **5**, 566 4) M.O. Forster & H.E. Fierz, JCS **91**, 1942 (1907) 5) L.K. Dyall & J.E. Kemp, AustJChem **20**, 1632 (1967) & CA **67**, 107911h (1967) 6) Altaf-al-Rahman et al, JCS B **1968**, 1516

1-Azido-2,4-dinitronaphthalene (2,4-Dinitro-1-naphthyl azide). $C_{10}H_5N_5O_4$, mw 259.18, N 27.02%, OB to CO_2 −114%; yel needles, mp 105° with decompn; prepd by the action of Na azide in boiling abs EtOH on 1-chloro-2,4-dinitronaphthalene, yield 75%

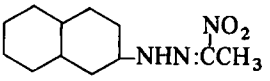
Refs: 1) Beil **5**, [460] 2) E. Muller & K. Weisbrod, JPraktChem [2] **113**, 30 (1926) & CA **20**, 2677 (1926)

Azo Derivatives of Naphthalene

1-Bromo-1-nitro-1-(2-naphthylazo)ethane.

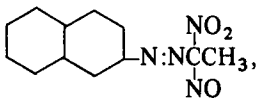


mw 308.14, N 13.64%, golden yel leaflets from EtOH, mp 168° with decompn; prepd by the action of Br on



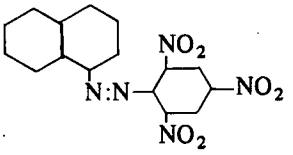
in warm EtOH (Refs 3 & 5)

1-(2-Naphthylazo)-1-nitro-1-nitrosoethane.

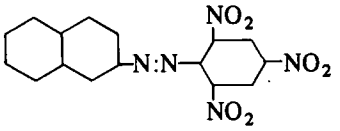


mw 258.23, N 21.70%, OB to CO_2 −161%; dark-red needles from EtOH, mp 141° with decompn; prepd by the action of Na nitrite and aq HCl on the same raw material as used above (Refs 3 & 5)

2,4,6-Trinitrophenylazonaphthalene-1, picrylazo-1-naphthalene. $C_{16}H_9N_5O_6$, mw 367.27, N 19.07%, OB to CO_2 −133%; red-yel needles, mp 226° with decompn; prepd by the oxidn of the hydrazine with chromic acid in glac acet ac (Refs 1 & 4)



2,4,6-Trinitrophenylazonaphthalene-2 (Picrylazo-2-naphthalene). Dull red needles from glac acet ac, mp 205° with decompn (Refs 3 & 4)



Refs: 1) Beil **16**, 78 2) Beil **16**, 80 3) Beil **16**, 81 4) C. Willgerodt & F. Shultz, JPrakt-Chem (2) **43**, 182 5) G. Oddo & G. Ampola, Gazz **23** I, 260 (1893)

Nitro Derivatives of Naphthalene

Mononitronaphthalenes (MNN), $C_{10}H_7NO_2$, mw 173.16, N 8.09%, OB to CO_2 −198%

1-Nitronaphthalene (Alpha-nitronaphthalene, 1-MNN). Yel needles from EtOH, mp 61.5° (Refs 1 & 6), bp 304° (Ref 4); CA Registry No 86-57-7

1-MNN is readily prepd from naphthalene by the action of a number of nitrating agents. Some which have been used are concd nitric ac in the cold for 5–6 days (Ref 3); N dioxide in the cold (byprods are also obtained) (Ref 5); nitrylsulfuric ac (O_2NSO_3H) in 100% nitric ac at 30°, yield quant (Ref 13); concd nitric ac and anhyd Zn chloride in pyridine at 130° (Ref 11); a suspension of Na nitrite in concd sulfuric ac at 110° (Ref 14); di-N tetroxide in concd sulfuric ac, yield 88.4% (Ref 15); and in low yield by heating with Bi trinitrate (Ref 12). On a coml scale the nitration is conveniently done with mixed acids such as 83g of nitric (d 1.38 g/cc) and 233g of sulfuric (d 1.83g/cc)/100g of naphthalene, yield 85% (Ref 19). Lab and coml prepns are summarized in Ref 22, p 350. In Ref 8 are discussed the effects of acid concns on the formn of mono- and polynitro compds by the mixed acid nitration of naphthalene. Other studies on the coml prodn of 1-MNN are in Refs 16, 20, 29 & 30

Analysis. 1-MNN is best identified by redn to the amine with Sn and 10% HCl, which is converted to the benzenesulfonamide, mp 167°; or the benzamide, mp 160° (Ref 36). The picrate, CA Registry No 29754-26-5, is also known (Ref 37). It has been found in crude TNT recovered from Comp B (probably arising from the presence of naphthalene in coml toluene), from which it was isolated by gas chromatography and identified by mass spec (Ref 40). Standard anal procedures for Mil grade 1-MNN are given in Ref 35

Flash Point. Closed Cup, 327°F (Ref 42)

Heat of Combustion. 1190.1kcal/mole at 15° (Ref 18)

Heat of Formation. Q_f^v −85cal/g, Q_f^p −68cal/g (Ref 27)

Mixtures. Frolova studied the system 1-MNN/TNT and found eutectics at 28.5 and 78.5% MNN, mp 58.8 and 45.5° respectively; and a dystectic point, mp 63.4°. He also found that the visc of liq TNT is decreased by the addn of MNN (Ref 23). A mp diagram with PA shows a 1:1 molar eutectic, mp 67° (Ref 21)

UV Spectrum. In EtOH there is a peak at 3650, in petr eth at 3700, and in benz at 3450Å (Ref 9)

Uses. While 1-MNN is not an expl and cannot be detond, mixts with expls have been used extensively. A mixt of PETN/1-MNN 95/5 is used as a detonator for mixts contg TNN (Ref 24). It has been found that addn of 0.2 to 0.4% 1-MNN to TNT and 0.4 to 0.6% to Comp B will inhibit crack formn in castings of these expls (Refs 31 & 35). A mixt with TeNMe contg 80.3% TeNMe has expl props: mp 58.8°, OB to CO_2 +0.34%, d 1.57g/cc, deton vel 8160 m/sec, power by Trauzl test 489cc, brisance by

Hess test (Ref 17) 65.95mm (Ref 33). A mixt with PA, called Trimonite or MMn (Fr) has the following props: comp 88–90% PA/10–12% 1-MNN, OB to CO_2 –62%, mp 90°, impact sensy BM app 60cm, PA app 10″; rifle bullet impact test unaffected; expln temp, decomps in 5sec at 315°; vacuum stab test, 9.9cc of gas evolved in 40hours at 120°; 200g bomb sand test, 44.2g of sand crushed; deton vel 7020 m/sec at a diameter of 1.0″ & d of 1.60g/cc. Prepd by melting PA and 1-MNN together in the correct proportions in a steam-jacketed kettle, with care being taken to avoid the formn of expl metal picrates. Used as a substitute for TNT in cast-loaded munitions (Refs 31 & 32). A comp of 61.7% AN, 8.0% of an equimolar mixt of 1-MNN and DNT, 0.8% guncotton, and 1.5% wood flour is an expl which can be safely mixed (Ref 28). AN is coated with 2–5% 1-MNN, 2–20% TNT is added, and the mixt agitated in a rotating drum as another 2–5% of TNT is added to give a w insoluble granular expl; deton vel 6000–7000m/sec, Trauzl test 525cc; gap test, above 6cm; suitable for borehole blasting (Ref 37). 1-MNN has been used in Ammonite expls (Vol **1**, A307). At a level of 1.5%, 1-MNN prolongs the stab of NC from 7.5 to 25.5hours as shown by the litmus test (Ref 25). The thermal decompn of dil solns of NC in 1-MNN was studied betw 165 and 200° by following the evolution of gas. It was found that 3.5 moles of gas were evolved for each glucoside unit present in NC (Ref 25)

2-Nitronaphthalene (Beta-Nitronaphthalene, 2-MNN). Long yel needles from EtOH & eth, mp 79° (Refs 2 & 7), bp at 14mm 180–4° (Ref 10); CA Registry No 581-89-5

2-MNN is obtained in 3–5% yield by the nitration of naphthalene and is present at this level in coml MNN. It is best prepd by indirect methods; for example, by the removal of an amino group from an appropriately substituted nitronaphthylamine. The amine is treated with Na nitrite and acid to form the diazonium salt which is replaced with a H atom by redn with EtOH (Ref 7). It may also be prepd by treatment of 6-nitro-1,2,3,4-tetrahydronaphthalene with Br to form a dibromo compn (probably the 1,4-isomer), followed by removal of two moles of H bromide by distn in the presence of base (Ref 10). 2-Naphthalenediazonium fluoroborate is decompd at room temp in the presence of Cu(I) chloride and Na nitrite to give 2-MNN (Ref 38). The UV spectrum in EtOH shows peaks at 3000, 3675 & 4250Å; and in petr eth at 3200, 3750 & ca 4300Å (Ref 9). A more recent prepn of 2-MNN is as follows: naphthalene is treated with 2 moles of hexachlorocyclopentadiene to give a 1,2:3,4-diadduct (DHA), mp 214–15° (Ref 26). Upon treatment with anhyd nitric ac in sulfuryl chloride or methylene chloride, a mixt of 13% 1-nitro and 87% 2-nitro-DHA is obtained which can be sepd by recrystn from aq acet. Upon heating to 250–400°, the 2-nitro-DHA is converted to 2-MNN in good yield (Ref 41). The picrate of 2-MNN (CA Registry No 29754-27-6) is described in Ref 39. Because it is difficult to produce, 2-MNN has had no coml or expl uses. It has been used to prep other nitrated naphthalenes

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Dinitronaphthalenes (DNN). $C_{10}H_6N_2O_4$, mw 218.16, N 12.84%, OB to CO_2 −139%

Below is collected info on mixts of DNN and on compds of unspecified structure. The nitration of naphthalene with mixed acid gives a 2:1 mixt of 1,8- and 1,5-DNN contg a small amt of the 1,3- isomer (Ref 54). This is the compn of the coml DNN used in the expls industry

Crude DNN can be detond when confined and heated, its explodability is lower than DNB or AN; its fire point is ca 350° (Ref 53). It also can be detond by an initiator when loosely packed in shells (Ref 57)

Preparation. On a coml scale the nitration of naphthalene is carried out in two steps using a cylindrical jacketed reactor 1.6 x 1m with a conical bottom. It is fitted with a discharge pipe 8cm in diameter and a stirrer which can be rotated at 85–90rpm. The jacket can be heated with steam or cooled with cold w. The cover is provided with an opening for the addn of naphthalene and a vent for the removal of gaseous prods

Procedure. a) The reactor is charged with 1150kg of mixed acid contg slightly more than 128kg of K nitrate. The comp should be nitric ac 12–14%, sulfuric ac 40–50%, and the remainder w. b) The mixt is agitated as 300kg of naphthalene is added in small portions over a 3 hour period as the temp is allowed to rise to 50°. When all the naphthalene is added, the reactor is heated to 55°, which melts the crude MNN. c) The stirrer is stopped, the mixt allowed to sep, and the mono-spent acid (which is depleted of K nitrate) is drained to a holding tank; the oily prod is transferred to a tank contg w at 70°, and fitted with a steam jet agitator. d) The prod is agitated for 30min with w and steam, allowed to sep, and the oil poured into trays where it solidifies, yield almost quant. In Ref 27 there is a slightly different proc: e) The MNN is broken into fist-sized pieces and added to the nitrator contg 1150kg of a mixt of 51% sulfuric ac, 26.5% K nitrate, and the remainder w, while being agitated at 85–90rpm. f) The temp is kept at 38–45° during the addn after which it is raised over a one hour period to 55°. g) The nitration is complete when the emulsion is replaced by uniform grains of DNN. h) The slurry is filtered thru a Nutsch filter and the filtrate recycled to step a. i) The crude DNN is washed with spent acid from step c, then with 6 portions of cold w. j) The DNN is transferred to a tank with a false bottom and agitated with 6 portions of cold w at 60°. k) The DNN is dried at 60° for 24hours, yield almost quant, w content ca 0.5% (Ref 24). The prod is 35–40% 1,5-, 60–5% 1,8- and 1–2% 1,3-DNN. It is an expl, but is less powerful than DNT

Toxicity. Workers wrapping or otherwise handling TNT/DNN mixts were found to have dermatitis as well as symptoms of systemic poisoning (Ref 47)

Uses. Mixts of DNN with expls have been used

as substitutes for TNT by many countries when the latter was in short supply. A mixt of 87.5% AN and 12.5% DNN (OB to CO_2 +12.5%), called **Schnéiderite** (Fr), **Sznajderyt** (Poland), and **Shnaiderit** (USSR), was used in WWI as a fill for HE artillery shells (Ref 61). Another comp of 78% AN and 22% DNN was used in Fr and the USSR (Ref 61). A compn contg 80% PA and 20% DNN, called **MDN** or **MDn** (Mélenite-Dinitronaphtaline) (Fr), melts near 105°, and was used as a cast filler for projs and bombs (Ref 60). Another series of comps of AN and DNN, called **Type N, Nos 1b, 1c, 1d, & 7** (Fr) are described in Ref 39. A mixt of 40% TNT, 30% HNDPhA, 20% DNN, and 10% powd Al (code name **KMA Block** or **Ersatz-sprengstoffe**) was used in Ger during WWII as a substitute for TNT (Ref 55). A mixt of 50% AN, 43% TNT, and 7% DNN, called **Nougat** or **MST** (It) was cast loaded into artillery shells (Ref 60, p 339); another comp of 72.8% AN, 17.6% TNT, and 10.5% DNN, called **Siperite** or **MNDT** (It) was similarly used (Ref 60, p 347). Other Italian formulations contg DNN are reported in Ref 40. Comps of 50/50 and 80/20 PA and DNN, code name **Onayaku** (Jap) were used as bursting charges in artillery ammo (Ref 56); DNN is one ingredient of **"Chanyaku"** expl (Jap) (see Vol **2**, C148); and a comp contg 79% AN, 10% DNN, 10% Na chloride, and 1% sawdust, code **Shoan Bakuyaku** (Jap) was used as a demolition expl (Ref 56, p 113). A similar comp of 51.5% PA and 48.5% DNN, code **Russian Alloy (Russki Splav)** (USSR) was used in WWII in artillery ammo

Recent Uses. Mixts of 15–45% DNN, 15–45% Hexogen, and 5–30% powd Al are useful blasting expls (Ref 37). AN (918g) is mixed with 80g of DNN or TNT in 80g of concd nitric ac, and gaseous ammonia passed in until the mist is neutral, to give an expl (Ref 44). A mixt of 26 parts polystyrene, 5 DNN, and 300 benz is added to 612ps of Pb dioxide, and the mixt dried to give a comp useful for match heads or fuses (Ref 51). At a level of 1.5%, DNN prolongs the life of NC by 6.5–7.5 hours at 106.5° as indicated by the litmus test (Ref 59). A comp of 87% AN, 4% DNN, 4% TNT, 2% Na stearate, and 3% starch is kneaded, pressed, and packed into cylinders (sticks), packing d 1.3g/cc, brisance equal to NG Dynamite (Ref 46)

1,2-Dinitronaphthalene (1,2-DNN). Brownish needles from EtOH, mp 158° (Refs 5 & 20); CA Registry No 24934-47-2. It is prepd by bromination of 5,6-dinitro-1,2,3,4-tetrahydronaphthalene followed by dehydrobromination (Ref 20), from 2-nitro-1-naphthylamine by the same procedure as used for the prepn of the 1,4-isomer (Ref 20)

1,3-Dinitronaphthalene (Gamma-dinitronaphthalene, 1,3-DNN). Bright yel needles from aq pyridine, mp 144°, bp subl (Refs 1 & 32); CA Registry No 606-37-1. It is prepd by the action of nitric ac/sulfuric ac on naphthalene at low temps (Refs 14 & 33); by the nitration of 1-MNN with a mixt of 17.3% nitric ac, 61.2% sulfuric ac, and 21.5% w, temp 59–75°, time 90min (Ref 52); by the action of powd Cu (Ref 18) or hydrazine (Ref 22) on 1-chloro-2,4-dinitronaphthalene; by the diazotization of 2,4-dinitro-1-naphthylamine followed by redn of the diazonium salt with EtOH (Ref 25); or by the action of Br on 5,7-dinitro-1,2,3,4-tetrahydronaphthalene followed by dehydrobromination (Ref 13). It is used to prep more highly nitrated naphthalenes

1,4-Dinitronaphthalene (1,4-DNN). Long yel needles from MeOH, mp 134° (Refs 6 & 34); CA Registry No 6921-26-2. It is prepd by the diazotization of 4-nitro-1-naphthylamine followed by treatment of the diazonium salt with powd Cu and Na nitrite (Ref 45)

1,5-Dinitronaphthalene (Alpha-dinitronaphthalene, 1,5-DNN). Six sided needles from acet ac, mp 219° (Refs 2 & 29, d at 18° 1.602g/cc (Ref 48); Q_c^p 1152.6kcal/mole (Ref 29), Q_f −61cal/g (Ref 34); CA Registry No 605-71-0. It is prepd by heating naphthalene with concd nitric ac (Ref 12); by treating naphthalene with sulfuric ac/nitric ac at −60 to −50° (Ref 14); or by the nitration of 1-MNN with a mixt of 1 part of nitric ac (d 1.4g/cc) to 2ps of concd sulfuric ac (Ref 16). It forms a solid ppt with Nitron (for structure of Nitron see Ref 50), mp 202° with decompn, which can be used for identification (Ref 41). Crystals of 1,5-DNN are monoclinic tablets whose crystallographic data, including n, interfacial angles, and X-ray diffraction data are given in Ref 42. A procedure is described in Ref 43 for the analysis of expls contg 1,5-DNN by solv extn. It is best extd with et acet

1,6-Dinitronaphthalene (Delta-dinitronaphthalene, 1,6-DNN). Crysts from acet ac, mp 166–67°, bp at 10mm 235°, 360° with decompn (Refs 2 & 31); CA Registry No 607-46-5. It is prepd by the nitration of 2-nitronaphthalene with nitric ac/sulfuric ac in hot acet ac (Ref 21); by diazotization of 5-nitro-2-naphthylamine followed by treatment of the diazonium salt with Na cobaltinitrite, yield 40% (Ref 36); or by removal of the amino group from 1,6-dinitro-2-naphthylamine by diazotization followed by redn (Ref 17). The temp of expln is 492° (Ref 17)

1,7-Dinitronaphthalene (1,7-DNN). Yellow crysts from EtOH, mp 156° (Refs 7 & 21); CA Registry No 24824-25-7. It is prepd by the nitration of 2-nitronaphthalene with nitric ac/sulfuric ac in hot acet ac (Ref 21); or by the diazotization of 8-nitro-2-naphthylamine, followed by treatment of the diazonium salt with Na cobaltinitrite (Ref 35)

1,8-Dinitronaphthalene (Beta-dinitronaphthalene, Peri-dinitronaphthalene, 1,8-DNN). Tablets from chlf or pyridine (Refs 4 & 16), mp 172.5–3.0° (Ref 29), d at 18° 1.575g/cc (Ref 48), Q_C^v 1164.45kcal/mole (Ref 28), Q_f –60cal/g (Ref 49), temp of expln 445° (Ref 19); CA Registry No 602-38-0. It is prepd by heating naphthalene with concd nitric ac (Ref 11); or by allowing naphthalene to stand in the presence of concd nitric ac for 24 hours, then warming the mixt on a w bath with concd sulfuric ac (Ref 15). It forms a eutectic with TNT contg 18.07% DNN, mp 73.4° (Ref 38). A procedure is described in Ref 43 for the analysis of expls contg 1,8-DNN by solvent extn. It is best extd with acet

2,3-Dinitronaphthalene (2,3-DNN). Yel needles from MeOH, mp 170.5–1.0° (Refs 8 & 23); CA Registry No 1875-63-4. It is prepd by bromination of 5,6-dinitro-1,2,3,4-tetrahydronaphthalene followed by dehydrohalogenation (Ref 23); or by nitration of a naphthalene-hexachlorocyclopentadiene adduct (Diels-Alder), followed by pyrolysis to regenerate the 2,3-DNN (Ref 58)

2,6-Dinitronaphthalene (2,6-DNN). Long yel needles from Ac_2O, mp 279° (Refs 9 & 30); CA Registry No 24824-26-8. It is prepd by the diazotization of 6-nitro-2-naphthylamine followed by treatment of the diazonium salt with powd Cu and Na nitrite (Ref 21), or Na cobaltinitrite (Ref 25); or from naphthalene-2,6-bis (diazonium salts) by treatment with nitrosylsulfuric ac ($ONSO_3H$) in concd sulfuric ac followed by cuprocupric sulfite (Ref 30)

2,7-Dinitronaphthalene (2,7-DNN). Yel crysts from Ac_2O, mp 234°; CA Registry No 24824-27-9. It is prepd by the decarboxylation of 3,6-dinitronaphthalene-1,8-dicarboxylic ac with powd Cu in boiling quinoline (Refs 10 & 26)

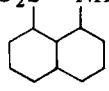
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Dinitronaphthalenesulfonic Acids, $C_{10}H_6N_2O_7S$, mw 298.23, N 9.39%, OB to CO_2 & SO_2 −96.6%

4,5-Dinitronaphthalene-1-sulfonic Acid. Yel needles from fuming nitric ac, mp explds on rapid heating (Ref 3). It is prepd by nitration of 5-nitronaphthalene-1-sulfonic ac with mixed ac at 15–20° (Ref 6). It is sl sol in cold w (Ref 3)

5,7-Dinitronaphthalene-1-sulfonic Acid. Needles from w, mp explds around 300° when heated on a Pt foil (Refs 1 & 5). It is prepd by the action of an excess of fuming nitric ac on the sultam: $O_2S—NH$



(Ref 5); or by sulfonation of 1,3-DNN with an excess of 100% sulfuric ac contg a small amt of oleum (Ref 7)

4,5-Dinitronaphthalene-2-sulfonic Acid. Crysts, mp explds on heating (Refs 2 & 4). It is prepd by sulfonation of 1,8-DNN with 20% fuming sulfuric ac at 140° (Ref 4), or by nitration of 2-naphthalenesulfonic ac with mixed ac at 0–15° (Ref 2)

4,8-Dinitronaphthalene-2-sulfonic Acid. Solid which explds on heating; prepd by nitration of 8-nitronaphthalene-2-sulfonic ac with mixed ac at 0–15° (Ref 2)

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Trinitronaphthalene, $C_{10}H_5N_3O_6$, mw 247.16, N 15.97%, OB to CO_2 −100%

Commercial Trinitronaphthalene (TNN, Naphtite). Yel cryst solid, mp 110–140° depending on prepn procedure used. It contains varying proportions of 1,2,5-, 1,3,5-, 1,3,8-, and 1,4,5-TNN (for descriptions of pure isomers see below)

Preparation. 1) By the nitration of naphthalene: on boiling with fuming nitric ac for 14 days, TNN, mainly 1,3,8- is formed (Ref 5); by nitration with nitric ac/sulfuric ac at −60°, the same TNN is formed along with MNN and DNN (Ref 25); and with excess N dioxide at 100°, 1,3,8-TNN is formed (Ref 22). 2) By the nitration of 1-MNN: 1800kg of mixed ac (55% sulfuric ac, 40% nitric ac, and 5% w), to which is added 800kg of spent ac from a previous run, is agitated at 55° as 850kg of molten 1-MNN is added slowly. After all is in, the mixt is stirred for 2hours at 55°, cooled to 40°, the TNN filtered from the spent ac which is recycled, and purified as is described above for DNN; yield is 120kg/100kg of MNN (Ref 19). 3) By the ni-

tration of DNN: 100kg of DNN is introduced rapidly with stirring into 400kg of mixed ac (71% sulfuric ac, 20% nitric ac, and 9% w) as the temp is held at 65° for 1 hour, then raised to 95° and held there 3hours. The crude prod is sepd and purified as for DNN, yield 110kg (Ref 20)

TNN is an expl, more powerful than DNN, but less than DNB. Theoretical expln press is 83% of TNT (Ref 14); and its deton vel is from 6470m/sec at d 1.60g/cc to 9600m/sec at d 0.9 g/cc, both at 180° (Ref 30). It shows only incipient deflagration to deton transition at d 0.55–0.63g/cc and 1200–1600atm (Ref 35). An expln, however, on 4 Apr 1940 in a plant at Sainte-Chamas, Fr, which was mfg TNN, caused the deaths of 11 workers (Ref 29)

Uses. Belg comps: **Sabulite.** 52% AN, 9% TNN, 9% K perchlorate, 4% TNT, and 26% Na chloride is a mining expl (Ref 36, p 196); **Minolite Antigrisouteuse:** 72% AN, 23% Na nitrate, 3% TNT, and 2% TNN is a currently-used permissable mining expl (Ref 12, p 194)

Fr comps: A mixt of 70% Na nitrate and 30% TNN was proposed in 1908 as a Mil expl (Ref 9); this was later revised to 58% Na nitrate, 27% TNN, and 15% AN. It is shock sens, can be compressed to a d of 1.4g/cc with 200 lb press, can be detond with a 0.5g MF cap, and is very hygroscopic (Ref 10). **Antigrisou No 3:** 82% AN, 13% Amm chloride, & 5% TNN (Ref 11, p 270). **Grisounite 1:** 91.5–5.5% AN & remainder TNN (Ref 11, p 276). **French Mining Explosive No 1a:** 95% AN & remainder TNN (Ref 11, p 277). **French Mining Explosive No 3:** 15% AN, 58% Na nitrate, & 27% TNN (Ref 11, p 277). Another comp of 83% AN and 17% TNN (OB to CO_2 –0.4%) is also used in mining (Ref 11, p 275). **Nitroferrite:** 93% AN, 2% TNN, 2% K ferricyanide, & 3% sugar is a safety mining expl (Ref 11, p 278). The following comps have been patented as mining expls: 59% AN, 13% TNN, 18% Na chloride, & 10% K perchlorate; 60% AN, 20% Na chloride, 10% TNN, & 10% gelatinized NG; and 59% AN, 18% Na chloride, 8% TNN, 5% TNT, & 10% K perchlorate (Ref 16)

It comps: **Piombite:** 75% Pb nitrate, 16% Ca silicide, 6.5% basic Pb carbonate, 1.5% TNN, & 1.0% vaseline was used in grenades during WWI (Ref 36, p 342); a similar formulation of 76% Pb nitrate, 5% Ca silicide, 16% TNN, & 3% vaseline has been used as a mining expl (Ref 36, p 342). **Vibrite:** 78% AN, 14% Ca silicide, & 8% TNN was similarly used (Ref 36, p 353)

Jap comps: A formulation of 51.5% Amm chlorate, 35.3% Ba nitrate, 8.2% of a mixt of oil and TNN, & 5.0% wood pulp was used in WWII as a booster in demolition bombs. It tends to expld when burned unconfined in large quants (Ref 28)

1,2,5-Trinitronaphthalene (delta-Trinitronaphthalene, 1,2,5-TNN). Colorl needles from EtOH, mp 112–13°, bp explds (Ref 3), d 1.576g/cc (Ref 32). It exists in two polymorphic forms: alpha, stable to 40°; and beta, stable above 40°. Crystallographic data for both forms are in Ref 26, p 196. It is 47.5% of the prod obtained by nitration of 1,5-DNN with mixed ac (Ref 18), and 70% of prod from nitration of 1,2-DNN with aq nitric ac for 3 hours (Ref 34). It can be sepd from coml TNN by extn with 70% EtOH in which it is more sol (Ref 8)

1,3,5-Trinitronaphthalene (alpha-Trinitronaphthalene, 1,3,5-TNN). Yel rhombic crysts from chlf, mp 122–3° (Ref 2), bp explds at 364° when heated in a glass tube (Ref 12). It exists in 5 polymorphic forms, but only two are readily obtainable. Alpha 1,3,5-TNN is the form stable at room temp, but the beta form is obtained by most recrystns up to the mp. Crystallographic data on all 5 forms are in Ref 26, p 199. It is obtained, along with a small amt of TeNN and 3-nitrophthalic ac, by heating pure 1,5-DNN with concd nitric ac (45° Bé) (Ref 7); or by refluxing 1,5-DNN with 70% nitric ac for 20hours. It is sepd from other nitrated naphthalenes by formn of a complex with beta-naphthol, followed by chromatography (Ref 33). It gives a red color with K hydroxide in EtOH (Ref 6). Thermal analyses and mp curves for mixts of 1,3,5-TNN with a number of other nitrated naphthalenes are given in Ref 13

1,3,8-Trinitronaphthalene (beta-Trinitronaphthalene, 1,3,8-TNN). Pale yel monoclinic crysts from EtOH, chlf, acet ac, or NB (Refs 1 & 24), mp 223° (Ref 27); crystallographic data are given in Ref 26, p 203; cryst d 1.42g/cc (Ref 23); Q_c^v –4223.9cal/g, Q_c^p –1190kcal/mole (Ref 17), Q_f^v –27cal/g, Q_f^p –11cal/g (Ref 31), $Q_{nitration}$ 35.28kcal/mole (Ref 17); impact sensy similar to TNT (Ref 24), power by BalMort

83% of TNT (Ref 24), thermal stab at 135°, no acid fumes or expln after 300 min, no expln below 360° (Ref 24); vacuum stab, 0.46cc of gas evolved/5ml of sample in 48hours at 120° (Ref 24); hygroscopicity at 25° & 90% RH, wt gain 0.05%, at 100% RH, wt gain 0.09% (Ref 24). Its sol in a number of solvs is given in Ref 15. 1,3,8-DNN may be isolated from coml TNN in yields from 33–57%. It is best prepd by the nitration of 1,8-DNN with concd nitric ac in sulfuric ac, yield 60%; or in aq nitric ac, yield 66% (Ref 34). It can also be prepd by the redn of 4-chloro-1,3,8-trinitronaphthalene with powd Cu in NB (Ref 13)

1,4,5-Trinitronaphthalene (gamma-Trinitronaphthalene, 1,4,5-TNN). Golden yel leaflets from nitric ac, mp 147–9° (Ref 4); Q_c^p −1122.7kcal/mole (Ref 21); CA Registry No 2243-95-0. It is isolated in 3–10% yield from coml TNN (Ref 18). It is best prepd by nitration of 1,5-DNN with nitric ac (d 1.5g/cc) in sulfuric ac (d 1.84 g/cc) below 30°, yield 94% (Ref 33); or in good yield by nitration of naphthalene with nitric ac in polyphosphoric ac (Ref 37). Its sol in a number of solvs is given in Ref 15

Refs: 1) Beil **5**, 563, (265) & [457] 2) Beil **5**, 563, (265), [457] & {1612} 3) Beil **5**, 563, & [457] 4) Beil **5**, 563, [458] & {1613} 5) Lautemann & A. deAguiar, BullFr (2) **3**, 256 (1865) 6) A. deAguiar, Ber **5**, 374 (1872) 7) A. deAguiar, Ber **5**, 897 (1872) 8) W. Will, Ber **28**, 377 (1895) 9) H. Dautriche, MP **15**, 150 (1909–10) 10) H. Dautriche, MP **16**, 1 (1911–12) & CA **6**, 1227 (1912) 11) Colver (1918) 12) R.L. Datta & N.R. Chatterjee, JCS **115**, 1007 (1919) 13) P. Pascal, BullFr (4) **27**, 388 (1920) & CA **14**, 2711 (1920) 14) J.E. Crawshaw, JFrankInst **189**, 607 (1920) & CA **14**, 1897 (1920) 15) L. Desvergnes, MonSci (5) **16**, 79 & 201 (1926) & CA **21**, 740 (1927) 16) A. Segay, FrP 645566 (1927) & CA **23**, 2036 (1929); BrP 299462 (1927) & CA **23**, 3346 (1929) 17) W.H. Rinkenbach, JACS **52**, 116 (1930) 18) Pascal (1930), 114 19) Vennin, Burlot, Lécorché (1932), 426 20) J. Pepin Lehalleur (1935), 192 21) M. Badoche, BullFr (5) **4**, 232 (1937) & CA **31**, 4196 (1937) 22) P.P. Shorygin et al, ZhObschKhim **8**, 981 (1938) & CA **33**, 3781 (1939) 23) G.B. Kistiakowski, "The Heats of Combustion of Explosives", **OSRD 702** (July 1942), Table II 24) R. McGill, "Evaluation of Explosives Submitted to the Explosives Research Laboratory in 1941", **OSRD 830** (Aug 1942), 64 25) H.E. Fierz-David & R. Sponagel, Helv **26**, 98 (1943) & CA **37**, 5961 (1943) 26) A.T. Blomquist, "Microscopic Examination of High Explosives and Boosters", **OSRD 3014** (Aug 1944) 27) H.H. Hodgson et al, JCS **1945**, 455 28) Anon, "Handbook of Japanese Explosive Ordnance", **OpNav 30-3M** (Aug 1945), 32 29) Anon, MP **34**, 389 (1952) & CA **49**, 4293g (1955) 30) L. Médard, MP **34**, 397 (1952) & CA **49**, 4293h (1955) 31) P. Tavernier, MP **38**, 329 (1956) & CA **51**, 15952c (1957) 32) P. Tavernier, MP **39**, 253 (1957) & CA **53**, 1717 (1959) 33) E.R. Ward et al, JCS **1959**, 487 34) E.R. Ward & C.D. Johnson, JCS **1961**, 4316 35) K.K. Andreev, Explosivst **10**, 203 (1962) & CA **58**, 3263c (1963) 36) PA, "Handbook of Foreign Explosives", US Army **FSTC 381-5042** (Oct 1965) 37) N.S. Koslov et al, IzvVysshUchebnZaved,KhimKhimTekhnol, **17**, 1043 (1974) & CA **81**, 120299 (1974)

Tetranitronaphthalenes, $C_{10}H_4N_4O_8$, mw 308.16, N 18.18%, OB to CO_2 −72.7%

Commercial Tetranitronaphthalene (TeNN). Yel cryst from acet ac, mp 200–20°, bp expl on rapid heating. It is prepd by nitration of DNN with mixed ac whose acid concns are tabulated in Ref 8, or by nitration of TNN with mixed ac contg an excess of oleum (Ref 12). As prepd in this way it is a mixt of isomers with the 1,3,6,8- predominating, with some 1,3,5,8- and 1,2,5,8-, plus a small amt of 1,3,5,7-TeNN (Ref 17). The yield is often low due to oxidn and other side reactions, hence TeNN has not been used in expls as much as other nitrated naphthalenes, although it is similar to TNT in expl props. It has been proposed as a filler for HE Arty shells, but has not been used as such, probably because of its expense (Ref 10). A mixt of 21.5% TeNN and 78.5% AN (OB to CO_2 +0.07%) has been proposed as a HE, but there is no ref to its use as such (Ref 10). More recently workers at Katalyst-Chemie claimed that naphthalene can be nitrated to TeNN with mixed ac if compds of Cr, Ga, In, Mo, Ni, Ta, V,

or W are used as catalysts (Ref 13); although there has been no ref to this work in the more recent literature. The expln press of TeNN has been reported as 3745kg/sq inch at a loading d of 0.3g/cc (this d seems low) (Ref 9)

1,2,4,6-Tetranitronaphthalene (1,2,4,6-TeNN). Pale yel plates from Ac_2O, mp 215° (Refs 4 & 16), decomps above its mp (Ref 16). It is prepd by nitration of 2,6-DNN with fuming nitric ac in concd sulfuric ac (Ref 16). The structure is somewhat uncertain as it was obtained in low yield. Its crystallographic props are given in Ref 16

1,2,5,8-Tetranitronaphthalene (1,2,5,8-TeNN). Mp 190–2° (Ref 22). It is prepd by nitration of 1,2-DNN or 1,2,8-TNN with mixed ac at 80° (Ref 22). Its power by the Pb plate test is similar to TNT (Ref 19). The TeNN, mp 310° with decompn, which was claimed to be 1,2,5,8-TeNN (Ref 7), was later shown to be 1,4,5,8-TeNN (see below) (Ref 15)

1,2,6,8-Tetranitronaphthalene (1,2,6,8-TeNN). Clusters of needles from bz/ligroin, mp 138°, decomps above the mp (Ref 16). It is prepd by nitration of 2,6-DNN with fuming nitric ac in concd sulfuric ac (Ref 22), and its crystallographic props are given in this Ref

1,3,5,7-Tetranitronaphthalene (alpha-Tetranitronaphthalene, 1,3,5,7-TeNN). Orange-yel bipyramids from Ac_2O, mp 260° (Refs 5 & 16), detons at 263–5° (Ref 16). It can be isolated in small amts from coml TeNN, but is best prepd by nitration of 2,6-DNN with mixed ac at 10°, or in 42% yield by nitration of 1,3,5-TNN with excess 92.3% nitric ac at reflux for 12hours (Ref 20). Its crystallographic props are given in Ref 16

1,3,5,8-Tetranitronaphthalene (gamma-Tetranitronaphthalene, 1,3,5,8-TeNN). Long needles from EtOH, mp 194–5°, bp explds (Ref 1), cryst d 1.54g/cc (Ref 15); CA Registry No 2217-58-5. It can be isolated from coml TeNN, but is best prepd by nitration of 1,7-DNN with mixed ac at 50°, yield 85% (Ref 16)

1,3,6,8-Tetranitronaphthalene (beta-Tetranitronaphthalene, 1,3,6,8-TeNN). Long needles from EtOH, mp 203.5–4.5° (Refs 2 & 24). There is no expln below 360° (Ref 14), but it explds violently on rapid heating (Ref 6); CA Registry No 28995-89-3. 1,3,6,8-TeNN is the principal component of coml TeNN and can be isolated from this source. It is best prepd, however, as follows: 1,8-DNN (10g) is added with stirring to a mixt of 50ml of fuming nitric ac (d 1.52g/cc) and 50ml of concd sulfuric ac at 20°, the mixt heated slowly to 80° over an horu and held at 80–90° for 3hours. The mixt is cooled, the solid filtered off, and the filtrate drowned in ice w. The 2 solids are combined and recrystd from 95% EtOH to give pure 1,3,6,8-TeNN (Ref 24). Q_c −1082.8kcal/mole, Q_f 1.5kcal/mole (Ref 15); hygroscopicity at 25° & 90% RH, wt gain is 0.07%; at 100% RH it is 0.3% (Ref 14); impact sensy is similar to Tetryl (Ref 14); power by BalMort is 101% of TNT (Ref 14); thermal stab at 135°, no acid fumes or expln after 300min; vacuum stab at 120°, 0.75cc of gas evolved/5g of sample in 48hours (Ref 14)

1,4,5,8-Tetranitronaphthalene (delta-Tetranitronaphthalene, 1,4,5,8-TeNN). Needles from NB (Ref 11), stout bars (Ref 21), mp darkens ca 280° (Ref 18), melts 340–5° with decompn (Refs 3 & 11), cryst d 1.80g/cc (Ref 21); CA Registry No 4793-98-0. More recently it has been claimed that the phys props in the literature were measured on impure material and that pure 1,4,5,8-TeNN has a phase change at 270° and decomps without melting above 450° (Ref 21). Because of its high mp and thermal stab at high temps, 1,4,5,8-TeNN was examined by workers at NOL as a heat resistant expl (Ref 23). Below is an improved proc developed at NOL for the prepn of this compd: a mixt of 1825ml of 90% nitric ac and 1825ml of 30% oleum are placed in a 5ℓ 3-necked flask, the mixt cooled to 20° with an ice bath, and 730g of 1,5-DNN added with stirring over ½hour. The mixt is stirred ½hour at 30°, the temp allowed to rise to 55–60°, held there until it begins to fall, then is stirred for 6½hours. The mixt is drowned in crushed ice, the solid filtered onto a coarse sintered glass filter, the cake digested with cold w, washed again with w, and dried overnight. The crude prod is digested twice with 2ℓ of hot acet to give 280g of crude 1,4,5,8-TeNN which can be recrystd from NB or 70% nitric ac (Ref 23, p 14). The material has the following props:

Detonation velocity. In ¼" Al tubes, 7013m/sec (Ref 21)

Differential thermal analysis. Gives a single endotherm at 250–60° showing the above-mentioned phase transition (Ref 23, p 3)

Gas volume produced on explosion. 780cc/g (Ref 21)
Impact sensitivity. NOL machine with a 2.5kg wt on sandpaper gives 99cm for 50% positives (Tetryl 32cm) (Ref 23, p 3)
Power by ballistic mortar. 101% of TNT (Ref 21)
Thermal stability. It discolors without melting at 360°; on heating rapidly on a hot stage, it shows no sign of melting to 450° (Ref 23, p 2)
Vacuum stability. At 280° gas evolution is 0.02cc/g/hr; at 300° 1.1cc/g/hr (Ref 23, p 2)

A discussion of the prepn of small particle size 1,4,5,8-TeNN and the reasons for its high mp and thermal stab are given in Ref 23, pp 8–12. As a prelude to its possible application in space missions, the effects of ionizing radiation on 1,4,5,8-TeNN were examined by workers at PA. After 40min irradiation in a nuclear reactor (GE Test Reactor at Pleasanton, Calif), the sample became dark brown, the phase change endotherm was shifted from 270 to 291°, and a DTA exotherm occurred at 381°; after 81min irradiation the phase change endotherm came at 313°, and the exotherm at 368°. Other minor changes in props were also noted (Ref 21, p 128)

Refs: 1) Beil **5**, 564 & [452] 2) Beil **5**, 564, [459] & {1614} 3) Beil **5**, 564 & {1614} 4) Beil **5**, [459] 5) Beil **5**, {1613} 6) Lautemann & A. deAguiar, BullFr (2) **3**, 261 (1865) 7) W. Will, Ber **28**, 369 (1895) 8) G. Patart, MP **11**, 152 (1901) 9) L. Vennin & G. Chesneau, "Les Poudres et Explosifs. Les Measures de Securetê dans les Mines & Houille", C. Beranger, Paris (1914) & CA **8**, 3629 (1914) 10) Colver (1918), 273–5 11) O. Dimroth & F. Ruck, Ann **446**, 125 (1926) & CA **20**, 1077 (1926) 12) Vennin, Burlot & Lêcorchê (1932), 427 13) Katalyst-Chemie AG, FrP 821767 (1937) & CA **32**, 3964 (1938) 14) R. McGill, "Evaluation of Explosives Submitted to the Explosives Research Laboratory in 1941", **OSRD 830** (Aug 1942), 57 15) G.B. Kistiakowski, "The Heats of Combustion of Explosives", **OSRD 702** (July 1942), Table II 16) J. Chatt & W.P. Wynne, JCS **1943**, 4314 17) Davis (1943), 156 18) J.S. Whitehurst, JCS **1951**, 220 19) D. Smoleński & W. Czbuda, ZeszytyNaukPolitechWrclawa No10, Chem **2**, 3 (1955) & CA **51**, 4712h (1957) 20) E.R. Ward et al, JCS **1959**, 488 21) L. Avrami & W.E. Voreck, "A Determination of Reactor-Radiation-Resistant Explosives, Propellants, and Related Materials", PATR **3782** (Nov 1959), 126, AD-506895 22) E.R. Ward & C.D. Johnson, JCS **1961**, 4314 23) H.G. Adolph, "Heat Resistant Explosives, XXIV. Selected Properties and Preparation of 1,4,5,8-Tetranitronaphthalene (TNN-1,4,5,8)", **NOLTR 67-11** (Apr 1967), AD-381547 24) J.H. Fendler et al, JOC **36**, 1749 (1971)

Higher Nitrated Naphthalenes, besides the claim by KatalystChemie, FrP 821767 (1937) & CA **32**, 3964 (1938), that penta- and hexanitronaphthalenes can be prepd by nitration of naphthalene if certain catalysts are used, no higher nitrated naphthalenes have been reported in the literature

Written by **C. H. McDONNELL**

Naphthalit. A Ger chlorate expl introduced during WWI. It contained not more than 80% K chlorate and aromatic hydrocarbons (such as naphthalene), and not more than 12% nitrohydrocarbons (but no trinitro compds), the remainder consisting of paraffins, fatty oils, flour or other combustibles. It might also contain not more than 4% blasting gelatin. The prefixes Gesteins- and Wetter- were applied if the expls were intended for rock or coal mine use
Ref: Marshall, Dict (1920), 65

Naphtalites. Fr safety expls containing nitronaphthalenes
Ref: Davis (1943), 157

Naphtite. Same as commercial Trinitronaphthalene (qv)

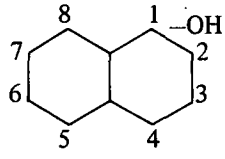
Naphtites. Expls proposed in Fr by the Société Générale Pour la Fabrication de la Dynamite, but not permitted to be manufd. These expls had properties between those of Grisoutines (see Vol **6**, G143-R) and Favier (see Vol **6**, F10-L ff) powders; *Naphtite No 1:* AN 88, NG 4 & MNN 8%; *Naphtite Grisoutine:* AN

92, NG 4 & MNN 4%. The first mixt could not be detonated completely, even by a cap containing 1.5g of MF
Refs: 1) H. Dautriche, MP **16**, 54–8 (1911–12) 2) Ibid, SS **7**, 96–7 (1912)

NAPHTHOL AND DERIVATIVES

Naphthols. (Hydroxynaphthalenes; Oxynaphthalins, in Ger). $C_{10}H_7.OH$, mw 144.19. Two isomers are known, 1–(or alpha) & 2-(or beta):

1-(or α)-Naphthol (1-Hydroxynaphthalene).



yellow monoclinic needles, mp 94–96°, bp 288° (subl), d 1.0989g/cc at 99/4°, RI 1.6224 at 99°. Sol in benz, alc & eth. Prepn from 1-naphthalenesulfonate by fusing with caustic soda, decomposing the melt with hydrochloric acid & distilling off the 1-naphthol in vacuo. Combustible. Q_c 8233cal/g, Q_f 31.3kcal/mole
Refs: 1) Beil **6**, 596, (304) & [572] 2) A. Leman & G. Lepoutre, CR **226**, 1976–8 (1948) & CA **42**, 8061 (1948) 3) CondChemDict (1971), 604 4) ChemRubHdb (1972–73), C-381

Benzeneazonaphthol. See Benzenazonaphthol & Derivatives in Vol **2**, B53-R ff

Benzeneazonitronaphthol. See Benzeneazonitronaphthol & Derivatives in Vol **2**, B54-R ff

1-Naphthol Additive Compounds

2,4,6-Trinitro-3-Methyl-Phenol + 1-Naphthol (2,4,6-Trinitro-m-cresol + 1-oxy-naphthalene). $HO.(O_2N)_3C_6H.CH_3 + C_{10}H_7.OH$, mw 387.33, N 10.85%, OB to CO_2 –142.51%, orange-yellow silky needles from dil alc, mp 159°. Sol in hot alc. Prepn by mixing hot saturated alc solns of the constituents & allowing the mixt to cool slowly. Expln temp 472°
Ref: Beil **6**, [578] & {2922}

2,4,6-Trinitro Phenol + 1-Naphthol (Picric Acid + 1-oxy-naphthalene). $(O_2N)_3C_6H_2.OH + C_{10}H_7.OH$, mw 373.30, N 11.26%, OB to CO_2 –126.44%, orange-red crysts from methanol & w, mp 190–190.5° (decompn). Sol in alc & eth, sl sol in chlf; v sl sol in cold w. Prepn by blending the compounds in alc until they are dissolved
Refs: 1) Beil **6**, 605, (306) & {2922} 2) T. Asahina & C. Shinomiya, JChemSocJapan **59**, 341, 342, 345 (1938) & CA **32**, 9075 (1938)

2-(or β-) Naphthol (2-Hydroxynaphthalene). White monoclinic leaflets, mp 123–24°, bp 295°, d 1.28g/cc at 20°. Sol in alc, eth, chlf, glyc, oils & alkaline solns. Prepn from 2-naphthalene sulfonate by fusing with caustic soda, decomposing the melt with hydrochloric acid & distilling off the 2-naphthol in vacuo. Flash point is 307°F, Q_c 8213cal/g, Q_f 34.2kcal/mole
Refs: 1) Beil **6**, 627, (310) & [591] 2) A. Leman & G. Lepoutre, CR **226**, 1976–8 (1948) & CA **42**, 8061 (1948) 3) CondChemDict (1971), 604 4) ChemRubHdb (1972–73), C-381

2-Naphthol Additive Compounds

2,4,6-Trinitro-3-Methyl-Phenol + 2-Naphthol (2,4,6-Trinitro-m-cresol + 2-Oxy-naphthalene). $HO.(O_2N)_3C_6H.CH_3 + C_{10}H_7.OH$, mw 387.33, N 10.85%, OB to CO_2 –142.51%, orange needles from dil alc, mp 124°. Sol in hot w & dil alc. Prepn by mixing hot saturated w solns of the constituents & allowing the mixt to cool slowly. Expln temp 452°
Ref: Beil **6**, [597] & {2969}

Mononitrocompounds of Naphthols

Only one of these compounds decomps at its mp:

8-Nitro-1-Naphthol (8-Nitro-1-oxy-naphthalene). $(O_2N)C_{10}H_6.OH$, mw 189.18, N 7.41%, OB to CO_2 –173.38%, mp 212° (decompn). Prepn from 1-naphthyl-m-nitrobenzene sulfonate by nitration with nitric acid in AcOH, then hydrolysis with piperidine
Refs: 1) Beil – not found 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 245

Other Derivatives of the Mononitrocompounds of Naphthols

1-Nitro-4,6-Dibromo-2-Naphthol (4,6-Dibromo-1-nitro-2-naphthol). $Br_2.C_{10}H_4(NO_2).OH$, mw 346.97, N 4.04%, OB to CO_2 −89.99%, yellow needles from alc, mp 148–50° (decompn). Prepn from 4,6-dibrom-2-naphthol by nitration with nitrous-nitric acid (d 1.5g/cc) in AcOH at RT

Ref: Beil **6**, 609

2-Nitro-4-Iodo-1-Oxy-Naphthalene (2-Nitro-4-iodo-1-naphthol). $(O_2N)C_{10}H_5(I).OH$, mw 315.09, N 4.45%, OB to CO_2 −101.56%, clear golden needles, mp 115° (decompn). Prepn from 4-nitro-2-acetoxymercuric-naphthol-(1) by reacting with iodine

Ref: Beil **6**, (586)

1-Nitro-3,4,6-Tribromo-2-Naphthol (1-Nitro-3,4,6-tribromo-2-oxy-naphthalene). $O_2N.C_{10}H_3Br_3.OH$, mw 425.87, N 3.29%, OB to CO_2 −71.38%, turns black at 135°, mp 136° (decompn). Prepn from 1,3,4,6-tetrabromo-1-nitro-2-naphthol by reaction with nitric acid, then alkali

Ref: Beil **6**, 655

Dinitrocompounds of Naphthols

Dinitro naphthols. $(O_2N)_2.C_{10}H_5.OH$, mw 234.17, N 11.96%, OB to CO_2 −123.00%

2,4-Dinitro-1-Naphthol (2,4-Dinitro-1-oxy-naphthalene). Yellow crysts, mp 139.5°. Sol in alc & chlf. Prepn from naphthalene as a by-product during nitration with dil nitric acid & Hg(II) nitrate. The **Lead Salt** of the above can be shown as $Pb[O.C_{10}H_5(NO_2)_2]_2$, mw 729.57, N 7.68%, OB to CO_2 −76.75%. The explosive sensitivity of this salt compared to PA is 49%

Refs: Beil **6**, 617, (308) & [586, 587] 2) A.H. Blatt & F.C. Whitmore, OSRD **1085**, 26 (1942) 3) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 247

4,5-Dinitro-1-Naphthol (4,5-Dinitro-1-oxy-naphthalene). Yellow needles from alc, mp 208° (decompn). Sol in alc, acet, alkaline & ammoniacal w soln; sl sol in w. Prepn from 5-nitro-naphthochinon-(1,4)-oxime (4) by reacting with basic K ferrocyanide soln at RT

Refs: 1) Beil **6**, 619 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 248

4,6-Dinitro-1-Naphthol (4,6-Dinitro-1-oxy-naphthalene). Crysts from methanol (as Na salt), mp 240°. Sol in chlf. Prepn from 1,4,6-trinitro-2-naphthylamine by diazotization in AcOH-sulfuric acid to yield 4,6-dinitro-2-diazo-1-naphthol; steam is passed thru the mixt to yield the naphthol

Refs: 1) Beil – not found 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 248

4,8-Dinitro-1-Naphthol (4,8-Dinitro-1-oxy-naphthalene). Yellow needles from 25% alc/w; mp, turns black at 200° & melts at 235° (decompn). Sol in alc, AcOH & cold Na carbonate soln. Prepn from 8-nitro-naphthochinon-(1,4)-oxime-(4) by oxidation with alkaline K ferrocyanide

Ref: Beil **6**, 619

1,5-Dinitro-2-Naphthol (1,5-Dinitro-2-oxy-naphthalene). Crysts from AcOH, mp 187° (decompn). Sol in hot benz. Prepn from 5-nitro-2-naphthyl-m-nitrobenzene-sulfonate by nitration with fuming nitric acid. Yield 24%

Refs: 1) Beil – not found 2) W. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 248

1,6-Dinitro-2-Naphthol (1,6-Dinitro-2-hydroxy-naphthalene). Pale yellow needles from chlf, mp 195° (decompn). Sol in eth, hot alc, chlf & py. Prepn from bis-(2-hydroxy-1-naphthyl) sulfide by nitration in AcOH at 55°. Yield 78%

Refs: 1) Beil **6**, 656, (316) & [610] 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 248 3) ChemRubHdb (1974–75), C-381

1,8-Dinitro-2-Naphthol (1,8-Dinitro-2-oxy-naphthalene). Brownish yellow leaflets or needles from alc, mp 198–99° (decompn). Sol in w, alc & chlf. Prepn from 1,8-dinitro-2-ethoxy naphthalene by heating with alc KOH

Ref: Beil **6**, 655–56, (316) & [610, 656]

4,5-Dinitro-2-Naphthol (4,5-Dinitro-2-oxy-naphthalene). Mp 238°. Prepn from 4-nitro-2-naphthyl-m-nitrobenzenesulfonate by nitration & hydrolysis with piperidine

Refs: 1) Beil – not found 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 249

2,7-Dinitro-8-Hydroxy-1-Acetoxy-Naphthalene (2,7-Dinitro-8-acetoxy-naphthol-(1), acetic acid-[2,7-dinitro-8-hydroxy-naphthyl-(1)-ester], [2,7-dinitro-8-hydroxy-naphthyl-(1)]-acetate). $HO.(O_2N)_2C_{10}H_4.OCOCH_3$, mw 292.22, N 9.59%, OB to CO_2 −149.81%, gold-green crysts from AcOH, mp 125–70° (decompn). Prepn from 2,7 (?)-dinitro-naphthalendiol-(1;8) by reaction with Ac_2O for one hour at RT

Ref: Beil **6**, {5285}

5,7-Dinitro-8-Hydroxy-1-Acetoxy-Naphthalene (2,4-Dinitro-8-acetoxy-naphthol-(1), acetic acid-[5,7-dinitro-8-hydroxy-naphthyl-(1)-ester], [5,7-dinitro-8-hydroxy-naphthyl-(1)-acetate]. $HO.(O_2N)_2C_{10}H_4.OCOCH_3$, mw 292.22, N 9.59%, OB to CO_2 −149.81%, gold prisms from AcOH, mp 200° (decompn). Sol in alc & boiling AcOH. Prepn from 1,8-diacetoxy-naphthalene by reaction with dil nitric acid (d 1.4g/cc) at 25–30°

Ref: Beil **6**, {5284}

2,4-Dinitro-1-Naphthol-7-Sulfonic Acid (5,7-Dinitro-8-hydroxy-naphthalene-2-sulfonic acid, Flavianic acid). $(HO_3S).C_{10}H_4(NO_2)_2.OH$, mw 314.23, N 8.92%, OB to CO_2 −76.38%, pale yellow needles from w, mp 140–50° (decompn). Sol in w, alc & butyl alc; sl sol in concd HCl. Prepn from the disodium salt (called naphthol yellow S) by heating with 40% concd sulfuric acid & recrystallizing from concd HCl, chlf & hot w. Q_c^v 3156cal/g; Q_c^p 3152cal/g; Q_f^v 916.5 cal/g. The **Dipotassium Salt** of the above can be shown as $(KO_3S).C_{10}H_4(NO_2)_2.OK+1.5H_2O$, mw 417.42, N 6.71%, OB to CO_2 −53.66%, golden yellow crysts; mp, turns red when heated & explds. Sol in w. Prepn from the disodium salt called naphthol yellow S by adding to a hot soln of the disodium salt an excess of a concd w soln of K chloride. Explosion temp is 270°. Q_c^v 2498cal/g; Q_c^p 2495cal/g; Q_f^v 1157.1cal/g; Q_f^p 1169.9cal/g. Heat test at 100° for 3 hours showed a loss of 0.1% in weight

Refs: 1) Beil **11**, 275 & [156] 2) E. Knecht & H. Hibbert, Ber **37**, 3475 (1904) 3) M. Badoche, Bull(Fr) [5] **13**, 10, 37 (1946) 4) L. Médard & M. Thomas, MP **34**, 426 (1952) 5) ChemRubHdb (1973–74), C-385

Trinitro-1-Naphthols

$(O_2N)_3.C_{10}H_4.OH$, mw 279.17, N 15.05%, OB to CO_2 −88.50%. All of the trinitro naphthols expld on heating. Some of their salts are also expl

2,4,5-Trinitro-1-Naphthol (2,4,5-Trinitro-1-hydroxy naphthalene). Yellow leaflets or prisms; mp 189–90°; bp, explds. Sol in hot AcOH, sl sol in hot w, alc, benz, eth acetate, xylene & cold AcOH. Prepn from 2,4-dinitro-naphthol by nitration, or from 4-chlor-1,3,8-trinitronaphthalene by heating with 0.1N NaOH in w or alc

Refs: 1) Beil **6**, 619, (309) & [587] 2) M. Rindl, JCS **103**, 1913 (1913) 3) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 249

2,4,7-Trinitro-1-Naphthol (2,4,7-Trinitro-1-oxy-naphthalene). Yellow prisms from AcOH or benz, mp 145° (decompn). Sol in AcOH & glac AcOH. Prepn from 2,4-dinitro-1-naphthol by mixed acid (nitric-sulfuric-acetic) nitration. The compound is extracted as the Na salt from the AcOH washings of the concd mother liq

Refs: 1) Beil **6**, 620 2) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold Ltd, London (1958), 250

2,4,8-Trinitro-1-Naphthol (2,4,8-Trinitro-1-oxy-naphthalene). Yellow prisms, mp 175°. Sol in cold w. Prepn from 8-nitro-naphthoquinone-(1,4)-oxime by heating with dil nitric acid

Ref: Beil **6**, 620 & (309)

2,4,6-Trinitro-5-Acetoxy-1-Naphthol (2,6,8-Trinitro-5-hydroxy-1-acetoxy-naphthalene, acetic acid-[2,6,8-trinitro-5-hydroxy-1-naphthyl-ester], [2,6,8-trinitro-5-hydroxy-1-naphthyl]-acetate). $(O_2N)_3C_{10}H_3(OCOCH_3).OH$, mw 337.22, N 12.46%, OB to CO_2 −87.78%, yellow needles from AcOH, mp 223° (decompn). Prepn from 1,5-diacetoxy-naphthalene by nitration with dil nitric acid at 40–50°

Ref: Beil **6**, {5275}

X,X,X-Trinitro-3-Chlor-1-Naphthol (X,X,X-Trinitro-3-chlor-1-oxy-naphthalene, X,X,X-trinitro-4-chlor-2-oxy-naphthalene). $(O_2N)_3C_{10}H_3Cl.OH$, mw 313.62, N 13.40%, OB to CO_2 −76.53%; crysts from AcOH with 1 mol AcOH as yellow-blue needles, mp ∿156°

(decompn). Sol in alc & AcOH. Prepn from 1,3-dichlor-X,X,X-trinitro-naphthalene by heating with alcoholic NaOH
Ref: Beil **6**, 664

Trinitro-2-Naphthols

1,6,8-Trinitro-2-Naphthol (1,6,8-Trinitro-2-hydroxy naphthalene). Light yellow crysts, mp 221°. Prepn from 7-chlor-1,3,8-trinitro-naphthalene by treating with NaOH soln in the presence of acet. Explds on heating
Refs: 1) Beil **6**, (610) 2) E.J. van der Kam, Rec **45**, 725 (1926)
X,4,6-Trinitro-2-Naphthol (X,4,6-Trinitro-2-oxy-naphthalene). Yellow needles from alc, mp 150° (decompn). Prepn from 4,6-dibromo-2-naphthol by nitration with nitrous-nitric acid. Rapid decompn occurs above 159°
Ref: Beil **6**, [610]
X,X,X-Trinitro-7,8-Dinitroso-2-naphthol (7,8-Dinitroso-X,X,X-trinitro-2-oxy-naphthalene). $(O_2N)_3C_{10}H_3(NO)_2.OH$, mw 337.18, N 20.78%, OB to CO_2 −59.21%, yellow crysts, mp 208° (decompn). Prepn from an AcOH suspension of 7-oxy-naphthochinon-(1,2)-dioxime by heating with nitric acid. Explds when heated above mp. The mono K salt (orange yellow crysts) explds with great violence when heated to about 260°. This salt, together with the Pb salt of trinitro-phloroglucinol, has been used as a priming compn for loading blasting caps, Flobert ammo & the like
Refs: 1) Beil **8**, 300 2) H. Rathsburg, BritP 190215 (Sept 10, 1921) & CA **17**, 3101 (1923)

Tetranitro-1-Naphthols

$(O_2N)_4C_{10}H_3.OH$, mw 324.18, N 17.29%, OB to CO_2 −64.20%
2,4,5,7-Tetranitro-1-Naphthol (2,4,5,7-Tetranitro-1-hydroxy naphthalene). Mp 180°, yellowish leaflets or needles. Sl sol in cold AcOH, better in hot AcOH; sl sol in benz (1p in 220p benz at 18°). Prepn from 4-brom-1,3,6,8-tetranitro naphthalene by heating on a w bath with an excess of Na carbonate soln. Explds on heating. Forms some expl salts
Refs: 1) Beil **6**, 620 2) V. Merz & W. Weith, Ber **15**, 2714 (1882)
4,X,X,X-Tetranitro-1-Naphthol (4,X,X,X-Tetranitro-1-oxy-naphthalene). Yellow needles from alc, mp 215°. Prepn from 4-nitro-1-ethoxy naphthalene by nitration
Ref: Beil **6**, 621
X,X,X,X,X-Pentanitro-X-Naphthol (X,X,X,X,X-Pentanitro-X-oxy naphthalene). $(O_2N)_5C_{10}H_2.OH$, mw 369.18, N 18.97%, OB to CO_2 −45.51%. Prepn from naphthalene by action of nitric acid & Hg nitrate followed by sulfuric acid
Refs: 1) Beil – not found 2) T.L. Davis, USP 1419027 (1922) & CA **16**, 2781 (1922) 3) A.H. Blatt & F.C. Whitmore, OSRD **1085**, 74 (1942)

Nitrosocompounds of Naphthols

There is only one nitroso compound that decomps at its mp:
4-Nitroso-1-Naphthol (Naphthochinon-(1,4)-monoxime). $ON.C_{10}H_6.OH$, mw 173.18, N 8.09%, OB to CO_2 −198.64%, pale yellow needles from benz or dil alc, mp 193–94° (decompn at 190° thru mp). Sol in alc, me alc, acet, eth, chlf & C disulfide. Prepn from 4-nitroso-1-methoxy-naphthalene by saponification with mineral acid. Q_c^v 1166.4cal/g-mole & Q_c^p 1166.5 cal/g-mole
Refs: 1) Beil **7**, 727, (386), [653] & {3700} 2) ChemRubHdb (1974–75), C-381

Peroxides of Naphthols

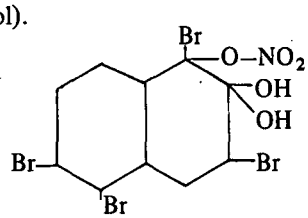
There is only one peroxide compound that explds (by rubbing):
7-Hydroxy-1,2-Dioxo-1,2-Dihydro-Naphthalene (7-Hydroxy-naphthochinon-(1,2), 7-Hydroxy-1,2-naphthoquinone). $(HO).C_{10}H_5:(O)_2$, mw 174.16, OB to CO_2 −183.74%, dark red microcrysts, mp 203–204° (decompn). Sol in alc & AcOH. Prepn from 1-amino-2,7-dioxy-naphthalene by oxidation with chromic-sulfuric acid
Refs: 1) Beil **8**, 299, (634) & {2542} 2) S. Mededeco & O. Bloch, ChemZtr (1935), 2670 3) Tobolsky & Mesrobian (1954), 179

Dihydroxynaphthalene and Derivatives

Note: These compounds are described in Vol **5**, D1294-L to D1295-L, however, more recent edi-

tions of Beil have revealed several additional derivatives, two of which are of particular interest:

(±)-1,3,5,6-Tetrabrom-1-Nitryloxy-1H-Naphthalendiol-(2,2) ((±-1,3,5,6-Tetrabrom-2,2-dihydroxy-1-nitryloxy-1,2-dihydro-naphthalene, (±)-1,3,5,6-tetrabromo-1-nitryloxynaphthalene-2,2(1H)-diol).



mw 538.78, N 2.60%, OB to CO_2 −51.97%, needles from benz, mp 121° (decompn). Sol in benz & alc. Prepn from an AcOH suspension of 1,3,5,6-tetrabrom-2-naphthol by warming with dil nitric acid (d 1.4g/cc)

Ref: Beil **7**, {3693}

2-Nitroso-Naphthalendiol-(1,8) (2-Nitroso-1,8-dioxy-naphthalene). $ON.C_{10}H_5.(OH)_2$, mw 189.18, N 7.41%, OB to CO_2 −173.38%, brownish yellow needles from benz; mp, turns dark at 170° & decomps at 183°. Sol (exhibiting a yellow color) in acet, eth, alc, ligr & benz. Prepn from 1,8-dioxy naphthalene by reaction with Na nitrite in AcOH. Explds when heated quickly

Ref: Beil **8**, [344]

Written by: **H. L. HERMAN**

Naphthylamines. See under Aminonaphthalenes and Derivatives in Vol **1**, A237-L to A238-L

Nationalite. A Brit coal mine expl of the Grisounite class (see Vol **6**, G-143-L). The original composition contained AN 92 & Di- and Trinitrotoluenes 8%. In order to pass the Rotherdam Test for acceptance on the permitted list, it was necessary to add alkali chlorides, resulting in the following formulations:

Table 1

	No 1	No 2
Date of Permit	6-22-1914	1-28-1915
Amm Nitrate, %	65.5	64.0
TNT, %	15.0	15.0
Na chloride, %	19.5	–
K chloride, %	–	21.0
Limit charge, oz	12	20
Power (BalPend swing, inches)	2.92	2.63

The permits were subsequently repealed

Ref: Marshall, Dict (1920), 65

National Transportation Safety Board. An independent agency of the US Government established under the Transportation Safety Act of 1974, reporting directly to the Congress with recomendations for legislation. It conducts a continuing review of safety in all modes of transportation, including hazardous materials. Thru its Hazardous Materials Safety Division, the Board evaluates the adequacy of safeguards and procedures concerning the transportation of hazardous materials as well as the performance of other government agencies charged with assuring the safe transportation of such materials. Although the Board has no regulatory authority, their recommendations and responses to these recommendations are published in the Federal Register

Ref: J. H. Reed, "Hazardous Materials Safety – Where Are We Going?", Transportation Association of America National Seminar, Denver, Colorado (June 1975)

Natriialmatrit No 19. See under Almatrites in Vol **1**, A140-L

Natural Barricade. See under Barricades in Explosives and Ammunition Installations in Vol **2**, B22-R

Natural Gas. See under Gas, Natural in Vol **6**, G27-R. Dangerous fire and expln hazard. Flash pt 900–1170°F; flammable limits in air 3.8–6.5% & 13–17% by vol (Ref 2). Stoichio-

metric natural gas-air mixts were exploded at pressures as low as 0.2 atm in a pipe 2 ft in diameter by 300 ft long. Measured expln pressures exceeded the theoretically predicted pressures of a detonation. The detonation hazard can be reduced by the proper application of water sprays in the region in which the detonation is being developed. The combination of water sprays and a large increase in the vol of the system stopped the established detonation (Ref 1)
Refs: 1) M. Gerstein, E.R. Carlson & F.V. Hill, IEC **46**, 2558–62 (1954) & CA **49**, 2736 (1955) 2) Anon, "Fire Protection Guide on Hazardous Materials", 5th Ed, 325M-85, National Fire Protection Association, Boston, Mass (1973)

Nauchoff's Explosives. Low freezing plastic expls patented prior to WWI by S.A.S. Nauchoff of Sweden. It was claimed that they were equal to Dynamites in performance. Examples are: (1) Liq TNT (gelatinized by dissolving 4p of NC in 96p of liq TNT, called "flüssige Tri" in German) 31, Amm perchlorate 43 & AN 26% (Ref 3); (2) Liq TNT (gelatinized) 31, AN 43 & Na nitrate 26% (Ref 1); and (3) Liq DNT (gelatinized) 31, Amm perchlorate 43, & Na or K nitrate 26% (Ref 2). One of these expls was called **Territ** (qv)
Refs: 1) S.A.S. Nauchoff, USP 1058891 (1913) & CA **7**, 1975 (1913) 2) Ibid, USP 1061774 (1913) & CA **7**, 2309 (1913) 3) Colver (1918), 247 & 681

Navez Chronograph. See under Chronographs, Chronoscopes, Chronometers and Other Devices Used in Measuring Velocities of Projectiles in Flight and of Detonation Velocities of Explosives in Vol **3**, C305-R

Navol Tank, Torpedo. A tank forming part of a torpedo assemblage, provided for the storage of solution of hydrogen peroxide in water. Decomposition of the hydrogen peroxide furnishes the oxygen required to effect combustion of the fuel, alcohol
Ref: Anon, OrdTechTerm (1962), 202-R

NBSX or ATX. Code designations for 1,7-Dinitroxy-1,3,5,7-tetramethylene-2,4,6-trinitramine or 1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, described in Vol **5**, D1295-R

NC. Abbr for Nitrocellulose
Ref: Anon, OrdTechTerm (1962), 202-R

N.E. Brit sporting smokeless proplnt introduced in 1912. It contains NC (insol) 50.0, NC (sol) 25.8, metallic nitrates 12.0, nitrohydrocarbons 7.0, vaseline 3.5 & moisture 1.7%
Ref: Marshall **3** (1932), 96

Nebelwerfer. Ger for "smoke thrower". A WWII Ger artillery piece that was originally designed to launch smoke shells, but was modified to launch rockets, including 150mm, 210mm and 320mm types. As many as six launchers were mounted on one vehicle. The total weight of the 150mm unit was about 1200 lbs, and the rockets had a range of up to 7750 yds. Nebelwerfers were first used on the Russian front in 1941
Refs: 1) Anon, OrdTechTerm (1962), 202-R 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 322

Neck. Cylindrical portion of cartridge case between mouth and shoulder (Ref 1). The part of a cannon immediately behind the swell of the muzzle (Ref 2)
Refs: 1) Anon, OrdTechTerm (1962), 202-R 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 322

Needle Gun. A gun that utilizes a needle-fire cartridge in which a needle penetrates thru the base of the cartridge and strikes the primer within the case, thus setting off the charge. Needle guns were of muzzle-loading and breechloading types, the best known of the latter being the **Dreyse rifle**, which was first used by the Prussians (see under Johann Nicolas von Dreyse in Vol **5**, D1544-R). It was a single-shot rifle with a bolt-breech action, and fired a conical

bullet encased in a paper cartridge with a powder charge. The bolt of the rifle contained a long needle that penetrated the paper cartridge, passed thru the proplnt, and detonated a primer attached to the base of the bullet. This weapon, in .607 cal, was adopted by the Prussian Army in 1840 and remained in service thru the wars with Austria (1866) and France (1870). Other needle guns included the **Chassepot** (see in Vol **2**, C154-L), **Needham** and **Chatauvillard**
Refs: 1) J.R. Newman, "The Tools of War", Doubleday Doran, NY (1943), 44 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 145 & 322

Neesen's Photogrammetric Apparatus. Invented in 1903 for determining the speed of rotation of projectiles. Also see under Neesen's Chronograph in Vol **3**, C306-L
Ref: Cranz **3** (1927), 315–21

Negro. A Ger manned torpedo of WWII. The pilot rode on a manually controlled electric torpedo with its warhead removed. He sat in a 20″ plastic dome which rode just above the water. Attached beneath this vehicle was a regular electric torpedo with a live warhead which could be launched by the pilot
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 322

Negro Powder No 2. Favier type permissible expl containing AN 57.0, TNT 15.0, Na chloride 27.5 & graphite 0.5%. Limit charge is 24 oz, and power by BalPend is 2.86″
Refs: 1) Marshall **1** (1917), 390 2) Colver (1918), 250

Nellite. Brit expl containing 70/30 Picric Acid (PA)/Dinitrophenol (DNP), used during WWII in shells and armor-piercing bombs. A 60/40 mixt, designated **MBT**, was used by the Italians for shell loading; and the same mixt, designated **DD**, was used by the French for loading shells and bombs. An 80/20 mixt was designated **Tridite.** All three mixts are suitable for melt-loading at temps below 100°, and therefore represent an improvement over the melt-loading of PA. Tridite is slightly inferior to PA as an expl, and DNP is somewhat objectionable because of toxicity
Ref: Anon, "Military Explosives", **TM 9-1910** (1955), 214

NENA. Code name for N-(β-Nitroxyethyl) nitramine. It is described as 1-Nitramino-2-ethanol Nitrate in Vol **1**, A201-L. See also **MeNENA** and **Me_2NENA** in this Vol, **EtNENA** in Vol **6**, E342-L, and **Iso-Me-NENA** in Vol **1**, A253-L

NENO. Code name for N,N′-Dinitro-N,N′-bis (2 hydroxyethyl)-oxamide Dinitrate (CA nomenclature). See in Vol **5**, D1244-L to D1245-R
Addnl Ref: A.J. Phillips, "Suitability of NENO as a Military Explosive", PATR **1441** (1944)

Néo (Poudres). Fr double-base proplnts containing diethyleneglycoldinitrate (DEGDN) and nitrocellulose

Neonals. Brit permissible expls; **No 1:** K perchlorate 14, NG 40, collodion cotton 2, woodmeal 4.5, Amm oxalate 39.5 & w 0.5%; power by BalPend 2.51″, limit charge 30 oz; **No 2:** K perchlorate 37, NG 21, collodion cotton 1, TNT plus DNT 0.2, woodmeal 15, Amm oxalate 25 & w 0.8%; power by BalPend 2.56″, limit charge 16 oz
Refs: 1) Marshall **1** (1917), 385 2) Barnett (1919), 137

Neonite. A fast burning, 30 grain, gelatinized smokeless powder introduced in 1907 by the New Explosives Co of Engl. It contains NC (insol) 73.0, NC (sol) 9.0, metallic nitrates 10.5, vaseline 5.9 & moisture 1.6% (Ref 1)

The same name was also given to a single-base proplnt, designed for small arms, developed by I.C.I. Ltd (Ref 2). The required ballistics for different types of ammo are obtained by surface treating the proplnt grains with methyl centralite, and in some cases, dibutylphthalate.

The coating penetrates into the base grain to some extent to give, in effect, a progressively increasing rate of burning as the grain burns away
Refs: 1) Marshall **3** (1932), 96 2) F.R.W. Hunt, Ed, "Interior Ballistics", Philosophical Library, NY (1951), 5

Neopentryl. 2-Nitro-2(3′,5′-dinitrophenyl)-propane-diol-1,3-Dinitrate. Its power is reported as 133% of TNT
Ref: D.P. MacDougall et al, OSRD **5746** (1945), 18

Neptune Powder. American expl prepd by A.J. Parker about 1878. It contains NG 33, Na nitrate 45, charcoal 17 & sulfur 5%
Ref: Van Gelder & Schlatter (1927), 619

Neu-Babelsberg Calorimeter. Apparatus constructed by Zentrallstelle für Wissenschaftlich-technische Untersuchungen G.m.b.H. at Neu-Babelsberg, near Berlin, in Ger, was used for the determination of heats of combustion of expls
Ref: Colver (1918), 615

Neudynamits. Austrian term for gelatin Dynamites. There were two types used: (1) NG (gelatinized) 66.00, K nitrate 24.82, woodmeal 8.84 and soda 0.34%; (2) NG (gelatinized) 45.00, K nitrate 40.15, cereal meal 14.30 and soda 0.55%
Ref: Naoûm, NG (1928), 329

Neugen. Polyethylene glycol laurate; used as an additive to prevent the expl reaction of Ba azide. See under Barium Diazide in Vol **1**, A524-L

Neumann, Egon (1884–1919). German ballistician & armament technologist. Especially known as a co-discoverer of the *shaped charge* or *cavity effect*, also known as the **Munroe-Neumann Effect** (See Munroe Effect; Detonation, Munroe-Neumann Effect, or Shaped Charge Effect in Vol **4**, D442-R to D454-L). This discovery, at a somewhat later date in Germany than in the USA (1910 for Neumann vs 1888 for Munroe), has been shown to be independent of the work of Munroe. Engineer, inventor, author, lecturer and well-known authority on explosives, his work, both basic & applied, covered many phases of the armament industry
Refs: 1) E.G. Neumann, GerP AmmW 36269 (1910) 2) E.G. Neumann, BritP 28030 (1911) 3) E.G. Neumann, ZAngewChem, 2238 (1911) 4) E.G. Neumann, SS **12**, 183 (1914) 5) Anon, SS **17**, 293 (1919) 6) Davis (1943), 20 7) Cook (1958), 226

Neumann's Classical Theory of the Plane Detonation Wave. See Detonation, Classical Theory of Plane Detonation Wave in Vol **4**, D237-R

Neu-Nobelit. (New Nobelite). Semi-plastic permissible expls which were used in Ger coal mines during the shortage of NG in and following WWI. However, for work with accompanying rock, the stronger gelatin permissible with 25 to 30% NG were preferred. One of the later types of Neu-nobelits was No XVI: NG 12, AN 54, woodmeal and coal 3, nitrocompounds 3, and alkali chlorides 28%. Its properties were: OB to CO_2 +2.9%, Trauzl block expansion 225.0cc, Pb block crushing 13.0mm, vel of deton 4600m/sec, Q_e 643.0cal/g, temp of expl 1828°
Refs: 1) Naoûm, NG (1928), 441 & 444 2) PATR **2510** (1958), Ger 117-L

Neutral Propellant Grain. A single piece of proplnt that maintains its burning surface constant, or approximately constant, during burning is said to have *neutral* geometry. Simple neutral geometries include sheets, squares or disks with webs small compared with surface dimensions, or with edges inhibited; long tubes, or tubes with ends inhibited. See also under Cannon Propellant in Vol **2**, C31-L
Refs: 1) Meyer (1943), 119 2) Anon, "Solid Propellants, Part One", EngrDesHnbk **AMCP 706-175** (1964), 17

Neutron Kill. A method of destroying objects, including enemy nuclear warheads in the atmosphere,

by means of a nuclear detonation. The *Sprint* interceptor missile of the *Safeguard ABM* program is intended to destroy incoming warheads by means of the neutron effect of its 1–2 kiloton warhead as well as by blast. The neutron emission of the interceptor's warhead is intended to trigger fission within the enemy warhead, thus generating very high temps which damage the warhead and prevent a normal detonation
Ref: H. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 138

Neutron Radiation. See under Radiation Effects on Explosives, Propellants and Pyrotechnics

Neuwestfalit. A Ger Favier-type permissible expl contg AN 70.3, DNT 10.9, Na chloride 16.8 & flour 2.0%. Trauzl test value 309cc; charge limit 540g
Refs: 1) Marshall **1** (1917), 391 2) Barnett (1919), 138 3) PATR **2510** (1958), Ger 117-b

New Explosive Co, Ltd. At Stowmarket, Engl, it was the first plant to manufacture compressed blocks of wet NC by Abel's method. These blocks were used as bursting charges in various projectiles as well as for demolition purposes. This facility also manufd Dynamites, Gelignite, Cordite, Carbonite, etc
Ref: Daniel (1902), 451

New Fortex. See under Fortex in Vol **6**, F174-L

Newit. A Rus pre-WWI mining expl contg NG (gelatinized with collodion cotton) 4, AN 78, K nitrate 5, Na chloride 8 & vegetable meal 5%
Ref: Anon, SS **12**, 431 (1917)

Newton Powder (Saxifragine). Belgian blasting expl patented in 1862 contg Ba nitrate 77, charcoal 21 & K nitrate 2%
Ref: Daniel (1902), 701

NG. Abbr for Nitroglycerin

NGk. Abbr for Nitroglycol

NGu. Abbr for Nitroguanidine

NGX. Code name for 1,2,3-Trinitroaminopropane

N.H. Powders. Abbr for nonhygroscopic powders

N-HMX. Code name for 1-Nitroso-3,5,7-trinitro-1,3,5,7-tetra-azacyclooctane

Nib. Abbr for Nitroisobutyl

NIBGTN. Abbr for Nitroisobutylglycerol Trinitrate

Nickel. Ni, at wt 58.71, at no 28, valences +2 & +3, five stable isotopes, 7 radioactive isotopes. Malleable, silvery metal; readily fabricated by hot and cold working; takes high polish; excellent resistance to corrosion. Mp 1455°; bp 2900°; d 8.908g/cc; electrical resistivity (20°) 6.844 microhm-cm; Moh's hardness 3.8; spec heat (100°) 0.1123; latent heat of fusion 73cal/g. Stable in air at ordinary temps; burns in O_2 forming NiO; not affected by w; decomps steam at red heat. Slowly attacked by dil hydrochloric or sulfuric acids; attacked by nitric acid. Not attacked by fused alkali hydroxides (Refs 5 & 6). The most comprehensive and modern monograph on Ni and its compds is Gmelin (Ref 3)

Ni is found in many ores in combination with S, As & Sb, the chief sources being the minerals chalcopyrite, pyrrhotite and pentlandite. Ni ores are of two types, sulfide and oxide, the former accounting for two-thirds of the world's consumption. Sulfide ores are refined by flotation and roasting to sintered Ni oxide, and either sold as such or reduced to metal, which is cast into anodes and refined electrolytically or by the carbonyl (Mond) process. Oxide ores are treated by hydrometallurgical refining, eg, leaching with ammonia. Much secondary Ni is recovered from scrap (Refs 6 & 7)

Probably the largest use of Ni is in the manuf of Monel metal, stainless steels, Ni-chrome resistance wire, in alloys for electronic and space applications, and as a catalyst (Raney Ni). It is also used as a fuel in pyrotechnics (Ref 2) and in delay powders as a Zr alloy (Ref 4)

Exposure to Ni may cause dermatitis (Ni itch) in sensitive individuals. Ingestion of large amts (even 1–3mg/kg of body wt) causes nausea, vomiting, diarrhea, & depression of the central nervous system. Its health hazard is, however, considered slight. The M.A.C. (max allowable concn based on continuous exposure for an 8 hr day) is 0.5 mg/ cu m (Refs 2 & 5)

Ni dust is expl and a dangerous fire hazard. It has an ignition temp above 700°, and burns with intense heat. When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. The amt of powdered metal which may become involved in a fire should be strictly limited. Fires must not be fought with ordinary streams of w because of the danger of liberating large quantities of hydrogen gas. Fires involving small amts of powdered Ni may be fought with fog nozzles or special extinguising powders (Ref 2)

The requirements for the US Armed Forces are detailed in the JAN Spec listed as Ref 1, which covers powdered Ni suitable for use in ammo. It specifies the following requirements:

Table 1

Free metallic nickel	95.0% min
Mercury	2.0% max
Moisture	0.2% max
Granulation	100% min thru a No 100 US Standard sieve
Average particle diam	1.5 ± 0.5 microns

Refs: 1) Anon, "Nickel, Powdered (For Use in Ammunition)", **JAN-N-412A** (30 June 1948) 2) Anon, EngDesHndbk, "Military Pyrotechnics Series, Part III – Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (1963), 214–17 3) Gmelin, SystNr 57 (about 3500 pp in 5 Vols published in 1965–67) 4) F.B. Pollard & J.H. Arnold, "Aerospace Ordnance Handbook", Prentice-Hall, Englewood Cliffs, NJ (1966), 270–74 5) Merck (1968), 727-R 6) CondChemDict (1971), 614-R 7) D.N. Considine, Ed, "Chemical and Process Technology Encyclopedia", McGraw-Hill, NY (1974), 765–69

Nickel (II) ammine Complexes. See under Ammine or Ammoniate and Coordination in Vol **1**, A275ff

Nickel Carbonyl (Ni tetracarbonyl). $Ni(CO)_4$; mw 170.73; colorl vol liq or needles; mp –25°; bp 43°; d at 17°, 1.318g/cc; vap press 400mm at 25.8°. Sol in alc, benz, chlf, acet, CCl_4& concd HNO_3; insol in w (Refs 3 & 4). Prepd by passing CO over finely divided Ni. Its vapor explds in air or O_2 at 20° and partial pressures as low as 15mm (Ref 1). It is highly toxic by inhalation, flammable, and a dangerous fire risk; tolerance 0.001ppm or 0.007mg/cu m of air (Ref 2). Trace levels of nickel carbonyl can be monitored using plasma chromatography (Ref 5)
Refs: 1) E.J. Badin et al, JACS **70**, 2055 (1948) & CA **42**, 7045 (1948) 2) Sax (1968), 956-L 3) Merck (1968), 727-R 4) CondChemDict (1971), 615-L 5) R.F. Wernlund & M.J. Cohen, Research/Development, 32–35 (July 1975)

Nickel-Hydrazine Nitrate Complex. $Ni(NO_3)_2.3N_2H_4$; rose-lilac colored cryst powder; deflagrates at 212–15°. Prepd by pouring slowly with stirring a 20–30% aq or alc soln of Ni nitrate into a 40% alc soln of hydrazine maintained at 10–20° until 4–5% excess hydrazine remains. The ppt is immediately filtered, washed thoroughly with MeOH or EtOH to remove excess hydrazine, and dried at 100° in a steam oven. It has a drop sensitivity of about 1.4m with a 2kg wt. In the Pb block test it gave a *coeff utilisation practique* of 87.7 & 85 (PA=100). In cellophane tubes 200mm long at d=0.62g/cc with a 0.4g MF detonator, the vel of deton by the Dautriche method for various tube diameters were: 2600m/sec at 6mm diam, 2900 & 3100 at 8mm, 2700 at 10mm, 2900 at 12mm, and 3500 at 15mm. It is not easily detonated by flame or heat in 2 to 2.5g charges even when mixed with Pb styphnate, Pb picrate or powdered Hexogen. In trying to improve the ignition quality, Ni styphnate-hydrazine complex was prepd and found more ignitable, with a drop sensitivity of about 2.6m with a 2kg wt
Ref: L. Médard & J. Barlot, MP **34**, 160–66 (1952) & CA **48**, 6125 (1954)

Nico Powder. Expl patented in 1889 in Engl by

Liardet and authorized for use in Australia. It was prepd by dissolving PA in half its weight of hot glycerin, and incorporating woodmeal and K nitrate
Ref: Daniel (1902), 406

Niepce's Incendiary Composition. Contained benz, petroleum or carbon disulfide with a small piece of metallic potassium or Ca phosphate as igniter. Potassium was later replaced with metallic sodium
Ref: Daniel (1902), 153

Nightingale and Pearson Powder. Mining expl patented in Engl in 1897. It contained K perchlorate 55–60, Na carbonate 25–29, sugar 6–10 and paraffin 5–20%. Potatoes or woodmeal could replace the sugar
Refs: 1) Daniel (1902), 452 2) Pérez Ara (1945), 212

Nigrosine. A dye consisting of a mixt of aniline, aniline hydrochloride and nitrophenol, or nitrobenzene and Fe. It was used in Ballistite proplnts in 0.05–0.10% concn (see under Ballistite in Vol **2**, B9-R)
Refs: 1) F.M. Rowe, "Colour Index", The Society of Dyers and Colourists, 1st Ed (1924), 216
2) L. Pauling, OSRD **3783** (1944)

Nike. Name applied to a system of US Army surface-to-air guided missiles designed to seek out, intercept, and destroy enemy aircraft. The *Nike-Ajax* was the first US operational supersonic antiaircraft guided missile. First deployed in 1953, it had a length of 31 ft (with booster), a launch wt of 2300 lbs, a ceiling of 60000 ft, and a range of 25 miles. Its successor, the *Nike-Hercules,* became operational in 1958. It had a length of 39 ft (with booster), a launch wt of 10000 lbs, a ceiling in excess of 150000 ft, and a range of over 75 miles. The *Nike-Zeus* increased the range to about 200 miles at an estimated speed of Mach 4. The *Nike-X* is the latest antimissile-missile system for defense against ballistic missiles, and a follow-on to *Nike-Zeus.* The system includes a multifunction array radar which performs target acquisition, discrimination, and tracking functions; a missile-site radar which performs missile command, target track and search functions; data processing equipment consisting of high speed digital computers; and *Sprint* missiles
Refs: 1) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 138-R
2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 325
3) R.T. Pretty & D.H.R. Archer, "Janes Weapon Systems 1974–75", Franklin Watts, Inc, NY (1975), 57

Nikles. Proposed an incendiary compn, called *"feu lorrain",* consisting of hydrochloric and sulfuric acids, and a soln of phosphorus in carbon disulfide. The mixt ignites, evolving heavy reddish fumes, when brought in contact with an ammoniacal soln
Ref: Daniel (1902), 154

Nilite. Trademark for a series of DuPont Co nitrocarbonitrate blasting agents
Refs: 1) Blaster'sHndbk (1969), 57ff 2) C.E. Gregory, "Explosives for North American Engineers", Trans Tech Publication, Cleveland (1973), 64

Niperit (Niperith, Niperyth). Same as PETN

Nipolit (Nipolite). A proplnt or expl compn developed during WWII at the Kraiburg plant of the Deutsche Sprengchemie GmbH. Two compns are reported: Nipolit (tubes) contain PETN 35, NC (12.6% N) 34.1, DEGDN 30, stabilizer 0.75, Mg oxide 0.05 & graphite 0.1%. Nipolit (sticks) contain PETN 50, NC (12.6% N) 29.1, DEGDN 20, stabilizer 0.75, Mg oxide 0.05 & graphite 0.1%. Nipolit is prepd by air-agitating a w slurry of NC and DEGDN in a Pb-lined vessel. After 15–20 minutes stirring, the mass is centrifuged to remove all but 25% of w. The resulting cake is kneaded at 50° in a Werner-Pfleiderer machine with the calculated amt of PETN, some w, Mg oxide and graphite. After 15 minutes of kneading, the paste is transferred to rubber-lined bags where it is allowed to age for 48–72 hrs. The aged paste is then passed 15–20 times thru a pair of vertical rollers maintained at 75° to produce a

sheet which is later extruded at a pressure of 200kg/sq cm and temp of 80°. The resulting tubes or sticks are then cut into desired lengths

In using Nipolit, the "stick" is wetted with acet and pushed into the "tube", of such a length that one end is flush, leaving a cavity in the other end to accommodate a detonator. This assembly was used as a booster charge in ammo (Refs 4 & 5)

As Nipolit-type expls were of interest to the US Ordn Corps, a study was initiated to modify the Ger manufg process which was considered to be hazardous because of the heated roller treatment. A new compn was developed consisting of RDX 35.9, NC (12.6% N) 24.5, NG 22.8, DNEtB 10.0, DBuPh 6.6 & DPhA 0.2%. It was tough and thermally stable, relatively non-hygroscopic, and insensitive to friction, impact and rifle fire. It was also superior to TNT in rate of detonation and brisance. A relatively simple and non-hazardous procedure was developed for its manuf. Another formulation variation was TNT 35, Comp A-3 35, M-1 proplnt powder 20, and DNEtB or TEGDN 10%. This was hard and tough at room temp, but softened at 65° (Refs 1 & 3)

Extrudable Nipolit-type expls were developed at PicArsn for use in the development of caseless bombs (Ref 2). Typical formulations contain RDX/Resin 83/17 and RDX/Al/Resin 80/10/10 or 60/23/17. Three resins, Marco MR-280, Laminac 4116 and Selectron 5003, were found to be satisfactory and interchangeable for use in these compns. These expls are thermally stable, relatively insensitive to mechanical shock, and have a brisance approaching that of Comp C-3. Weight-drop impact tests indicate them to be of the order of sensitivity of TNT

Refs: 1) Anon, ETO OrdnTechIntelligence Rept No 323 (June 20, 1945) 2) A.L. Forchielli & J.H. Veltman, PATR **1855** (1951) 3) J. Veliky & M. Epton, PATR **2056** (1954) 4) B.T. Fedoroff et al, PATR **2510** (1958), Ger 117 5) Anon, "Handbook of Foreign Explosives", **FSTC 381-5042**, US Army Foreign Science and Technology Center (1965), 285–6

Nisser Powders. One of the early perchlorate expls, patented in 1865, contg K perchlorate 10.5, K nitrate 44.5, K dichromate 2.0, K ferrocyanide 1.5, charcoal 19.6, sulfur 15.5 and sawdust 6.5% (Ref 2). Nisser also patented in 1870 a mixt contg a chlorate, K ferrocyanide, K bitartrate and charcoal (Ref 1)

Refs: 1) Daniel (1902), 452 2) Pérez Ara (1945), 219

Nital. A soln of 1–5ml of nitric acid (d 1.42 g/cc) in 100ml of 95% alc, used for etching metals. A nital soln contg about 15% by vol of Grasselli reagent, nitric acid and ethanol, used for etching Bi, decomposed vigorously. Explns were also reported when nital mixts came in contact with other metals. It is believed that the decompn was caused by the reduction of the nitric acid to oxides, which catalyzed the decompn (Ref 1). A possible additional cause is the formation of a highly unstable salt, similar to fulminate, by the action of nital on metals. In order to prevent future incidents, it is recommended that methanol be used in lieu of ethanol in nital mixts (Ref 2)

Refs: 1) H.H. Fawcett, C&EN **27**, 1396 (1949) & CA **43**, 5593 (1949) 2) F. Fromm et al, C&EN **27**, 1958 (1949) & CA **43**, 7229 (1949)

Niter. Same as Potassium Nitrate

Niter Cake. Same as Sodium Bisulfite

Nitetra. Fr designation for Tetramethylammonium Nitrate. It is called *Tetrsalz* in Ger

Ref; A. LeRoux, MP **35**, 121–32

Nitramex. Trademark for an AN based blasting agent developed by the duPont Co for use in dynamiting very hard rock, in quarry work, and in stripping operations where the toe is difficult to break. It is not detonated by rifle bullet impact, sledge hammers or heat, but rather by specially constructed primers. Nitramex is stronger and denser than *Nitramon* (see in this Vol), another duPont Co commercial blasting agent

Refs: 1) Blaster'sHndbk (1969), 47 & 51 2) CondChemDict (1971), 618-L

Nitramides. Expls similar in composition to

Favier expls described in Vol **6**, F10-Lff. Also see under Amides and Imides, Organic, Nitrated in Vol **1**, A171-L
Ref: Daniel (1902), 297

Nitramidon. Fr for Nitrostarch

Nitramin. Another name for Tetryl

Nitramindine. Expl compd prepd in 1845 by Dumas by the nitration of paper or cardboard, and proposed for use in the manuf of cannon cartridges (gargousses in Fr). This material was prepd prior to the discovery of NC by Schönbein
Ref: Daniel (1902), 453

Nitramines. See under Amines, Nitrated and Nitrited in Vol **1**, A174-R to A177-R, and Amine, Catalyzed Nitration in Vol **1**, A174-L
Addnl Refs: 1) R.J.J. Simkins, M.A. Simpkins & G.F. Wright, "Nitramine Abstracts", 4 Vols, Univ of Toronto (1953) [An unclassified collection of paper and patent abstracts on the chemistry of nitramines and their isomers, including primary nitramines, their **N-** and **O-**alkyl derivs, pernitroso compds, nitrimines, and nitrosohydroxylamines and their ethers]
2) Urbański **3** (1967), 15–127 [aliphatic, aromatic and heterocyclic nitramines]

Nitraminoalcohols. See under Aminoalcohols, Nitrated and Nitrited in Vol **1**, A179-L to A180-L

Nitraminobenzenes. See under Aminobenzenes and Derivatives in Vol **1**, A185-L

Nitraminoethane, N-Nitroethylamine or Ethylnitramine. See in Vol **1**, A199-R

1-Nitramine-2-ethanol Nitrate, N-(β-Nitroxyethyl) nitramine or NENA. See in Vol **1**, A201-L

Nitraminoimidazoles, Nitraminoimidazolidines, Nitraminoimidazolines.
See under Aminoimidazoles in Vol **1**, A218-R, etc

Nitraminopropanol Nitrate, 1-Nitramino-2-nitroxypropane or IsoMeNENA. See under Aminopropanols and Derivatives in Vol **1**, A253

6-Nitramino-s-triazine-2,4-diol. See under Ammelide and Derivatives in Vol **1**, A273

5-Nitraminotetrazole of Lieber and Its Salts. See in Vol **1**, A260-L

5-Nitraminotetrazole of O'Connor and Its Disodium Salt. See in Vol **1**, A259-R

Nitramita de la Fábrica de Galdácano (Spanish). See under Coal Mining Explosives, Permissible in Vol **3**, C455-L

Nitramita Espanola de la Fábrica de Granada (Spanish). See under Coal Mining Explosives, Non-Permissible in Vol **3**, C442-L

Nitramite. Trademark for a series of nitrocarbonitrate blasting agents developed by the duPont Co. Nitramite 2 was developed to provide a lower cost supplemental charge in columns of Dynamite for large diameter boreholes. It has become a popular blasting agent, and is frequently used for column loads where column build-up or a moderate degree of w resistance is required. Its d ranges from 1.07 to 1.14g/cc, it will sink in w, and is frequently used as a bottom load in wet holes. Nitramite 2 provides excellent performance for top loading in quarries and open pits, and is well adapted for stripping operations in both vertical and horizontal holes (Refs 2, 3 & 4)

The name Nitramite was also applied to a group of expls proposed by P. deWilde and patented by the Société Suisse d'Explosifs. *Nitramite No 1* was prepd by passing the gas obtained during the catalytic dehydrogenation of ammonia-methanol thru nitric acid. Its compn was AN 70–80% and a mixt of the nitrates of mono-, di- and trimethylamines 30–20%. Its properties, as detd in 1935–36 at the Laboratoire Central des Poudre were as follows: mp ca 120°;bp ca 230°; hygroscopic; sensitivity to shock: 50% explns with 10kg wt dropping 2.50m, difficult to inflame; gap test: 1 cm between 50g cartridges at d 1.20g/cc; French Trauzl test (c.u.p.) 115 (PA 100); vel of deton (max) 3200m/sec at d 1.20 to 1.30g/cc. *Nitramite No 2* contd AN 70–80 & methylamine nitrate 30–20%. Vel of deton (max) 3250m/sec at d 1.25g/cc (Ref 1)

See also under Italian Ammonals in Vol **1**, A291-R, Italian Explosives in Vol **7** & Spanish Explosives

Refs: 1) A. LeRoux, MP **34**, 130–32 (1952) 2) Blaster'sHndbk (1969), 50–1 3) Cond-ChemDict (1971), 618-R 4) C.E. Gregory, "Explosives for North American Engineers", Trans Tech Publications, Cleveland, Ohio (1973), 64

Nitramon. Trademark for a series of nitrocarbonitrate blasting agents developed by the duPont Co. They cannot be detonated by the strongest commercial blasting caps, a line of detonating cord, flame, shock, friction, or the impact of ball ammo or of heavy steel wts. Their blasting energy is released by the use of *"Nitramon"* primers, also manufd by DuPont. *Nitramon* has given outstanding results in the quarrying of almost every type of material, including limestone, sandstone, granite, trap rock, cement rock and shale. It is also used in stripping the overburden from both hard and soft coal, and in open pit mines for ore blasting as well as stripping

There are several grades of *Nitramon,* including A and HH, as well as S and S-EL, intended for seismic prospecting, and WW and WW-EL, for use in seismic prospecting at sea

Nitramon A has the highest d (1.27 to 1.48 g/cc) and is comparable in performance to 60% Special Gelatin

In anthracite coal strip fields, it becomes necessary at times to blast burning rock formations overlying the coal. In the removal of burning mine refuse banks, fused material that requires drilling and blasting is often encountered. Some of this may have temps above normal due to continued burning. As a result, temps of several hundred degrees are encountered in large diameter drill holes. The use of Dynamite under such conditions becomes extremely hazardous, and *Nitramon* HH was developed to meet this need

Nitramon S possesses strength and vel of the same magnitude as the gelatin Dynamites normally employed in seismic prospecting. Actual field tests have demonstrated that comparable seismograph records are obtained when a given wt of 60% gelatin is replaced by a column of *Nitramon* S and a primer of equal wt and length. *Nitramon S-EL* provides approx 65% greater useful seismic energy return than does *Nitramon S*

Nitramon WW has a d of approx 1.2g/cc, which allows it to sink readily in w, but at the same time does not require an excessive amt of buoyant material for suspended charges. *Nitramon WW-EL* returns about 65% greater useful seismic energy than *Nitramon WW*

Ref: Blaster's Hndbk (1969), 47–55

Nitranaftita. Expl manufd by La Dinamita Nobel Italiana contg RDX 80 & MNN 20%

Ref: Vivas, Feigenspan & Ladreda **2** (1946), 288

Nitranilic Acid. See 3,6-Dinitro-2,5-dihydroxy-1,4-benzaquinone in Vol **5**, D1290-L

Nitrasols. Family of castable composite solid proplnts contg plastisol binders composed of plastisol NC and certain liq nitrate esters. The liq esters serve as a platicizer for the NC, yielding an elastomeric binder of very high energy

The work that led to the development of Nitrasol proplnts began at the US Naval Ordn Test Station (NOTS) in 1955 with a program of research on elastomeric proplnts, in which the aim was to tie the plasticizer chemically to the NC to prevent migration of the plasticizer to the inhibitor. In attempting to solve processing problems met in the formulations under investi-

gation, NOTS took advantage of work done on plastisol NC by the Atlantic Research Corp, which had been the first to prepare this material and use it in proplnts. NOTS modified an Atlantic Research Corp procedure and began to prepare plastisol NC to meet its own specifications. At the same time that NOTS began producing its own plastisol NC, binder studies showed that a 40/40/20 mixt of Pentaerythritol Trinitrate (**Petrin**), NC, and dibutyl phthalate held considerable promise as an elastomeric proplnt binder. Later, binders were developed contg only the high-energy nitrate esters **Petrin** and Trimethylolethane Trinitrate (**TMETN**), with no dibutyl phthalate

The following table shows the formulation, physical and ballistic properties of two Nitrasol proplnts with widely differing applications. The H3515 formulation is a high energy proplnt, while P3500 is an application to gas-generator proplnts

Table 1

TWO REPRESENTATIVE NITRASOL PROPELLANT FORMULATIONS

Ingredient	Propellant formulation, % composition	
	High Energy, H3515	Gas generator, P3500
Plastisol nitrocellulose (12.6% N)	14.25	18.2
Pentaerythritol trinitrate	35.00	16.4
Dibutyl phthalate	–	19.5
Ethyl centralite	0.75	1.2
N-methyl-p-nitroaniline	–	1.0
2-Nitrodiphenylamine	–	0.1
Cellulose acetate	–	4.6
Poly(methyl methacrylate)	–	4.0
Ammonium nitrate	–	35.0
Ammonium perchlorate	35.00	–
Aluminum	15.00	–
Tensile strength at 77°F, psi		
Maximum	164	270
At rupture	164	201
Elongation at 77°F, %		
At maximum tensile strength	124.6	12.2
At rupture	124.6	23.2
Modulus of elasticity at 77°F, psi x 10^3	0.78	5.26
Density, lb/cu inch	0.064	0.0602
Impact sensitivity of ground propellant, 50% point with 2-kg hammer, cm	8	170
Friction sensitivity, kg-cm	56	–
Electrostatic sensitivity, joules	41.6	–
Strand burning rate at 70°F and 1000 psi, in/sec	0.42	0.48
Pressure exponent	0.68	0.79
Temperature coefficient ($\pi p/r$), %/°F	0.22	1.97
Specific impulse (Isp), lbf-sec/lbm	255[a]	156[b]
Adiabatic flame temperature, 0°K[b]	3450	955

[a]Measured value corrected to 1000 psi

[b]Calculated

The P3500 contains AN as the solid oxidizer. Since the Nitrasol binder was used in this proplnt, only 35% AN was required to obtain a relatively clean and cool-burning proplnt. Comparable proplnts require 70% or more solid oxidizer to achieve the same burning properties. P3500 is thus relatively immune to the two major problems, phase changes and hygroscopicity, that exist with proplnts contg large proportions of AN

The physical properties of Nitrasol make it applicable to the motors of very large missiles. Cracking under the stresses of ignition is eliminated, because Nitrasol has an elongation two to three times that of other composite proplnts now in use. In case-bonded rocket motors this property prevents cracking from temp changes. Nitrasol has a relatively high tensile strength, and can be easily cast into well-defined shapes, making it particularly well-suited for the fabrication of grains of intricate design

Nitrasol can be mixed in standard equipment, with precautions to exclude moisture not being necessary. It is cast without vacuum in the mold or press in the mixer. Since neither the mixing nor the curing involves any chemical reactions, there are no exotherms. In mixing Nitrasol, the liq ingredients are weighed and thoroughly mixed. The plastisol NC is placed in a sigma-blade or similar type of mixer, and approx 40% of the liquids are added. These ingredients are mixed until the plastisol NC agglomerates have been broken up and all the particles have been wetted; this requires approx 15 minutes. The remainder of the liq ingredients are added, and mixing is continued for 30 minutes under vacuum. The Al is added and mixing is resumed until all the Al has been wetted. The AP is added and the mixing and degassing are again resumed for 30 minutes. During the last 15 minutes of the mixing period, warm w is run thru the mixer jacket to raise the temp of the finished proplnt mix to 110°F. The proplnt is then poured directly from the mixing vessel into the casting mold without the aid of press or vacuum. The proplnt is presently cured by maintaining it at a temp of 185°F max for from one to two hours (Ref 1)

Electrical vol resistivity techniques have been employed to follow the course of the hardening of Nitrasol expls (Ref 3). The air blast effectiveness of Nitrasol as a high expl indicated it is a better expl than Pentolite and a poorer one than H-6 (Ref 2), and its use as an underwater expl has been investigated (Ref 4)

Refs: 1) Anon, "Nitrasol – A New Family of Solid Propellants", **NOTS 2059** (15 July 1958) 2) E.M. Fisher & J.F. Pittman, "Air Blast Effectiveness of Nitrasol as a High Explosive", **NAVORD 6891** (23 July 1960) 3) R.W. Warfield & A.H. Rosen, "The Plasticization and Hardening of Nitrasol Explosives", **NOLTR-61-184** (26 Jan 1962) 4) M. Stosz, "The Development of Nitrasol as a New and Superior Underwater Explosive", **NOLTR-62-204** (29 Jan 1963)

LIST OF NITRATE COMPOUNDS

Ammonium Nitrate. See in Vol **1**, A311 to A340 *Addnl Ref:* US Specification **MIL-A-50460** (15 Sept 1973)

Barium Nitrate. See in Vol **2**, B20-R to B21-L *Addnl Ref:* US Specification **MIL-B-162D** (7 Feb 1968)

Calcium Nitrate (Lime Nitrate, Nitrocalcite, Lime Saltpeter, Norwegian Saltpeter). (a) $Ca(NO_3)_2$, mw 164.10, N 17.07%, OB to CaO & N_2 +48.8%, deliq granules, mp 561°, d 2.36g/cc. Can be prepd by neutralizing lime with nitric acid. Sol in w (102p at 0°, 376p at 151°), in alc (14p at 15°) and amyl alc. (b) $Ca(NO_3)_2.4H_2O$, mw 236.1, white deliq mass, mp 42°, d 2.36g/cc, v sol in w. Strong oxidizing agent and dangerous fire risk in contact with organic materials; may expl if shocked or heated. Used in expls, pyrots, matches & fertilizers (Refs 6, 7 & 8)

Naoûm (Refs3 & 5) patented blasting expls made by dehydrating Ca nitrate at temps above 100°, cooling and grinding it, followed by mixing with TNT, NG, charcoal & sawdust. The Ca nitrate content varied from 62–70%. Stoops (Ref 2) patented expls contg hydrated Ca nitrate mixed with AN & K nitrate in Amm perchlorate, and absorbed on sawdust. Haid et al (Ref 4) claimed that a Ca nitrate mixt dried at 120° was superior to a saltpeter blasting powder

There is no US Specification for Ca nitrate

Refs: 1) Gmelin, SystNr **28** (1956), 59–69 & 341–82 2) R.I. Stoops, USP's 1671792 & 1671793 (1928) & CA **22**, 2665 (1928) 3) P. Naoûm, GerP 513654 (1930) & CA **25**, 4710 (1931) 4) Haid et al, JahresberCTR **8**, 115–118 (1930) & CA **26**, 3114 (1932) 5) P. Naoûm, USP 1865382 (1932) & CA **26**, 4475 (1932) 6) Merck (1968), 194-L 7) CondChemDict (1971), 157-R 8) Hackh's (1972), 124-R

Cellulose Nitrate. See in Vol **2**, C100-L to C126-L

Cellulose Benzoate Nitrates. See in Vol **2**, C99-L

Ceric Ammonium Nitrate (Cerium Ammonium Nitrate, Ammonium Hexanitratocerate). $Ce(NO_3)_4.2NH_4NO_3$, mw 548.3, small prismatic yellow crysts, sol in w & alc. Prepd by electrolytic oxidation of cerous nitrate in nitric acid soln, and subsequently mixing solns of cerium nitrate and AN, followed by crystn. It is a strong oxidizing agent and a dangerous fire risk in contact with organic materials

In the expls laboratory it is used for the detn of Pb Azide (LA) in primer mixts. The reaction proceeds as follows (Ref 2):

$$PbN_6 + Ce(NO_3)_4.2NH_4NO_3 \rightarrow 3N_2 + Pb(NO_3)_2 + 2Ce(NO_3)_3 + 4NH_4NO_3$$

with the quant production of nitrogen gas which is collected in an azotometer (measuring tube) and used for the detn of the azide radical (see Vol **1**, A566-L). It can also be used for the destruction of LA or other azides. There is no US Specification for Ceric Ammonium Nitrate

Refs: 1) Mellor **5** (1924), 644 4) CondChemDict (1971), 184-R

Ethyl Nitrate. See Vol **6**, E143-R

Lead Nitrate. $Pb(NO_3)_2$, mw 331.23, N 8.46%, OB to PbO & N_2 +24.2%, colorless cubic or monoclinic crysts, mp (decompn) 470°, d 4.53g/cc, sol in w and alc. Prepd by dissolving Pb scale or litharge in hot dil nitric acid of d 1.35g/cc, and partially evapg the soln

It is a strong oxidizing agent, *highly toxic,* and a dangerous fire risk in contact with organic materials

Pb nitrate is used in matches, in some military expls (Macarite, Triplastite, etc), and in the manuf of LSt & LA. According to Taylor & Rinkenbach (Ref 1), the use of Pb nitrate in the manuf of expls has been minimal mainly because of its tendency to decomp on slight heating or in contact with other chemicals. This disadvantage offsets the advantages of being less hygroscopic than other nitrates, except for K nitrate, and of contg more oxygen per unit vol than any other common oxidizing substance. As it gives off poisonous fumes on expl, its use in composite expls has been prohibited in Engl

US Mil Spec **MIL-L-20549A**, "Lead Nitrate, Technical" (15 Jan 1968) contains the following requirements: Pb nitrate shall be white in color and conform to these chemical characteristics: Assay as $Pb(NO_3)_2$, 98.0% min; w content, 1.25% max; w-insol matter, 0.20 max; acidity (as HNO_3), 0.50% max; Cu, 0.002% max

Refs: 1) C.A. Taylor & W.H. Rinkenbach, US-BurMinesBull **219** (1923), 25–26 2) Thorpe **4** (1949), 464 3) Merck (1968), 613-R 4) CondChemDict (1971), 510-L

Lithium Nitrate. $LiNO_3$, mw 68.95, N 20.32%, colorl deliq granules, mp 261°, d 2.38g/cc, sol in w & alc. Prepd by reaction of nitric acid with Li carbonate. It is a strong oxidizing agent and a dangerous expln risk when shocked or heated. It is used in pyrots as an oxidizer to color burning compns red. There is no US Specification for Li nitrate

Refs: 1) Anon, EngrDesHndbk, "Military Pyrotechnics Series, Part Three – Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963) 2) Merck (1968), 623-L 3) CondChemDict (1971), 525-L

Magnesium Nitrate. $Mg(NO_3)_2.6H_2O$, mw 256.43, N 10.93%, OB to MgO & N_2 +68.6%, colorless deliq crysts, mp 95°, d 1.464g/cc, loses $5H_2O$ at 330°. Sol in 8p w, freely sol in alc. Prepd by the action of nitric acid on Mg oxide with subsequent

crystn. It is a strong oxidizing agent and a dangerous fire and expln risk in contact with organic material. It has been used in pyrots
Refs: 1) Merck (1968), 636-R 2) CondChemDict (1971), 535-R 3) Anon, "Fire Protection Guide on Hazardous Materials", 5th Ed, National Fire Protection Assoc, Boston, Mass (1973)

Mercuric Nitrate (Mercury Nitrate, Mercury Pernitrate). $Hg(NO_3)_2.H_2O$, mw 342.61, OB to HgO and N_2 +26.4%; wh deliq powd or colorl crysts, mp 79°, bp dec, d 4.39g/cc. Sol in w and nitric acid, insol in alc. Prepd by action of hot nitric acid on alc. Highly toxic and a dangerous fire risk in contact with organic materials. It has been used for the nitration of aromatic organic compds and in the prepn of MF

US Mil Spec **MIL-M-51273**, "Mercuric Nitrate, Monohydrate, Analyzed Reagent" (15 Jan 1968) contains the following requirements: Mercuric nitrate, monohydrate shall be a white granular powder and conform to these chemical characteristics: Assay as $Hg(NO_3)_2.H_2O$, 99.0% min; residue after ignition, 0.029% max; chloride, 0.005% max; sulfate, 0.010% max; iron, 0.001% max; foreign metals, as Pb, 0.002% max; mercurous Hg, as Hg, 0.15% max
Refs: 1) Merck (1968), 660-L 2) CondChemDict (1971), 553-L

Mercurous Nitrate (Mercury Protonitrate). $HgNO_3.H_2O$, mw 280.64, OB to HgO & N_2 +17.1%, mp 70° dec, bp explds, d 4.78g/cc. Short prismatic crysts; effloresces and becomes anhydrous in dry air; sensitive to light. Sol in small quantities of warm w (hydrolyzes in larger quantities), w acidified with nitric acid. Prepd by action of cold dil nitric acid upon an excess of Hg with slight warming. Highly toxic; may explode if shocked or heated. There is no US Specification for Mercurous Nitrate
Refs: 1) Merck (1968), 662-L 2) CondChemDict (1971), 555-L

Methyl Nitrate. See in this Vol under Methyl Nitrate

Potassium Nitrate (Saltpeter, Nitre, Sal Prunella, Niter). KNO_3, mw 101.10, N 13.86%, OB to K_2O & N_2 +39.6%, colorless prismatic or rhombohedral crysts, d 2.1062 to 2.109g/cc, mp 333°; bp, decomps at 400° with evolution of O_2 and deflagration, RI 1.5038 for rhombohedral crysts (Refs 9, 12 & 13)

K nitrate was first obtained, in admixture with Na nitrate, by Boyle in 1667. The oldest method of prepn, which is still used in India and Egypt, is in the so-called "nitre plantations". Such plantations are usually located near towns or villages, where urine and other organic material find their way into the calcareous soil, owing to imperfect systems of sewage disposal. Due to the action of micro-organisms on urea, etc, some ammonia, which is first formed, is oxidized to nitric acid and this, reacting with Ca carbonate of the soil, forms Ca nitrate. This material is leached with w and the resulting soln is boiled with wood ashes, which contain K carbonate:

$$Ca(NO_3)_2 + K_2CO_3 \rightarrow CaCO_3 + 2KNO_3$$

The filtrate on evapn deposits saltpeter, which is purified by crystn

Saltpeter may also be obtained from specially constructed "heaps" of nitrous earth from which it is leached with w. This method is still in use in India (Ref 1, p 57)

Production as practiced in Chile consists of leaching residues from their Na nitrate operation to produce a weak brine of K nitrate which is concd by solar evapn. When the proper concn of K nitrate is achieved it is recovered by crystn (Ref 14)

A process for production of K nitrate from K chloride and nitric acid, after several years of development, was placed in commercial production in the USA in 1963. The overall process is represented by the following equation:

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \rightarrow 2KNO_3 + Cl_2 + H_2O$$

It is rather complicated and details cannot be given here, but the key to its success is the oxidation of nitrosyl chloride according to the reaction:

$$NOCl + 2HNO_3 \rightarrow 3NO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

The nitrogen dioxide product is converted to nitric acid for recycle in the process. The process has been described in detail by Spealman (Ref 11)

Solubility (Ref 3)

Water (grams K nitrate per 100g w)

°C	Solubility
0.40	13.43
14.90	25.78
25	38.45
30.80	47.52
44.75	74.50
60.05	111.18
76	156.61
91.65	210.20
114 (bp)	311.64

Abs Methanol. Practically insol

Aq Methanol (grams per 100g of satd soln at 30°)

Grams CH_3OH	Grams KNO_3
0	31.3
7.8	23.3
17.3	16.3
27.8	11.2
38.4	7.7
57	3.8
98.58	0.43

Absolute Ethanol. Practically insol

Aq Ethanol (Grams per 100g of satd soln at 30°)

Grams C_2H_5OH	Grams KNO_3
10.1	20.7
23.8	12.1
32.2	9.0
43.1	6.1
56.9	3.3
76.8	0.88
92.3	0.15

Ether. Practically insol

Trichloroethylene. 0.01g K nitrate per 100g solvent at 15°

Hydrazine (anhydr). 14g K nitrate per 100ml solvent at RT

Liq Ammonia. 100g of satd soln contains 9.52g K nitrate and 10.52g NH_3 at 0°; 9.42g and 10.4g, respectively, at 25°

Hygroscopicity (Ref 6)

The weight gain of K nitrate in mgs/g at RT after equilibrium was established in vacuum desiccators is shown below:

Table 1

% Rel Humidity	65		75		86		93	
Time	24hrs	equil	24hrs	equil	24hrs	equil	24hrs	equil
Specification Grade	–	< 1	–	0.2	–	–	55.2	–
Purified Material	–	–	–	–	–	< 0.1	–	< 0.1

The critical relative humidity of Specification grade K nitrate is 91.7% at 20°; purified material, 91.8% at 26.2°

Moisture absorbed by 2.0g of CP K nitrate at 25° as a function of fineness is shown below:

Table 2

Fineness	Hours Exposure	H_2O Absorbed, g
40–80 mesh	2.75	0.0147
	18.75	0.1136
	25.25	0.1527
	42.75	0.2687
	47.00	0.2896
Ground Very Fine	7.25	0.0453
	16.50	0.1056
	40.50	0.2580

Specification grade K nitrate gains 0.76% by wt at 70°F and 90% relative humidity

Toxicity. Ingestion of large amounts may cause violent irritation of the intestinal lining. Prolonged exposure to small amounts may result in anemia and nephritis. Moderately poisonous on ingestion or inhalation (Refs 9 & 10)

Fire and Explosion Hazard. Dangerous, as K nitrate is both a fire and expln hazard. As a strong oxidizer it can give up its oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decompn. It is sensitive to shock, can be very easily detonated, and when mixed with flammable materials becomes very sensitive (Refs 6 & 10)

Properties. The products of decompn, from 650 to 750°, are KNO_2+O+traces of NO_2. At 800° decompn is more extensive with KNO_2 decomposing to form K_2O, N and O (Ref 5). For DTA and TGA data, see Ref 4

When dried and powdered K nitrate is thrown on red-hot charcoal, or when powdered charcoal is sprinkled on fused K nitrate, rapid combustion occurs, possibly:

$4KNO_3+5C \rightarrow 2K_2CO_3+3CO_2+2N_2$, so that 1

vol of solid K nitrate will give on decompn nearly 3000 times its vol of gas (Ref 2). It is this fact that makes K nitrate so valuable an ingredient of BlkPdr and other expl mixts

Uses. K nitrate is used in the manuf of BlkPdrs, time fuzes, matches, and blasting expls, with or without NG. In proplnts, it is employed as an additive to avoid or diminish flash, and to make the proplnt more ignitable (Ref 7). Aside from use in BlkPdr and some starter mixts, its main pyrotechnic application is as the oxidizer in B/K nitrate ignition pellets (Ref 8)

The US Dept of Defense Mil Spec for K nitrate is **MIL-P-156B** (18 April 1956) with Amendment 1 (31 July 1974). Three classes are specified: Class 1 – for use in black powder and chemical munitions; Class 2 – for use in pyrotechnic compositions; and Class 3 – for use in propellants. The chemical requirements for these classes are given below:

Table 3

Property	Class 1 Percent	Class 2 Percent	Class 3 Percent
Moisture, max	0.2	0.2	0.2
pH value	7 ±1	7 ±1	7 ±1
Water insol material, max	0.1	0.1	0.1
Grit	None	None	None
Chlorides, as KCl, max	0.07	0.07	0.07
Chlorates & perchlorates, as $KClO_4$, max	0.5	0.5	0.5
Iron & aluminum, as oxides, max	0.5	0.5	–
Calcium & magnesium, as oxides, max	0.5	0.5	0.5
Sodium, as oxides, max	0.25	0.25	–
Ammonium compounds	None	None	–
Nitrogen, min	13.77	13.77	13.77

The potassium nitrate shall be odorless, and the crystals white in color

Granulation requirements specify that Class 1 material shall be furnished in lump form, while Class 2 and 3 material shall comply with the following, using US Standard sieves:

Table 4

Sieve No	Percent, min, thru specified sieve	
	Class 2	Class 3
60	99.9	–
80	–	99.9
100	40	–

Refs: 1) Marshall **1** (1917) 53–66; **2** (1917), 717–18; **3** (1932), 9–11 2) Mellor **2** (1922), 809 & 820 3) Seidell **1** (1940), 833–50 4) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 5) E.S. Freeman, JACS **79**, 838 (1957) 6) Anon, EngrDesHndbk, "Military Pyrotechnics Series, Part Three– Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 247 7) Anon, EngrDesHndbk, "Solid Propellants, Part I", **AMCP 706-175** (1964), 50 8) Ellern (1968), 339 9) Merck (1968), 855R 10) Sax (1968), 246–8 11) I. Spealman, "Farm Chemicals Handbook", Meister Publ Co (1970), 134 12) CondChemDict (1971), 723-R 13) Hackh's (1972), 540-R 14) J.A. Kent, Ed, "Riegel's Handbook of Industrial Chemistry", 7th Ed, VanNostrand Reinhold, NY (1974), 550-R

Propyl Nitrates. See under Propane

Sodium Nitrate (Chile Saltpeter, Cubic or Soda Niter, Caliche, Nitratine). $NaNO_3$, mw 85.01, N 16.48%, OB to Na_2O and N_2 +47%; colorless, transparent crysts, white granules or powd; mp 308°; bp, dec at 380°, *explodes at 1000°F,* d 2.267g/cc, RI 1.5874. One g dissolves in 1.1ml w, 0.6ml boiling w, 125ml alc, 52ml boiling alc, 3470ml abs alc, 300ml abs methanol (Refs 5 & 7)

Na nitrate occurs native in large deposits in the rainless districts of Chile, hence it is often called "Chile saltpeter" or "Chile niter". The Na nitrate in the deposits constitutes from 20 to 50% in a distinct stratum of earth known as "caliche". The caliche is crushed and lixiviated in large tanks of w heated by steam. The settled soln is run off to crystallizers, where crude nitrate separates, the mother liquors being run back to the lixiviators. The crysts are washed with a little w and dried in the sun; they contain 95–96% Na nitrate (Ref 1)

In the early days of fixation of atmospheric N_2, when the arc process was used in Norway to produce NO from air, the effluent from the arc furnaces was cooled to about 50°, the NO was oxidized by the same air to NO_2, and the NO_2 was absorbed in an aq soln of soda ash

which reacted with NO_2 to form both Na nitrate and nitrite in the soln:
$Na_2CO_3+2NO_2 \rightarrow NaNO_3+NaNO_2+CO_2$
Then air was blown thru the soln to oxidize the Na nitrite to nitrate after which the soln was concd by evapn, and Na nitrate was recovered by crystallization

Later, when nitric acid was manufd from synthetic ammonia at relatively low cost, synthetic sodium nitrate was made from it either thru the reaction between nitric acid and soda ash, or by direct absorption of nitrogen dioxide in an aq soln of Na carbonate (see above equation). The Na nitrate-nitrite soln was then heated with excess nitric acid to convert the nitrite to nitrate, and the NO thus produced was recycled to the nitric acid plant (Ref 6)

$Q_f^{298°}$ is −111540cal/mole; specific heat, 0.262cal/g at 25°; latent heat of fusion is −5355cal/mole at 310° (Ref 6)

Hygroscopicity (Ref 3): Na nitrate deliquesces in moist air. The critical relative humidity of purified material is 82.7% at 20°. The wt gain of purified Na nitrate (41μ size) at 70°F after 120 hours exposure is 11% at 70% RH and 25.75% at 90% RH. Water absorbed by 2.000g of 40–80 mesh material at 25° is:

Hours	g H_2O absorbed
3	0.0713
5.5	0.1355
7.5	0.1970
16	0.3924

Fire and Explosion Hazard. Na nitrate is a dangerous fire and expl hazard. It can ignite on friction. When heated above 1000° or when heated with reducing materials, particularly cyanides, it emits toxic fumes on decompn (Ref 3)

Properties. When molten Na nitrate is heated, it begins to decomp at 380°. At 400–600°, it gives off N_2 and O_2. NO appears at 700°. The rate of decompn increases with temp. From 775 to 865°, small amts of NO_2 and N_2O are also formed. The residue of the decompn is Na_2O. For DTA & TGA data see Ref 2

Uses. Na nitrate is an oxidizing agent containing more available oxygen per unit wt than K nitrate, and for this reason it is a suitable ingredient of expls such as black blasting powders (introduced by duPont) and some Dynamites (see Vol **5**, D1584ff). A more extensive use of it could be made if it were not so hygroscopic. In pyrotechnics, the oxidizer of choice for high-energy white flares is Na nitrate. It fulfills several important functions: the reaction with Mg leads to the formation of white Mg oxide particulates which enhance light reflection; the heat of reaction per g of components is high because of the high oxygen content of the nitrate and the low equivalent wt of the Na; and the Na exhibits luminescent properties that add significantly to useful light production (Ref 4)

The US Dept of Defense Mil Spec for Na nitrate is **MIL-S-322C** (5 Feb 1968). Three grades are specified (A, B & C) based on chemical requirements, and three classes (1, 2 & 3) based on granulation requirements. The chemical requirements are given on the following page

In addition to the granulation requirement, the average particle diameter of Class 2 Na nitrate shall be 30±15 microns by the procedure specified in **MIL-STD-1233**, Method 100

Refs: 1) Partington (1950), 694 2) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 3) Anon, EngrDesHndbk, "Military Pyrotechnic Series, Part Three–Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 272–73 4) Ellern (1968), 104 5) Merck (1968), 962-R 6) Kirk & Othmer **18** (1969), 494–95 7) CondChemDict (1971), 806-L

Table 1

Property	Grade A Percentage		Grade B 1/ Percentage		Grade C Percentage	
	Max	Min	Max	Min	Max	Min
Moisture	0.75	–	0.5	–	0.75	–
Insoluble Matter	0.5	–	0.1	–	0.5	–
Alkalinity (as Na_2O)	0.05	–	None	–	0.06	
Nitrates (as $NaNO_3$)	–	97.0	–	99.5	–	97.0
Chlorates (as $KClO_3$)	0.06	–	None	–	0.06	–
Calcium (as CaO)	0.3	–	0.1	–	0.3	–
Magnesium (as MgO)	0.15	–	0.06	–	0.15	–
Sulfates (as Na_2SO_4)	0.5	–	0.2	–	0.45	–
Chlorides (as NaCl)	–	–	0.15	–	0.15	–

1/ The percentages indicated, except the percent of moisture, are to be obtained in the sodium nitrate after the sample has been dried to constant weight at 150±3°

Granulation requirements follow:

Table 2

US Standard Sieve Number	Class 1 Percent thru	Class 2 Percent thru	Class 3 Percent retained on
	Minimum	Minimum	Minimum
20	–	–	80.0
60	98.0	–	–
100	–	98.0	–
200	–	–	–
325	–	–	–

Strontium Nitrate. $Sr(NO_3)_2$, mw 211.65, N 13.24%, OB to SrO and N_2 +37.8%, white granules or powd, mp 570°; bp decomps 580–600°; d 2.99g/cc, RI 1.5878. A white monoclinic tetrahydrate, $Sr(NO_3)_2.4H_2O$, also exists, having a d of 2.2g/cc. Methods reported for making Sr nitrate are by (1) treating strontianite with nitric acid, (2) digesting celestite with soda ash followed by treatment with nitric acid, and (3) digesting celestite with coal in a rotary kiln to form a sol sulfide, followed by treatment with nitric acid. Sr nitrate solns so formed are purified, and a commercial Sr nitrate crystal of high purity is prepd by crystn. Sol in 1.5p w, sl sol in alc or acet (Refs 3, 5 & 6)

Hygroscopicity. The critical relative humidity of purified Sr nitrate is 82.7% at 20°; for Spec grade material, 82.9% at 26.2° (Ref 2)

Fire and Explosion Hazard. Sr nitrate is a fire and expln hazard. As an oxidizer it can give up oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decompn. May expld when shocked or heated (Refs 2 & 6). For DTA or TGA data see Ref 1

Uses. The main use for Sr nitrate is for producing red colors in pyrotechnics, railroad fusees, marine signals, tracer compositions and in matches (Refs 2, 4 & 7). A high degree of purity is required, for the contamination of Sr nitrate with

Na or Ca salts tends to lighten the scarlet red flame to reddish yellow (Ref 5)

The US Dept of Defense Spec for Sr nitrate is **MIL-S-20322B** (19 Apr 1973). Two grades are specified, Grade A for use in pyrotechnic compns, such as flares, and Grade B, for use in tracer compns. The chemical and physical requirements are given below:

Table 1

Property	Requirement Grade A	Grade B
Strontium nitrate (including any barium nitrate), %, min	99.5	99.5
Moisture, %, max	0.05	0.05
Hygroscopicity, %, max	0.05	0.05
Acidity (pH)	6.0–7.0	6.0–7.0
Water-insoluble matter, %, max	0.02	0.02
Grit, %, max	0.02	0.02
Chloride (as Cl), %, max	0.003	0.003
Ammonium compounds (as NH_3), %, max	0.01	0.01
Sulfur (total), %, max	0.01	0.01
Barium, %, max	0.05	1.5
Calcium, %, max	0.003	0.003
Magnesium, %, max	0.003	0.003
Sodium, %, max	0.003	0.003
Iron, %, max	0.003	0.003
Bismuth, %, max	0.003	0.003
Lead, %, max	0.003	0.003
Copper, %, max	0.003	0.003

The granulation requirements for Grade A material is 95% thru a US Standard No 100 sieve; for Grade B material, 99.9% min thru a US Standard No 50 sieve, and 70.0% min retained on a US Standard No 140 sieve

Refs: 1) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 2) Anon, EngDesHndbk, "Military Pyrotechnics Series, Part Three–Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 283–4 3) Merck (1968), 987-R 4) Ellern (1968), 104, 136, 302 & 340 5) Kirk & Othmer **19** (1969), 52 6) CondChemDict (1971), 829-R 7) K.O. Brauer, "Handbook of Pyrotechnics", Chemical Publishing Co, NY (1974), 165

Tin Nitrate. Stannic nitrate, $Sn(NO_3)_4$, has been reported, but its existence is questionable. A soln contg stannic tin (Sn^{4+}) can be made by dissolving Sn in nitric acid. It decomps on aging, heating or dilution. The existence of stannous nitrate, $Sn(NO_3)_2$, must also be questioned. A soln of stannous tin (Sn^{2+}) in nitric acid can be made which must be kept cold. It is unstable to heat, dilution and aging (Ref 3)

In view of the above modern ref, it is interesting to note that Daniel (Ref 1) reported that tin nitrate (Nitrate d'étain in Fr) could be prepd by pouring a thin layer of nitric acid (d 1.2g/cc) onto a Sn surface and allowing it to stand for a while. A soln of Cu nitrate could be used in lieu of nitric acid. The resulting grayish-white deposit could be gently scraped with a non-sparking metal blade and dried. After drying, the material proved to be extremely sensitive to heat, impact or friction (Ref 1)

The above Sn nitrate (?) deserves mention because it was thought to be a fire and expln hazard in industrial accidents. For example, at the Spandau plant in Ger, several fires erupted in areas where wet NC came in constant contact with soldered bronze joints. In order to prevent further incidents, all soldered joints were examined and were found to be corroded with a coating contg Sn and nitrate ions. It was also found that the corroded material exploded when removal with a chisel was attempted

Ellern (Ref 2) mentions that in the presence of w, cupric nitrate and Sn foil, on prolonged and intimate contact, will produce flaming and sparking

Refs: 1) Daniel (1902), 480 2) Ellern (1968), 46 3) Kirk & Othmer **20** (1969), 314 & 317

Uranyl Nitrate (Uranium Nitrate, UNH, Yellow Salt). $UO_2(NO_3)_2.6H_2O$, mw 502.18, N 5.58%; yellow rhomb crysts, greenish luster by reflected light; mp 60.2°, bp 118°, d 2.807g/cc, RI 1.4967. Sol in 1.5p w, freely in alc and eth. Prepd by the action of nitric acid on U octoxide. When shaken, rubbed, or crushed, the crysts show remarkable triboluminescence with occasional detonations. It is highly toxic, and a severe fire and expln risk when shocked or heated,

and in contact with organic materials. Solns of U nitrate in eth should not be allowed to stand in sunlight as expln may occur
Refs: 1) V.N. Ivanov, JRussPhysChemSoc **44**, 678–9 (1912) & CA **6**, 2368 (1912) 2) L. Andrews, JACS **34**, 1687 (1912) & CA **7**, 702 (1913) 3) Merck (1968), 1094-R 4) Kirk & Othmer **21** (1969), 34 5) CondChemDict (1971), 914-R

Zinc Nitrate. $Zn(NO_3)_2.6H_2O$, mw 297.49, colorless tetragonal crysts, mp 36.4°, loses $6H_2O$ from 105° to 131°, d 2.065g/cc. Sol in w and alc. Prepd by action of nitric acid on Zn or Zn oxide. It is a strong oxidizing agent, a dangerous fire and expln risk, and may expld if shocked or heated

The US Dept of Defense Spec for Zinc Nitrate, Reagent is **MIL-Z-11143** (10 May 1951), and specifies the following chemical requirements:

Table 1

Requirement	Percent by weight
Assay, as $Zn(NO_3)_2.6H_2O$	99.0 minimum
Maximum impurities	
Insolubles	0.005
Free acid (as HNO_3)	0.03
Chloride (Cl)	0.005
Phosphate (PO_4)	0.001
Sulfate (SO_4)	0.010
Alkalies & Alkaline Earths	0.20
Iron (Fe)	0.001
Lead (Pb)	0.005

Physical requirements state that the material be in the form of crysts or fragments, and that its color be white or colorless
Refs: 1) Merck (1968), 1129-L 2) Kirk & Othmer **22** (1969), 608 3) CondChemDict (1971), 951-L

Zirconium Nitrate. $Zr(NO_3)_4.5H_2O$, mw 429.33, N 13.05%; white hygr crysts or white pieces or scales; decomps at 100°, sol in w and alc. Prepd by the action of nitric acid on Zr oxide (Refs 1, 2 & 3)

The US Dept of Defense Spec for Zirconium Nitrate, Reagent is **MIL-Z-11144** (10 May 1951), and specifies the following chemical requirements:

Table 1

Requirement	Percent by weight
Assay, as ZrO_2	45.0 minimum
Maximum impurities	
Solubility	To pass test
Chloride (Cl)	0.001
Sulfate (SO_4)	0.7
Alkalies & Alkaline Earths	0.10
Heavy metals (as Pb)	0.010
Iron (Fe)	0.020

The solubility test consists of dissolving 1.000g of the specimen in 20ml of w. If the soln is not completely clear or possesses more than a very slight opalescence, the specimen does not comply with the requirement

Physical requirements state that the material be a crystalline powder, and that it be white in color
Refs: 1) Merck (1968), 1132-R 2) Kirk & Othmer **22** (1969), 649 3) CondChemDict (1971), 956-L

Nitration

I. Introduction

Nitration is a chemical reaction by which *nitro* (NO_2) groups are introduced into organic compds. It is basically a substitution or double exchange reaction in which one or more NO_2 groups of the *nitrating agent* replace one or more groups (usually hydrogen atoms) of the compd being *nitrated.* It is customary to distinguish three types of nitration reactions as follows:

C-nitration, in which a nitro group is attached to a carbon atom to form a *nitro compd,*

$$-\overset{|}{\underset{|}{C}}-NO_2;$$

O-nitration, in which a nitro group is attached to an oxygen atom to form a *nitrate ester,*

$$-\overset{|}{\underset{|}{C}}-ONO_2;$$

N-nitration, in which a nitro group is attached to a nitrogen atom to form a nitramine,

$$-\overset{|}{\underset{|}{\overset{|}{\underset{|}{C}}}}-NNO_2$$

Nitration plays an important role in the prepn of expls. For example, the most commonly used military and commercial expls compds, such as TNT, RDX, NG, EGDN, Tetryl, PETN, NC, and many others are all produced by nitration (chemical names for these and other "common" names are given in Table 1 of Section III). Nitration reactions are also used to produce many commercially important non-expl organic chemicals and intermediates. In addition to their obvious importance in commerce and synthesis, nitration reactions have contributed greatly to the development of chemical theory – particularly in the formulation of substitution rules for organic compds and the elucidation of reaction mechanisms. Clearly, *nitration* in all its aspects is a vast subject and much too broad to cover in a single article. In what follows we will therefore limit ourselves primarily to examining nitration from an expl-oriented point of view. After a brief summary of the *Early History of Nitration* (Section II), we will list *Typical Explosives Produced by Nitration* (Section III), enumerate the *Nitrating Agents* used in producing these and other expls (Section IV), examine *Typical Spent Acid Compositions* and how they affect yield and waste products (Section V), describe the *Nitration Process* both batch and continuous (Section VI), review *Nitration Thermochemistry* (Section VII) and *Nitration Mechanisms* (Section VIII), briefly summarize *Selected Recent Literature on Nitration* (Section IX), and conclude with a short discussion of *Safety in Nitrations* (Section X). The following general refs are highly recommended to the reader requiring greater detail than presented here:

Annual Reviews of Nitration: IEC **40**, 1627 (Sept 1948); IEC **41**, 1889 (Sept 1949); IEC **42**, 1716 (Sept 1950); IEC **43**, 1967 (Sept 1951); IEC **44**, 2039 (Sept 1952); IEC **45**, 1998 (Sept 1953); IEC **46**, 1861 (Sept 1954); IEC **47**, 1894 (1955); (no review in 1956); IEC **49**, 1534 (1957); IEC **50**, 1380 (1958); IEC **51**, 1123 (1959); IEC **52**, 545 (1960); IEC **53**, 401 (1961)

T. Urbański, "Chemistry and Technology of Explosives", Vols **1**, **2** & **3** (Refs 74, 75 & 82), an *excellent* presentation of the prepn, properties and chemistry of nitrated compds and the technology and mechanisms of nitrations

T.L. Davis, "The Chemistry of Powder and Explosives", (Ref 29), a less detailed, older, but still useful overview of nitrations

L.P. Kuhn et al, "Unit Processes in Organic Synthesis", (P.H. Groggins, Ed), Chapter on Nitration, McGraw-Hill, NY (1958), summarizes the chemical technology of nitrations, but mostly for non-expl materials

Houben-Weyl, "Methoden der Organischen Chemie, Vierte Auflage (Eugen Müller, Ed), Stickstoff-Verbindungen **I**, $-NO_2$ $-NO$ $>N-O-$, Georg Threine Verlag, Stuttgart (1971) is a comprehensive modern review of the prepn of nitro compds

Ph. Naoúm, "Nitroglycerin und Nitroglycerinsprengstoffe", Springer, Berlin (1924) is the standard reference on NG, EGDN & other nitrate esters

L.F. Albright & C. Hansen, Eds, "Industrial and Laboratory Nitrations", ACS Symposium Series 22, ACS, Washington, DC (1976). Excellent modern review. Ten chapters emphasize various aspects of the chemistry and mechanism of nitrations, including oxidation and *ipso*-nitration side reactions. Six chapters discuss the chemistry and physical transfer steps between phases. Eight chapters discuss plant operation-improvements, safety features, and new operations. The final chapter is devoted to vapor phase nitrations

W. Foerst, Ed, "Ullmanns Encyklopädie der technischen Chemie" **12**, 3rd Ed, Urban & Schwarzenberg, Berlin (1960), 768–84. Nitrobenzene, Nitrotoluene and Nitroxylene

L.F. Albright, Ed, "Kirk-Othmer Encyclopedia of Chemical Technology" **13**, 2nd Ed, Interscience, NY (1967), 784–96 (Nitration) & 834–53 (Nitrobenzene & Nitrotoluenes)

Refs to nitrated materials, eg **Cellulose Nitrate, Cyclonite** etc., already described in this Encyclopedia will be found in Sections II & III

In view of the definition of nitration presented above and the concepts to be developed in Section VIII, discussion of nitrate salts such as $H_2NNH_2.HNO_3$ or $CH_3NH_2.HNO_3$ etc is not included in this article

II. Early History of Nitration and Nitrated Compounds

According to Urbański (Ref 74), "Nitration is one of the earliest known organic chemical reactions. It is mentioned in the writings of the alchemists.

As early as in the first half of the XVIIIth century Glauber obtained picric acid by acting on wool and horn with nitric acid. Soon reactions between nitric acid and a variety of organic substances became one of the alchemical reactions most frequently used. They were usually carried out by heating a substance with nitric acid, often to boiling point. Thus picric acid was obtained from certain organic substances such as indigo, silk, resins, etc

"In 1833 Braconnot obtained nitric esters of cellulose and starch by acting with nitric acid on plant fibres and starch, at low temperature. In 1834 Mitscherlich nitrated benzene to nitrobenzene. But it is only since 1842, when Zinin reduced nitrobenzene to aniline, that rapid development of the chemistry of nitro compounds and their application to organic industry has occurred"

Indeed it can be stated that the history of modern expls begins with the discoveries of nitroglycerin (**NG**) and nitrocellulose (or more correctly cellulose nitrate or **NC**) nearly 125 years ago, and their application to military and commercial usage. An excellent review of the early history of **NC** is given by T.L. Davis (Ref 29, pp 244–56). The early histories of **NG** and **EGDN** (discovered in 1870) are summarized, respectively, in Vol **6**, G99-R to G100-R and E259-R, and in the Naoûm reference cited above

TNT appears to have been first prepd by Willbrand (Ref 2) in 1863 and its prepn was further developed by Beilstein & Kuhlberg (Ref 3). By the beginning of this century it was already in general use as a military expl

RDX or **Cyclonite** was first prepd by Henning (Ref 6) for medicinal use in 1899. Its value as an expl was not recognized until 1920 (Ref 11). Much of the development for its large-scale production was done early in WWII (see Vol **3**, C611-L)

PETN was first described in 1894 (Ref 5). Methods for its large-scale production were developed in the late 1920's and early 1930's (Refs 15 & 17)

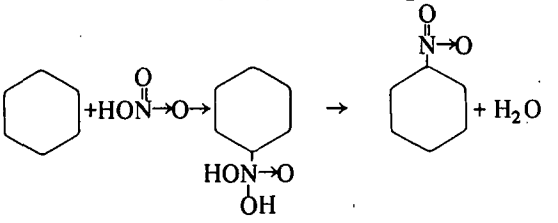
The use of mixed acid (mixt of nitric and sulfuric acids) as a nitrating agent was first described in 1846 by Muspratt & Hoffman (Ref 1). The sulfuric acid in their mixt was considered to be a "dehydrating agent", a view first advanced by Spindler (Ref 4) and developed further by Markovnikov (Ref 7) & Sapozhnikov (Ref 8). The modern concept of the role of sulfuric acid in mixed acid (MA) nitrating agents was first advanced by Hantsch (Ref 9). Although Hantzsch's ideas are no longer totally accepted, he was the first to point out that in the presence of sulfuric acid (or any acid stronger than nitric) – nitric acid acts as a base in accord with the Brönsted theory of acids and bases. According to Hantzsch:

$$NO_2OH + H_2SO_4 = NO(OH)_2^+ + HSO_4^-$$

$$NO_2OH + 2H_2SO_4 = N(OH_3)^{++} + 2HSO_4^-$$

In their more familiarly written form $NO(OH)_2^+ = H_2NO_3^+$ and $N(OH)_3^{++} = H_3NO_3^{++}$ are respectively the *nitracidium* and *hydronitracidium* ions. For further discussion of early theories of species existing in MA the reader is referred to Urbański (Ref 74, pp 12–14). Modern concepts will be examined in detail in Section VIII

Early nitration theories considered nitration as an addition reaction in which the initial step was the direct addition of the nitrating agent to the molecule undergoing nitration, eg:



These theories are reviewed in Urbański (Ref 74, pp53–60). Modern views of the mechanism of nitration will be examined in detail in Section VIII

III. Typical Explosives Produced by Nitration

As already mentioned (Section I), the prepn of most of the commonly used high expl compds involves one or more nitration reactions. Indeed, except for ammonium nitrate (AN), primary expls, and BkPdr, it is difficult to bring to mind any expl in common use (or even a laboratory curiosity) that was not prepared by nitration. In Table 1, we list the most important military and commercial high expl compds produced by nitration. We have grouped these compds by nitration type, ie C-nitration, O-nitration, and N-nitration. Note that either nitric acid or mixed acid are the nitrating agents principally employed in industry. This will be discussed further in the next section. The Table also gives Encyclopedia references for those compounds already described in previous Encyclopedia volumes

Table 1

Some Typical Explosive Compounds Produced by Nitration

C-Nitration

Compound	Common Name or Abbreviation	Usual Nitrating Agent*	Encyclopedia Reference
Trinitrotoluene	TNT**	MA	–
Hexanitrostilbene	HNS	MA	Vol **5**, D1456-R (f)
Trinitrophenol	Picric Acid	NA (a)	–
Trinitroresorcinol	Styphnic Acid	NA (a)	Vol **5**, D1276-R (g)
Hexanitrodiphenylamine	Hexyl	NA or MA	Vol **5**, D1434-R
1,3 Diamino-2,4,6-Trinitrobenzene	DATB	NA	Vol **5**, D1130-R (h)
Nitromethane**	NM	NA (b)	–
Tetranitromethane	TNM	NA + acet anhyd	–

O-Nitration

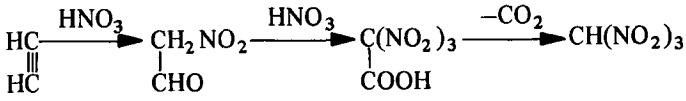
Compound	Common Name or Abbreviation	Usual Nitrating Agent*	Encyclopedia Reference
Glyceroltrinitrate	NG**	MA	Vol **6**, G98-R
Ethyleneglycoldinitrate	EGDN	MA	Vol **6**, E259-R
Diethyleneglycoldinitrate	DEGDN	MA	Vol **5**, D1232-L
Cellulose nitrate (c)	NC**	MA	Vol **2**, C100-L
Diethanolnitraminedinitrate (d)	DINA	NA + acet anhyd	Vol **5**, D1240-R
Pentaerythritoltetranitrate	PETN	NA	–
Nitrostarch	NS	MA	–
Mannitol hexanitrate	Nitromannitol	MA	–

N-Nitration

Compound	Common Name or Abbreviation	Usual Nitrating Agent*	Encyclopedia Reference
Cyclotrimethylene-trinitramine	RDX**, Cyclonite	NA + AN	Vol **3**, C611-L
Cyclotetramethylene-tetranitramine	HMX	NA + AN	Vol **3**, C605-R
Ethylenedinitramine	Haleite, EDNA	NA or MA + acet anhyd	Vol **6**, E238-R
2,4,6 Trinitrophenyl-methylnitramine (e)	Tetryl**	MA	–

*MA = mixed acid = mixt of nitric & sulfuric acids
NA = nitric acid
AN = ammonium nitrate
**Manufacture discussed in some detail in Section VI
(a) Sulfonation followed by nitration
(b) Vapor phase nitration
(c) A mixt of the di- & trinitrates
(d) Also an example of N-nitration
(e) Also an example of C-nitration
(f) Two moles of TNT condense to form one mole of Hexanitrostilbene
(g) Also see D.A. Salter & R.J. Simkins, GerP 1959930 (1970) & CA **73**, 76860 (1970)
(h) Also see J.A. Hoffman & C.F. McDonough, USP 3278604 (1966)

A somewhat unusual type of C-nitration can occur in reactions between nitric acid and unsaturated hydrocarbons. An example of the nitration of unsaturated hydrocarbons is Quilico's scheme (Ref 31) for the formation of nitroform ($CH(NO_2)_3$):



IV. Nitrating Agents

Nitration can be carried out either directly by introduction of the nitro group in place of a hydrogen atom or by adding it to a double bond, or else indirectly, by introducing into a compd a group which can readily be replaced by or converted to the nitro group

The following nitrating agents are most frequently used in industry for the direct introduction of the nitro group:

(1) concd nitric acid

(2) mixts of concd nitric acid and concd sulfuric acid or oleum in different proportions – these are usually known as "mixed acids", and much less frequently:

(3) alkali nitrates in the presence of sulfuric acid

(4) dil nitric acid

(5) nitrogen dioxide

(6) a soln of nitrogen dioxide in sulfuric acid

(7) nitrogen dioxide in the presence of catalysts

For lab prepns, and occasionally in industrial use, more expensive nitrating agents may be employed, as for example solns of nitric acid in inert organic solvents (chlf, carbon tetrachloride, eth, nitromethane, etc), or a soln of nitric acid in phosphoric or acetic acids or in acetic anhydride, trifluoroacetic anhydride or trifluoromethanesulfonic acid (Ref 94)

For nitrating on the lab scale, mixts of nitric acid esters or acyl nitrates, eg acetyl nitrate (CH_3CONO_3) and sulfuric acid may also be used

Several lesser known nitrating agents, which have been used on a lab scale are metal nitrates in the presence of acetic acid or acetic anhydride, tetranitromethane and hexanitroethane in an alkaline medium, and nitroguanidine in soln in sulfuric acid, used for the nitration of aromatic amines and phenols. For details see Ref 74, Chapt III

The most common indirect nitration method, often used in nitrating phenols, consists of sulforating the compd and then replacing the sulfo group by a nitro group. The usual nitrating agent for these reactions is concd nitric acid

Other indirect nitration methods applied on an industrial scale for nitrating phenols involve introducing a nitroso group into the phenol and then oxidizing it to the nitro group. Another method involves the oxidation of a primary amino group to the nitro group

In exptl work, indirect methods of introducing nitro groups find wide application as, for example, the replacement of a halogen (iodine or bromine in an alkyl iodide or bromide) by the nitro group, by means of silver nitrite (the Victor Meyer reaction)

In aromatic compds, an amino group may be replaced by the nitro group by diazotization and reaction with nitric acid in the presence of cuprous salts (the Sandmeyer reaction). This method is used for lab work only and is described in standard textbooks on preparative organic chemistry

The most widely used nitrating agents in the prepn of important military and commercial high expls are the mixed acids (MA) consisting of various mixts of $HNO_3/H_2SO_4/H_2O$. Consequently the remainder of this section will be devoted to a discussion of mixed acids. In view of the obvious importance of its use in the prepn of military expls, there is a US Military Specification for *Mixed Acid* (for use in nitration of explosives): **MIL-A-50210(MU)** (6 December 1968). The "Requirements" for mixed acid prescribed in this specification are:

3.1 *Materials.* The mixed acid shall be made with sulfuric acid conforming to JAN-A-179, and nitric conforming to JAN-A-183

3.2 *Residue on evaporation.* 0.5 percent, max

3.3 *Acid content.* As specified by contract or purchase order

3.4 *Total sulfuric acid.* As specified by contract or purchase order

3.5 *Total nitric acid.* As specified by contract or purchase order

3.6 *Nitrosylsulfuric acid.* As specified by contract or purchase order

3.7 *Actual sulfuric.* As specified by contract or purchase order

3.8 *Actual nitric acid.* As specified by contract or purchase order

3.9 *Water.* As specified by contract or purchase order

The appropriate mixed acid compns for the nitration processes that produce militarily and industrially important expls will be described in Sections V & VI. Typical MA compns for *aromatic nitrations* contain 110 to 200% nitric acid over the stoichiometric requirement. For the nitration of toluene to MNT & DNT, a typical MA compn in round figures is: 30% HNO_3, 60% H_2SO_4, 10% H_2O. For the nitration of DNT to TNT the MA contains no water and is approx: 20% HNO_3, 80% H_2SO_4

Nitrate esters such as NG & EGDN are made using MA contg 30–70% HNO_3, 35–70% H_2SO_4 and 0–10% H_2O. The nitric acid content of the MA is usually 20% in excess of stoichiometric

The ratio of the quantities of components of the nitrating acid (HNO_3, H_2SO_4 and H_2O) is obviously important. The fact that water is formed during the nitration process, thus diluting the nitrating mixt, must be taken into consideration. Since sulfuric acid is the principal "dehydrating" component of MA, the amount of H_2SO_4 must be chosen in such a proportion that it can take up most of the matter formed during the nitration. Otherwise nitration might be incomplete. A commonly used measure of the effectiveness of the sulfuric acid in doing this is the **DVS** or *dehydrating value of sulfuric acid.* DVS is defined by:

$$DVS = \frac{H_2SO_4}{(H_2O)_i + (H_2O)_f}$$

where $(H_2O)_i$ is the initial concn of water in the nitrating mixt before nitrating and $(H_2O)_f$ is the concn of water formed during nitration

The DVS of a given MA should be as high as possible in order to obtain complete nitration. However, as discussed in the next section, compromises must often be made in order to *minimize* the solubility of the nitrated product in the *spent acid,* ie, the acid in equilibrium with the nitrated product, as well as the solubility of spent acid in the product

Gillespie and Miller (Ref 33) arranged various nitrating agents in order of increasing nitration effectiveness, namely:

$C_2H_5O.NO_2$	ethyl nitrate
$HO.NO_2$	nitric acid
$CH_3COO.NO_2$	acetyl nitrate
$NO_3.NO_2$	nitric anhydride
$Cl.NO_2$	nitryl chloride
$H_2O.NO_2^+$	nitracidium ion
NO_2^+	nitronium ion

According to Urbański (Ref 74, Chapt 2), this order seems to require some alteration. For example, nitryl chloride has been found to be a definitely weaker nitrating agent than nitric acid and should have been placed before it. The nitronium ion, NO_2^+, occurs in many mixed acid compns

V. Spent Acid

Acid compns for practical nitrations must be formulated in such a manner that the *spent acid* must:

a) be readily separable from the nitrated product

b) have a minimum solubility for the nitrated product

c) be such that traces of the acid are readily removable from the crude nitrated product

d) be such that traces of product are readily removable from the spent acid

It is obvious that the nitrated product must be separated from the acid in equil with it (spent acid). If the product and the spent acid form two immiscible liq phases, eg, NG, EGDN, or molten TNT, separation is effected by gravity or centrifuging. If the product and spent acid form a solid and a liq phase, eg PA, NC or PETN, separation is effected by centrifuging (PA & NC) or filtration (PETN). If the nitration is carried in the vapor phase (NM), separation is effected by distillation

To keep product yield at a maximum it is important that the solubility of product in the spent acid be kept to a minimum. This also facilitates removal of traces of product from the spent acid so that it can be either fortified and reused, reused to make lower nitro compds, or neutralized and discharged as *non-polluting* waste material

Traces of acid in the product almost always degrade product stability and in some cases can lead to self-ignition and expln. The usual methods of removing traces of spent acid is by washing with water and/or dil alkali solns followed by a water wash

Typical nitrating acid and spent acid compns used in the manufacture of selected high expls are shown in Table 2

As illustrations of the loss of yield that can occur if spent acid compns are not adjusted to maintain minimum solubility of product, consider the data in Fig 1. These show a 2–3 fold increase in **NG** solubility in spent acid contg 7–16% HNO_3 and 16–19% H_2O over that dissolved in spent acid contg 16% HNO_3 and 13–15% H_2O

Similarly, TNT is very soluble in conc H_2SO_4 as shown in Table 3 (from Ref 19), and considerably less soluble in spent acid contg small amts of nitric acid, as shown in Table 4 (also from Ref 19). According to Orlova (Ref 62) TNT is very soluble (100–800%) in conc HNO_3

It is also important to minimize the solubility of acid in the product. Fig 2 (from Ref 61) shows the solubility of HNO_3 in NG. The numbers at the right of the curves are the % HNO_3 in the spent acid. The vertical line corresponds to the mole ratio of H_2O/H_2SO_4 to form the monohydrate $H_2SO_4.H_2O$. Note that the max HNO_3 solubility for each curve occurs close to this vertical line. It is clear that both water content and HNO_3 content of the spent acid should be kept low in order to minimize HNO_3 solubility in the NG

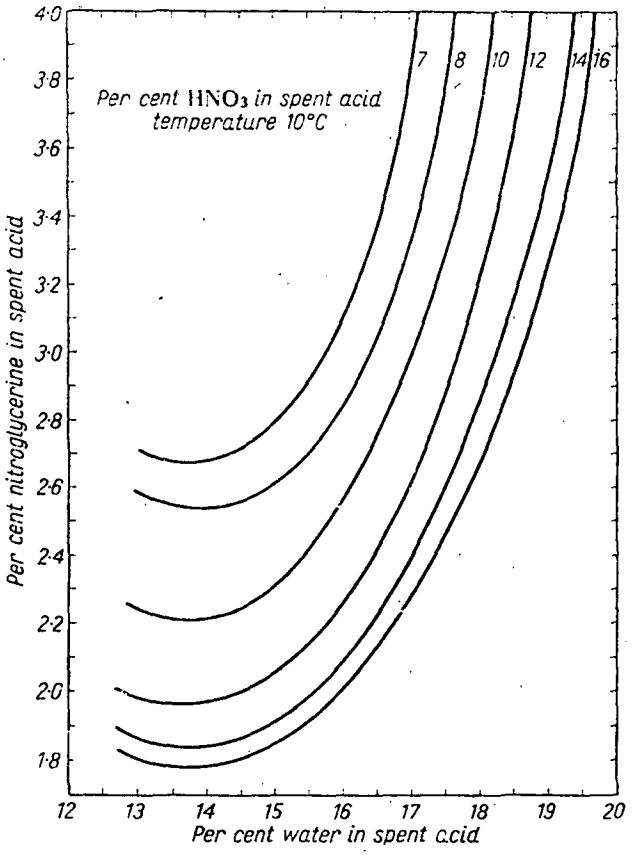


Fig 1 Solubility of nitroglycerine in spent acid, according to Klassen and Humphrys (Ref 40)

Table 2

Representative Nitrating Acid and Spent Acid Compositions* for Some Common Explosives

Product	Nitrating Acid (%)	Spent Acid (%)
MNT (a)	28/56/16 $HNO_3/H_2SO_4/H_2O$	70/30 H_2SO_4/H_2O
DNT (a)	28/64/8 $HNO_3/H_2SO_4/H_2O$	2/76/22 $HNO_3/H_2SO_4/H_2O$
TNT (a)	20/80 HNO_3/H_2SO_4	4/86/10 $HNO_3/H_2SO_4/H_2O$
TNT (b)	8/90/2 $HNO_3/H_2SO_4/H_2O$	—
PA (a) (c)	70/20/10 $HNO_3/H_2SO_4/H_2O$	4/76/18/2 $HNO_3/H_2SO_4/H_2O$/other
NG (a)	50/50 HNO_3/H_2SO_4	13/71/16 $HNO_3/H_2SO_4/H_2O$
NG (b)	50/50 HNO_3/H_2SO_4	—
DEGDN (a)	65/35 HNO_3/H_2SO_4	29/45/22/4 $HNO_3/H_2SO_4/H_2O$/DEGDN
PETN (a)	99/1 HNO_3/H_2O	30/70 HNO_3/H_2O (d)
NC (a)	22/68/9 $HNO_3/H_2SO_4/H_2O$	19/70/11 $HNO_3/H_2SO_4/H_2O$
Tetryl (a)	78/6/16 $HNO_3/H_2SO_4/H_2O$	1/0.5/82.5/16 $HNO_3/NO_2/H_2SO_4/H_2O$

*These are approximate "average" compns for several different processes

(a) Batch nitration (b) Continuous nitration (c) Final step (d) Water is added to ppt the PETN

Table 3
SOLUBILITY OF α-TRINITROTOLUENE IN SULFURIC ACID (IN %)

Concentration of H_2SO_4, % / Temperature °C	70	75	80	85	90	95	100
0	–	0.3	0.4	0.6	2.0	3.5	13.0
10	–	0.3	0.45	0.75	2.2	4.0	13.5
20	–	0.3	0.50	0.85	2.5	4.8	15.0
25	–	0.32	0.55	0.95	2.6	5.2	15.5
30	–	0.35	0.60	1.0	2.7	6.0	16.5
40	0.2	0.4	0.65	1.3	3.0	7.0	18.0
50	0.2	0.45	0.70	1.7	3.5	8.5	21.0
60	0.22	0.50	1.0	2.3	5.2	11.0	24.8
70	0.35	0.7	1.6	3.3	7.0	13.5	29.0
80	0.6	1.3	2.4	4.8	10.0	18.0	26.5

Table 4
SOLUBILITY OF α-TRINITROTOLUENE IN MIXED ACID

Composition of the mixture, %			Solubility, %		
H_2SO_4	HNO_3	H_2O	at 20°C	at 50°C	at 70°C
60	0	40	0.20	0.52	0.70
80	0	20	0.59	1.25	2.07
90	0	10	2.55	4.70	7.63
60	1	39	0.22	0.41	0.62
80	1	19	0.55	1.08	1.68
90	1	9	1.85	4.35	7.49
60	5	35	0.25	0.55	1.23
80	5	15	0.73	1.48	1.85
90	5	5	1.76	4.49	7.53

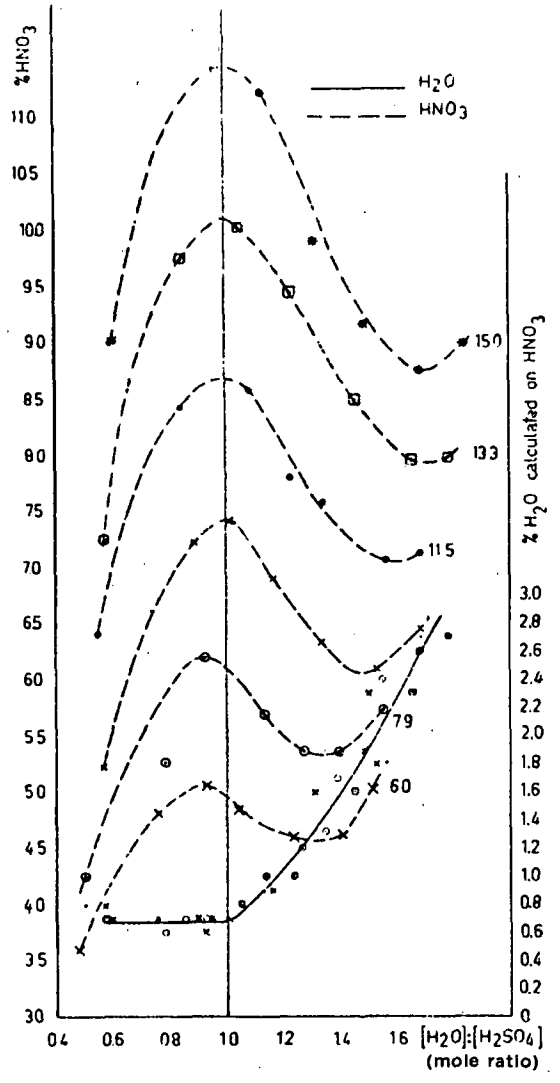


Fig 2 Solubility of **NG** in Spent Acid (Ref 61)

The original ref does not specify the temp at which the data of Fig 2 were obtained, but presumably it was at 20° since most of the other measurements in their investigation were made at 20°

VI. Technology of Nitration

Industrial nitrations are carried out either in discrete batches or continuously. Modern practice tends to continuous methods, but many nitrated materials are still produced by batch processes. Below, we will describe the technology of manuf of: **TNT** and **NM**, examples of *C-nitration:* **NG** and **NC**, examples of *O-nitration,* and **RDX** and **Tetryl**, examples of *N-nitration.* **NG, NC** and **RDX** (cyclonite) production has already been described in previous Encyclopedia articles (see Table 1 of Section III for references): here we shall examine these processes more fully. **NM** is included because it is a good example of vapor phase nitration, and because its expl properties have been studied so extensively. (see under Methane and Derivatives in this Vol). In general we will tend to emphasize modern continuous methods since the older batch processes are well described in the literature (eg, in Refs 29, 50, 74, 75 & 82)

TNT. Because TNT is so important in military and commercial use, its manuf will be described in some detail. The nitration of toluene is carried out in successive stages, eg, Toluene→ MNT→DNT→TNT. This method permits the use of spent acid from a higher stage of nitration, after it has been fortified with additional nitric acid, for a lower stage nitration. Moreover, the lower stage nitrations are thus accomplished with less degradation with a MA that has a higher water content than that required for the last nitration stage, as discussed below

The presence of a methyl group in toluene greatly facilitates its nitration as compared with benzene. The reaction of introducing the first nitro group therefore proceeds very quickly, however the methyl group is readily oxidized. Mononitration also leads to oxidation of the ring and the formation of cresols (as in the case of benzene, which is oxidized to phenol). Other oxidation reactions proceed especially readily under drastic conditions which introduce several nitro groups at a high temp

Sometimes, for example, if the MA is poor in nitric acid, or if an insufficient amount of MA is used, tar formation may take place. For this reason it is preferable to use mixts rich in HNO_3, and to use a distinct excess of MA. On the other hand, both excess HNO_3 and excess MA favor oxidation processes. Thus a trade-off must be achieved

Kostevich and Sapozhnikov have carried out extensive studies on the nitration of toluene to mononitrotoluene, using nitrating mixts of various compns and determining the compn of mixts leading to dinitrotoluene. Their results are shown in the ternary diagram of Fig 3

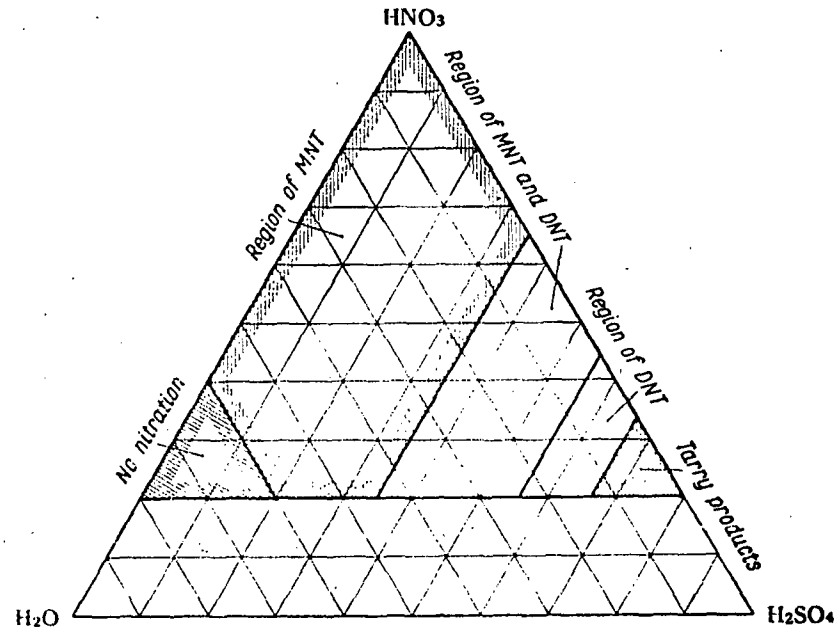


Fig 3 Nitration of toluene with MA (Kostevich and Sapoznikov, as shown in Ref 74, p 266)

An important aspect of nitrating toluene to nitrotoluene is the very low solubility of toluene and nitrotoluenes in nitrating mixts. Therefore the nitration proceeds in a two-phase system and the rate of nitration depends greatly on dispersion, which in turn depends on keeping the two phases efficiently stirred. This is emphasized in Fig 4, which gives the yield of MNT for a 11/64/25% nitric acid/sulfuric acid/water MA and a nitration time of 30 minutes as a function of stirring speed

Fig 5 shows the yield of MNT as a function of acid/toluene ratio for a MA of 27/55/18% nitric acid/sulfuric acid/water and a nitration time of 50 minutes at 30°

The rate of nitration of toluene to MNT increases with increasing temp, but over the range of 20–75° this rate increase is less than 2-fold (cf Fig 6)

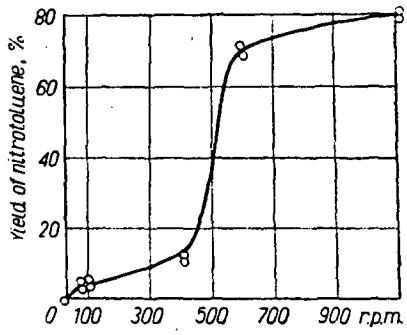


Fig 4 Influence of the rate of stirring on the rate of nitration of toluene (Orlova, Ref 62)

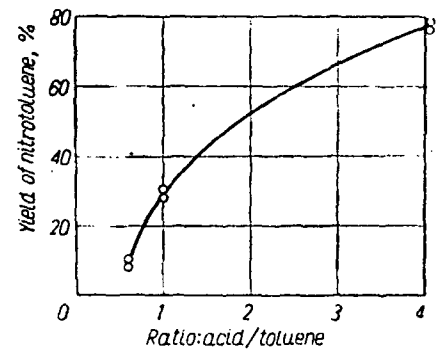


Fig 5 Change of yield of MNT with the ratio acid/toluene (Orlova, Ref 62)

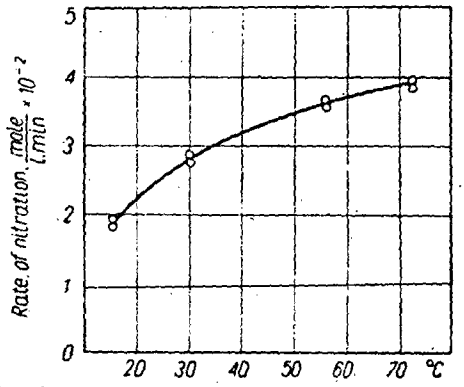


Fig 6 Change of the rate of nitration of toluene with temperature (Orlova, Ref 62)

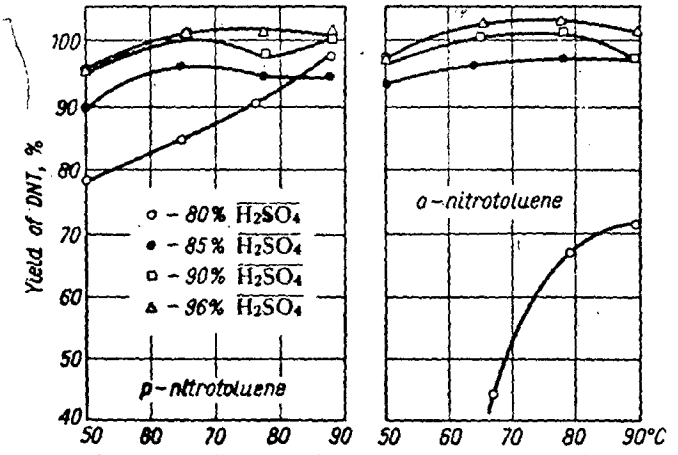


Fig 7a Influence of temperature on the yield of DNT. Nitration of o- and p-nitrotoluenes in nitrating mixtures with various concentrations of sulfuric acid (Kobe, Skinner and Prindle, Ref 45)

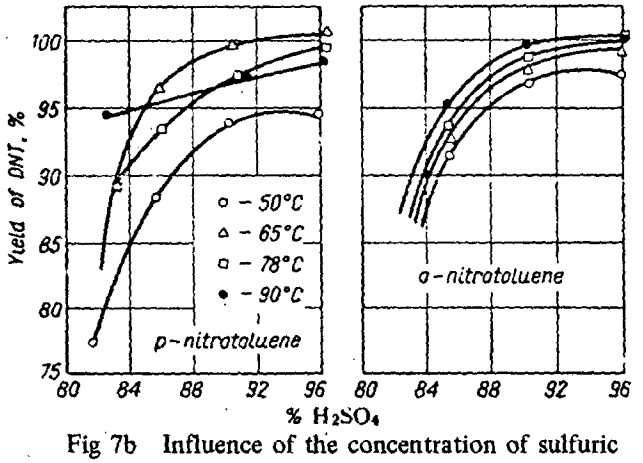


Fig 7b Influence of the concentration of sulfuric acid on the yield of DNT. Nitration of o- and p-nitrotoluenes (Kobe, Skinner and Prindle, Ref 45)

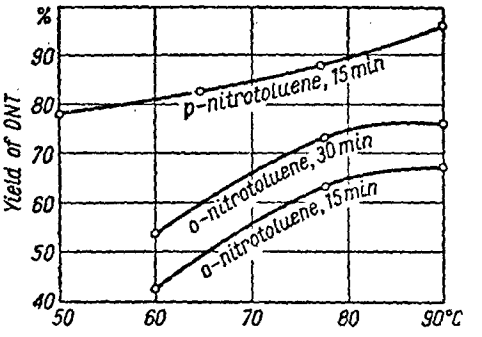


Fig 7c Influence of temperature and time on the yield of DNT. Nitration of o- and p-nitrotoluenes (Kobe, Skinner and Prindle, Ref 45)

The nitration of nitrotoluenes to DNT has been studied by Kobe, Skinner & Pringle (Ref 45). Their results are presented in Figs 7a, b and c

As in the case of MNT, agitation is important in increasing the MNT to DNT nitration rate. Orlova's data for the nitration of p-nitrotoluene with 4/74/23% nitric acid/sulfuric acid/water at 70° are shown in Fig 8

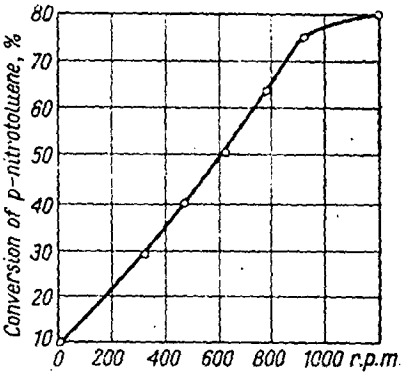


Fig 8 Influence of the intensity of stirring on the rate of nitration of p-nitrotoluene (Orlova, Ref 62)

Factors affecting the rate of nitration of DNT→TNT will be discussed in Section VIII

Urbański (Ref 74) lists several processes for the batchwise manufacture of TNT (eg, the "French", "British", "USSR" etc). All of them are essentially similar with only minor differences in MA compns and methods of separating the crude TNT from its spent acid. These processes have been largely replaced by continuous nitration techniques. The Biazzi and Bofors continuous processes for the manuf of TNT are described briefly under **Continuous Methods of Manufacturing Explosives** in Vol 3, C501-L. The Swedish-Norwegian continuous process and the Hercules process are discussed below

Swedish-Norwegian Chematur and Norsk Spraengstoffindustri Continuous Process: This process, patented in Sweden in 1953 (Ref 42), employes stepwise nitration of mono- and/or di-nitrotoluene to trinitrotoluene in a series of counter-current units, each unit consisting of a nitrator and a separator

The principle of design and operation of the unit is given in Fig 9. The nitrator N consists of a U-vessel with two legs or shanks (1) and (2), joined by pipe (6). The components of the

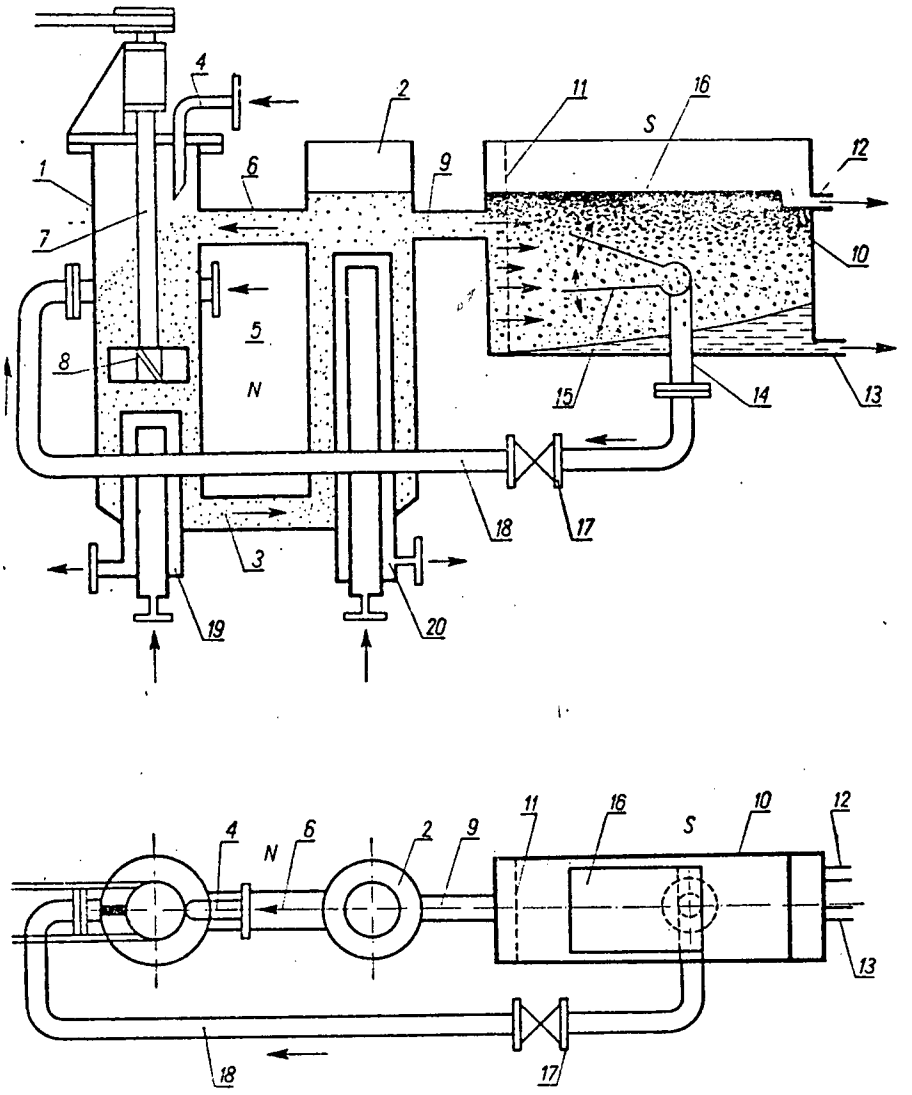


Fig 9 Nitrator for continuous manufacture of TNT (Chematur method, Ref 42)

reaction are introduced thru inlets (4) and (5). Liq can be kept in circulation from leg (1) to leg (2) and back by the turbine-wheel (8) on the drive-shaft (7). By regulating the speed of the turbine (8) and adopting suitable proportions for pipes (3) and (6) it is possible to keep the liq at a higher level in leg (2) than in leg (1). Separator S communicates with the nitrator thru pipe (9). The separator is a rectangular box (10) with a distributor (11) for the mixt coming from the reactor, an outlet (12) for the separated light component and an outlet (13) for the heavy component. At some distance from the inlet, and between the levels of the outlets for the separated components, there is also another outlet (14) for partly separated emulsion. This outlet has adjustable plates (15) and (16) to make it possible to adjust the opening of the outlet with reference to its level in the separator. The partly-separated emulsion is led back to the reactor thru pipe (18) and regulating valve (17). To control the temp of the reaction mixt the unit is equipped with heat exchangers (19) and (20). The separator may also have a heat exchanger jacket, not shown in the diagram

The unit is operated in the following way: The reactants (see Table 5 for mixed acid compn) are introduced thru inlets (4) and (5), mixed with the help of turbine (8) and circulated thru pipe system (1), (3) and (6), chemical reaction and physical exchange being simultaneously effected. They are continuously transported to the separator in the form of an emulsion. In the separator the components are separated, the light component (nitro compounds) rising to the surface and flowing off continuously thru (12). The heavier spent acid sinks to the bottom and is removed continuously thru (13). In the area between the separated components the partly separated emulsion is withdrawn and led to the mixing part of the reactor. This transport is possible because the level of the liq in the separator thru leg (2) is higher than in leg (1). The rate of feed of partly separated emulsion can be regulated by means of valve (17)

If eighteen nitrating units are used, the compn of the nitrating mixts and the temp during the process will be as shown in Table 5. The multiple unit arrangement is shown in Fig 10

Table 5

Nitrators Nos.	Composition of nitrating mixtures, %			Temperature °C
	HNO_3	H_2SO_4	H_2O	
1–3	0.9	89.2	9.9	65
4–6	3.0	90.1	6.9	75
7–9	7.9	87.8	4.3	80
10–12	7.5	89.8	2.7	85
13–15	7.5	91.4	1.1	90
16–18	7.7	91.8	0.5	90

The yield of TNT is as high as 97–99% of theory

If an unfractionated mixt of the mononitrotoluene isomers is used (ie, the product of straight nitration of toluene), TNT with a mp of 78.7° is produced. If the starting material is free from m-nitrotoluene, TNT with a mp of 80.6° is claimed

Prime (Ref 73) describes a seven-stage continuous TNT nitrator that has been in operation since 1963. It is based on a joint design by CIL and AB Chematur and is claimed to give yields consistently above 87%. Each nitration stage consists of an agitated U-shaped vessel with the organic phase flowing counter-current to the nitrating acid (similar to the flow sheet in Fig

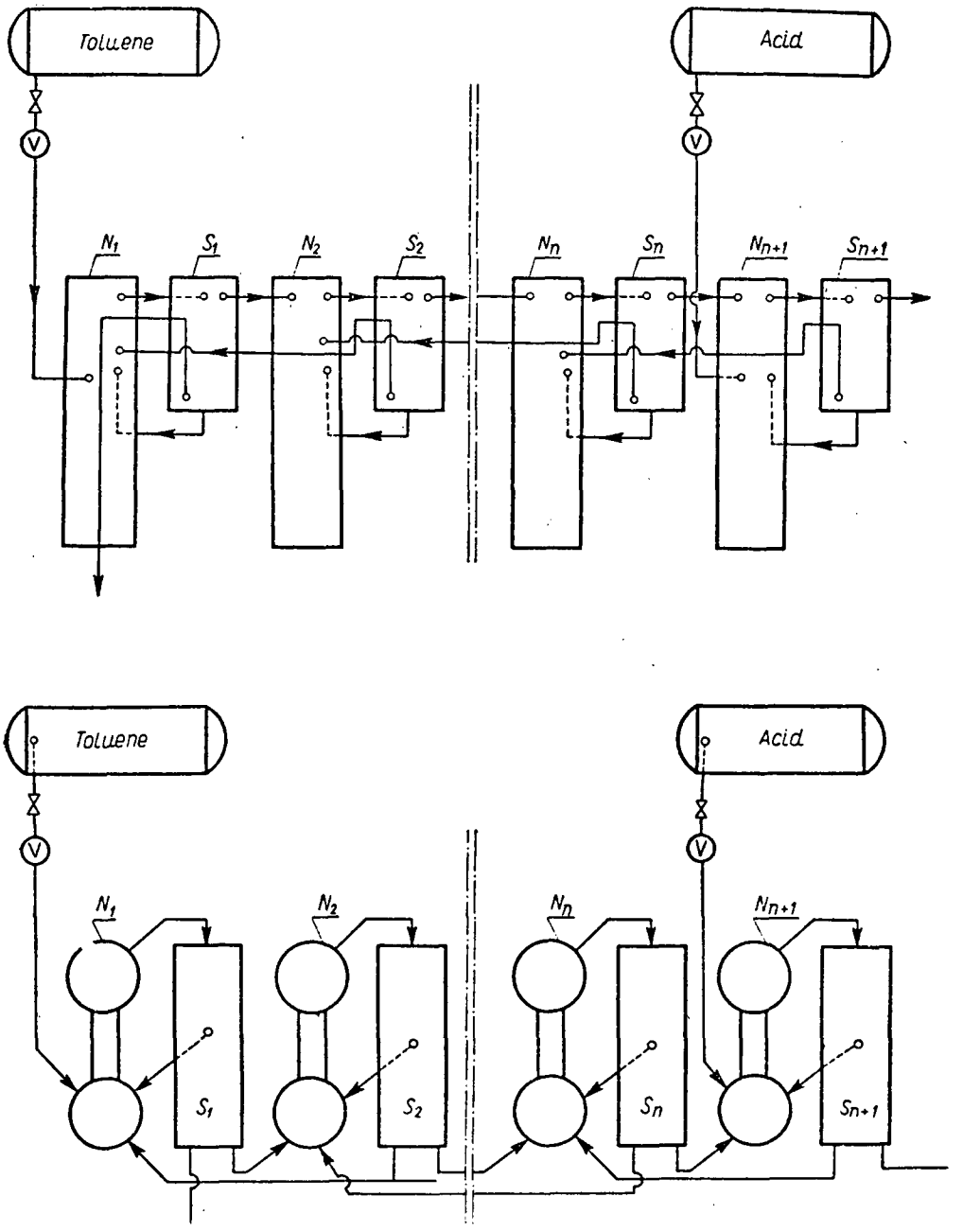


Fig 10 Diagram of a system of nitrators (N) and separators (S) in the Chematur method of continuous manufacture of TNT (Ref 42)

10). Most of the nitrated product is in the form of an emulsion and consequently is much safer to handle. The toluene that enters stage 1 leaves stage 7 as crude TNT, while the strong acid that enters stage 7 comes out as weak acid in stage 1. Man-power requirements are kept to a minimum even for 10 million pounds/year production

Hercules Continuous Process: Kouba et al (Ref 60) describe a novel tubular nitration procedure and app by which toluene is nitrated in two stages to form trinitrotoluene. In the first stage of nitration according to this invention, toluene is partially nitrated to an average nitrogen content between about 14.5% and about 16.5%, and in the second stage of nitration partially nitrated toluene is further nitrated to form trinitrotoluene

They claim that in substantially all of the prior art processes, the operation is really a modified batch process in that high hold-up vessel-type nitrators are employed. Moreover, extensive circulation, recirculation, and a relatively long residence time of the reaction mixt in the nitrating zone are characteristics of a majority of the previously proposed methods, and such features are inherently undesirable because they favor degradative side reactions, which occur at all stages of the nitration of toluene to trinitrotoluene, and particularly in the final stage

Advantages claimed for the Hercules process are: (1) minimization of the amount of nitrated material in the process at any time, (2) rapid nitration with a minimum of side reactions, (3) simplicity of apparatus and equipment, and (4) process is easily controlled

The essentials of the process are described by: "(a) continuously feeding a stream of toluene thru a tubular path to a tubular reaction zone, (b) simultaneously and continuously feeding a stream of nitrating acid containing between about 60% and about 85% sulfuric acid, between about 10% and about 30% nitric acid, and between about 3% and about 16% water by weight on a contaminant free basis thru a second tubular path to the tubular reaction zone, (c) impinging the separate streams of toluene and nitrating acid upon each other to form a reaction mixture stream in the tubular reaction, (d) continuously advancing the resultant reaction mixture stream thru the tubular reaction zone while regulating the temperature of the reaction mixture stream between about 40°C and about 140°C until the toluene has been partially nitrated to an average nitrogen content between about 14.5% and about 16.5% by weight, and (e) continuously discharging the reaction mixture stream into a separating zone and there separating spent nitrating acid from partially nitrated toluene having an average nitrogen content between about 14.5% and about 16.5% by weight. The above combination of process steps (a) to (e), inclusive, constitutes the first stage of nitration. The partially nitrated toluene product obtained in the first stage of nitration is composed substantially of dinitrotoluene, with relatively minor amounts of mononitrotoluene and trinitrotoluene. It is quite similar in composition to the product heretofore known in the art as "Bi-Oil", employed as an explosive ingredient in various high explosive formulas, and has been found to be a satisfactory equivalent to Bi-Oil as a high-explosive ingredient

However, for trinitrotoluene manufacture, the partially nitrated toluene is then subjected to a second stage of nitration by (f) continuously feeding a stream of the separated partially nitrated toluene product from step (e) at a temperature above its melting point and under pressure thru a tubular path to a high temperature tubular reaction zone maintained at a temperature between about 90°C and about 140°C, (g) simultaneously and continuously feeding a stream of trinitration acid (60–95% H_2SO_4 and 5–40% HNO_3) under pressure thru a second tubular path to the high temperature tubular reaction zone, (h) impinging these separate streams upon each other under pressure in the high temperature reaction zone, (i) continuously advancing the resultant reaction mixture stream under pressure thru the high temperature tubular reaction zone until substantially all of the partially nitrated toluene product has been nitrated to trinitrotoluene, (j) continuously advancing the reaction mixture stream under pressure thru a tubular cooling zone to cool it below about 100°C, and (k) thereafter separating trinitrotoluene from spent trinitration acid, the pressure in step (i) being sufficient to prevent any substantial vaporization of nitric acid during the nitration reaction"

In actual practice the temp in the region of the converging streams of the second stage reactor is kept between 90 and 120°, and the rest of the tubular reactor between 110 and 140°. In both stages, turbulent flow of the impinging streams is very desirable. The spent acid of the second stage, upon separation of the TNT, is fortified with aq nitric acid and is reused as the nitrating acid for the first stage

An important characteristic of this process is that there are no moving parts in either the first-stage or second-stage tubular reactors. "Turbulent flow is relied upon for effectuating intimate dispersion of toluene in first-stage nitrating acid and for effectuating intimate dispersion of partially nitrated toluene and anhydrous trinitrating acid in second-stage nitration, and for maintaining the respective reaction mixtures in emulsified form in their respective tubular reactors. The rates of flow of the reactant feed streams of toluene and first-stage nitrating acid in first-stage nitration and of partially nitrated toluene and anhydrous trinitrating acid in second-stage nitration are regulated so that upon impingement upon each other, they form turbulent reaction mixtures in the respective tubular reactors. No further mixing is required. The first-stage nitration reaction is highly exothermic, commencing immediately upon mixing the toluene with the first-stage nitrating acid and is very rapid, being substantially complete within a matter of 10 seconds or less under the preferred conditions of the invention, and seldom, if ever, requiring any longer than 60 seconds. The second-stage nitration reaction is somewhat slower than first-stage nitration, but is nevertheless quite rapid in comparison to prior art methods, being substantially complete within a matter of from about two to six minutes under the preferred conditions of the invention, and seldom, if ever, requiring longer than about 12 to 15 minutes"

It is claimed (Ref 60) that separation of product and MA in both first and second stages can be accomplished by gravity or by centrifugal separators

The Hercules continuous TNT process is the basis for three continuous TNT lines which went into operation at the Radford Army Ammunition Plant in Virginia in 1968. The lines were designed by CIL and represent improvements over their plants in Canada, which in turn are improvements over the original AB Chematur process. Details of the actual *Radford Continuous TNT Process* are described in Refs 86a & 90a

The most recent UK Royal Ordnance Factory (ROF) continuous process for the manuf of TNT is described by Thomas (Ref 90b). It uses "a novel method of achieving continuous countercurrent contacting between heavy and light phases in the trinitration section and some of the washing stages". The plant is also designed to operate based on the use of 96–100% sulfuric acid in the trinitration stage instead of the oleum used at Radford

TNT Purification.

Crude TNT produced by either batch or continuous methods requires purification. The ultimate objective of TNT purification is to remove all those products which are more reactive than TNT itself (isomers, nitrocresols, nitrobenzoic acids, etc), or which can easily give oily exudation products, such as isomers or lower nitrated substances

The oil exudation product (TNT-oil) is very undesirable for the following reasons:

(a) Exudation produces porosity of the TNT charge and reduces its density. This reduces its expl effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and premature expln

(b) The oily products can penetrate into the threaded parts of the shell and form "fire channels" thru which the ignition of proplnt can ignite the charge

(c) The oily products can penetrate into the detonating fuze if the explosive of the fuze is unprotected by a metal envelope, and reduce the detonating power of the fuze

In the purification of TNT the following impurities have to be removed: (1) traces of nitric and sulfuric acids; (2) unsymmetrical isomers; (3) products of incomplete nitration; (4) by-products (tetranitromethane, trinitrobenzene, nitrobenzoic acids, nitrocresols, etc)

The first purification step is thorough washing of the TNT with hot water, in washing tanks or by emulsification, followed by neutralization with Na bicarbonate soln. This removes residual acids

Before WWI neutralized TNT was further purified by crystn from solvents such as mixts of alc and benz. This method added to production cost and increased the fire and expln hazard due to the presence of flammable vapors. Solvent crystn of TNT is no longer used

Modern purification methods employ Na sulfite solns to react with the β and γ -TNT isomers to form water soluble substances which can then be washed out of the desired α-TNT. However, these water washes form a blood-red soln – the bothersome "red-water" of TNT plants. Modern methods of disposing of "red-water" will be described in Section X

Nitromethane. The industrial method of producing NM is based on a vapor phase reaction of propane and 70% nitric acid. The reaction is carried out at around 410° and 115–175psi press. In essence the production of NM involves five steps: 1) nitration; 2) product recovery; 3) product purification; 4) product separation; 5) reactants recovery

According to Ref 50, nitration is carried out in an "adiabatic" nitrator in which the heat of reaction is utilized to vaporize the nitric acid. A small excess (over stoichiometric) of nitric acid is sprayed thru several nozzles into a stream of hot propane. This excess of nitric acid is kept small in order to minimize oxidative and degradative reactions. The nitrated products are cooled to condense the nitroparaffins and the chamber press is reduced to one atm. The crude products are then scrubbed with a solvent to remove some of the oxidation products. The solvent is then stripped off the crude nitroparaffins in a steam-heated column. The solvent and the oxides of nitrogen in the off gases are recycled. This keeps the yield, based on nitric acid, high – about 90 moles of nitroparaffins per 100 moles of nitric acid. The crude nitroparaffins are decanted from the water that they contain and sent to rectification. The first rectification (distn) removes any remaining low boiling oxidation products, such as ketones and aldehydes. The nitroparaffins are then treated chemically and water washed, with the wash water then removed by decantation. The final sepn is a distn in four successive stages at atm press. The first stage distills off the NM. Nitroethane, 2-nitropropane, and 1-nitropropane are recovered successively in the next three stages. The product distribution is approx 25% NM, 10% nitroethane, 40% 2-nitropropane and 25% 1-nitropropane

NG. Batch-wise production of NG is described in Vol **6**, G99–102, and continuous methods such as the Schmidt-Meissner and Biazzi processes are discussed in Vol **3**, C501–505. The Swedish injector process and the Hercules tubular nitrator will be described below, but before doing this we will discuss certain aspects of glycerin nitration that are common to both batch and continuous methods, and then contrast the main features of the batch process vs the continuous process

The usual MA for batch-wise and early continuous methods of glycerin nitration consists of 45–50% nitric acid and 50–55% sulfuric acid. The MA for the recent continuous methods contains up to 12% water and less nitric acid than above. The MA should be prepd from pure acids, and spent acids are not reused in most installations. The DVS of the MA should be kept high to avoid incompletely nitrated products which are subject to exothermic oxidation reactions. Similarly, it is imperative to maintain the proper MA-to-glycerine ratio. If the amount of glycerine gets to be too high, exothermic decompn and oxidation reactions can occur and temp control becomes most difficult. The proper MA-to-glycerine weight ratio ranges from 5.5 to 6.5

Effective temp control is an absolute necessity. Small scale nitration can be carried out at temps as high as 40°, but NG yield is reduced at these temps. Low temps favor yield but increase nitration time. In the older methods, temps in the 15–25° range are usually maintained

In the USA it is common practice to nitrate mixts of glycol and glycerine. These mixed nitrations are essentially similar to pure glycerine nitrations and require no further comment

The really great advantage of the continuous methods over the batch methods is the much smaller accumulation of NG in any given plant location in the former process. Additional advantages accrue from faster production, better control, lower labor costs, etc. Klassen and Humphrys (Ref 40) compare the Biazzi con-

Table 6

	Nitrators producing 1200 kg nitroglycerine/hr	
	Biazzi	batch
Nitrator capacity, l.	125	305
Total cooling surface, m^2	10	23
Unit cooling surface, m^2/l.	0.08	0.0075
Time in nitrator, min	10	50
Heat transfer, kcal/m^2°C hr	800	365
Brine inlet temp., °C	−5	−25 to −20
Nitroglycerine in nitrator (at 4.7:1 acid ratio), kg	80	1590
	Raw materials and labour per 100 kg dry nitroglycerine	
Glycerine (and ethylene glycol 50:50), kg	42.2	42.2
Sulphuric acid (100%), kg	101	99
Nitric acid (100%), kg	104	99
Sodium carbonate, kg	6.0	1.7
Operating, labour-man-hours	0.04	0.18
Maintenance, labour-man-hours	0.01	0.08

tinuous process with batch nitrations. In Table 6 we give a more recent comparison given by Urbański (Ref 75, p114)

In a recent review of NG manufacture, Pennie (Ref 66) claims that there are no overwhelming advantages to scrapping operational batch processes and installing continuous equipment. However, in building a new plant, he recommends the installation of a continuous process

The Swedish *Nobel Aktiebolaget* process for nitrating glycerine consists of an injector nitrator and a centrifugal separator for separating NG from spent acid. As described in Refs 47, 57 and 75, p 114, the flow of nitrating acid thru an injector sucks in the correct amount of glycerine mixed with air. NG forms an emulsion with the spent acid. After cooling, the emulsion flows into a centrifuge. Here NG is separated from the spent acid and transferred to the washing house

The main features of this process, which has been in industrial use since 1956, are:

Mixed acid is a mixt of the conventional 50/50 NG-MA and spent acid, such that it contains about 27% nitric acid and 10% water or about 1.7 parts of spent acid to 1 part of MA

Glycerine flow into the injector is controlled by the acid flow (much like the suction in a water aspirator). Thus, if the acid flow is reduced by some equipment malfunctioning the glycerine flow is automatically decreased

A novel feature of this process is the *high temp* at which it operates, namely 45–50°. This is achieved by preheating the glycerine (or glycerine-glycol mixture) to this temp before it enters the injector and cooling the input acid to 0°. The heat of reaction then maintains the fluid temp in the injector in the 45–50° range. Automatic controls give warning or shut down the operation if the temp rises a few degrees above the normal range

The NG-acid emulsion enters a *cooling system* immediately after leaving the injector and the temp of 45–50° is maintained for only about half a second. During the next 80–90 secs the mixt is cooled to 15°. In the following 30 secs the NG is separated from the spent acid

A continuous centrifugal separator separates NG from the spent acid. The centrifuge operates at 3200 rpm. For a unit with a capacity of 2500ℓ/hr the quantity of NG in the separator bowl during operation is only 3.5 kg. The separated acid-free NG is emulsified immediately by a wash-jet to form a non-expl mixt and is removed continuously from the separator house to the NG wash-and-weigh house

The spent acid from the separator contains a small amount of emulsified NG. The portion of spent acid which is to be used to prepare fresh mixed acid need not be separated further, since when nitrating acid is added the emulsified oil redissolves and returns to the cycle

A flow sheet of the process, as given by Urbański (Ref 75, his Fig 53), is shown below

According to Urbański: "To start the nitration, current from the switch (18) is applied to the electromagnet (6), which closes the air inlet to the injector. Mixed acid is admitted by opening the valve under the acid rotameter (4). The injector now comes into operation. The manometer (13) must show full vacuum. The needle valve (7) is then opened and the vacuum adjusted to about 300mm Hg. The glycerine-glycol mixture is sucked in thru the rotameter (3) to the injector from (2)

The exact setting of the acid and glycerine rotameters is adjusted by means of the corresponding valves and the nitrating temperature is checked. It should be 40–45°C higher than the temperature of the incoming mixed acid

Through the inspection glass, nitroglycerine can be seen leaving the separator within about 2 mins after nitration has begun

To stop the process the circuit through the electromagnet (6) is broken at (18), so that air rushes into the injector and the glycerine in the pipe and in rotameter (3) runs back to (2). Mixed acid should be allowed to flow for 1 min in order to flush the pipes and cooling system. The separator is stopped about 10 min later and empties automatically

The contents of the separator are collected in a special small separation vessel. The emulsified explosive oil is separated and delivered

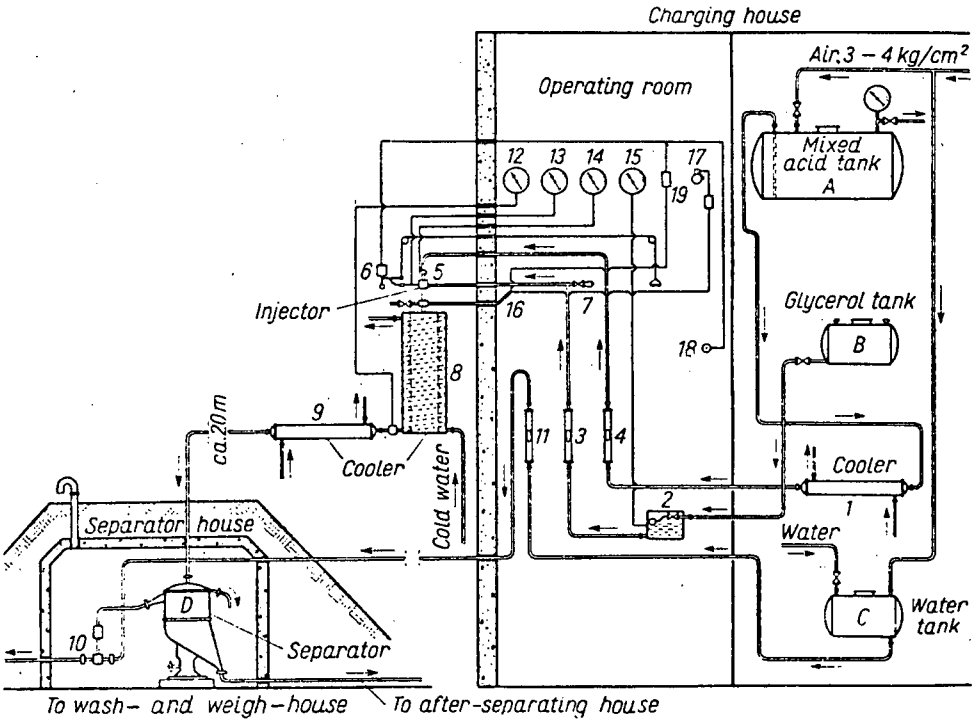


FIG. 53. Flow-sheet of injector nitration of glycerine and centrifugal separation of nitroglycerine at Gyttorp (Nitroglycerin Aktiebolaget Gyttorp, Sweden): *1* and *9*—tubular coolers (−12°C), *2*—glycerine suction tank with a constant level, *3*—glycerine rotameter, *4*—acid rotameter, *5*—injector-nitrator, *6*—electromagnet, *7*—needle valve for the air inlet to the injector, *8*—cold water cooler, *10*—injector to supply nitroglycerine-water emulsion, *11*—rotameter supplying water to *10,12,14,15*—thermometers, *13*—vacuum-meter, *16*—glass thermometer, *17*—alarm bell, *18*—current switch, *19*—relay to electromagnet *6*.

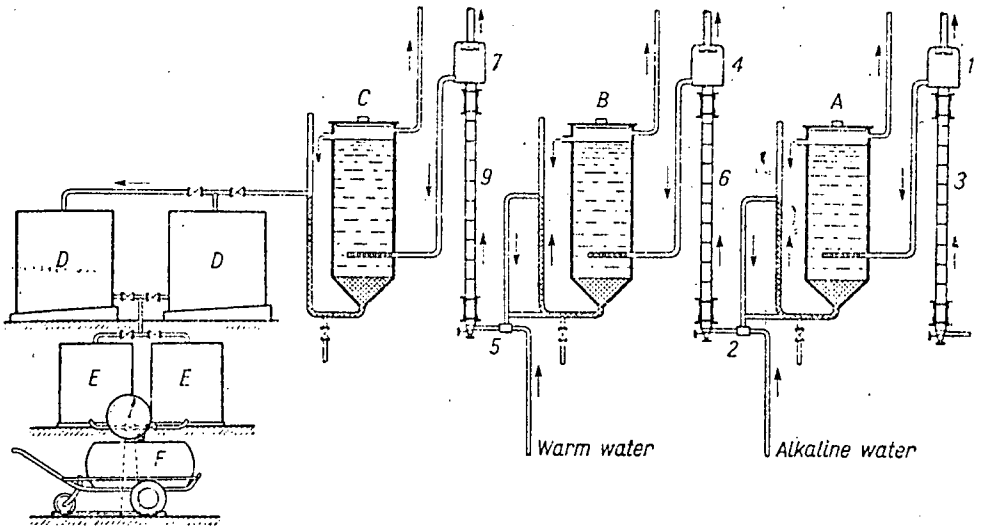


FIG. 59. Flow-sheet of washing nitroglycerine at Gyttorp: *A*—separator of acid wash-water, *B*—separator of alkaline wash-water, *C*—separator of warm wash-water, *D*—storage tanks, with wash-equipment, *E*—storage tanks with refrigerating coils, *F*—nitroglycerine waggon on a balance, *1*, *4*, *7*—air separators, *2*, *5*—injectors, *3*, *6*, *9*—wash-columns.

direct to the wash jet (10). After rinsing with separated spent acid, the separator is ready to be restarted"

Urbański describes the washing procedure as follows:

"Continuous washing of nitroglycerine is carried out in three wash columns: (3), (6), and (9) (his Fig 59)"

Operating characteristics of the Gyttorp injection nitrator are: production: 500–650kg NG/hr; acid consumption: 2600–3400kg/hr; glycerine consumption: 216–281kg/hr; and the yield of NG-nitroglycol mixt is 231–232.5kg of expl oil, ie, 93.9–94.5% of theoretical

Hercules Tubular Nitrator. Like the Gyttorp injector nitrator, the Hercules tubular nitrator involves no mechanical mixing devices and thus minimizes impact and friction hazards during nitration. It also operates on a very short nitration cycle, thus minimizing side reactions and producing exceptionally pure products. Further advantages of the tubular nitrator (again similar to the injector process) are minimum amounts of product in process at any time, positive control of the reagents and relatively inexpensive equipment. McKinney's basic patent (Ref 59) describes the process as follows:

"Generally described, the continuous manufacture of explosive liquid nitric acid esters of polyhydric alcohols in accordance with this invention comprises continuously feeding a stream of polyhydric alcohol through a tubular path to a tubular reaction zone, simultaneously and continuously feeding a stream of precooled nitrating acid through a second tubular path to the tubular reaction zone, causing the separate streams of polyhydric alcohol and precooled nitrating acid to impinge upon each other at sufficient flow rates to form a turbulent reaction mixture stream in the tubular reaction zone, continuously advancing the resultant reaction mixture stream through the tubular reaction zone at a flow rate corresponding to a Reynolds Number of at least about 1000 until substantially all of the polyhydric alcohol has reacted with the nitrating acid to form explosive liquid nitric acid ester, and thereafter separating explosive liquid nitric acid ester of polyhydric alcohol from spent nitrating acid

In a preferred embodiment of the invention, the tubular reaction zone is uncooled and the temperature of the reaction mixture in the tubular reaction zone is controlled within safe operating limits by regulating the temperature

of the precooled nitrating acid and by regulating the proportions, respectively, of the nitrating acid and of the polyhydric alcohol which are mixed together by impingement to form the reaction mixture. Operating with an uncooled tubular reaction zone promotes a more rapid reaction which is desirable, and in fact is an important advantage of the present invention. Moreover, although not necessary in practicing this invention, it has been found desirable to cool the mixture of explosive liquid nitric acid ester and spent nitrating acid upon completion of the nitration reaction and prior to separation, since this promotes a more complete recovery of the product. While cooling can be effected in a separate vessel following discharge of the reaction mixture from the tubular reaction zone, such cooling is more conveniently and efficiently accomplished in a tubular cooling zone forming an extension of the tubular reaction zone. Preferably, but not necessarily, the reaction mixture stream is advanced through the tubular reaction zone, and the tubular cooling zone when employed, at a flow rate corresponding to a Reynolds Number of at least about 2,100 and sufficient to maintain turbulent flow in the reaction mixture"

A simplified flow sheet (taken from the above Patent) is shown below (his Fig 2), and the

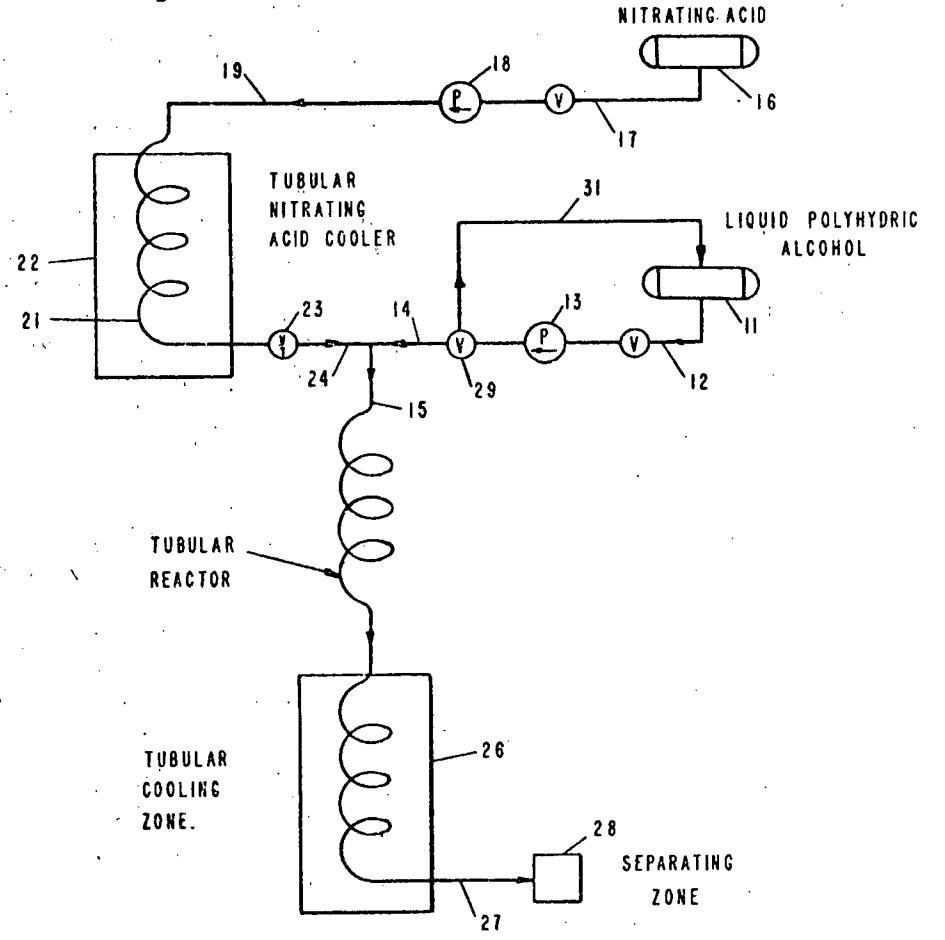


FIG. 1

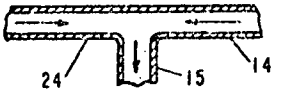


FIG. 2

operation is described as follows:

"Liquid polyhydric alcohol from supply tank 11 via valved line 12 is fed through metering pump 13 in predetermined proportions via line 14 to tubular reactor 15. Simultaneously, nitrating acid from supply tank 16 via valved line 17 is fed through pump 18 in predetermined proportions via line 19, tubular nitrating acid cooling coil 21, and valved line 24 to tubular reactor 15. 22 is a conventional heat exchange means such as a refrigerating brine bath or the like. Although it is convenient to cool the nitrating acid as illustrated, the invention is not limited in this respect. The only requirement is that the nitrating acid should be cooled before it enters the tubular reaction zone. Accordingly, therefore, cooling means can be employed to cool the nitrating acid at any desirable and convenient point along the path of flow of nitrating acid in the system before the nitrating acid reaches the reaction zone. For example, the nitrating acid can be cooled at supply tank 16, or even at some point before the acid reaches supply tank 16. Valve 23 in line 24 is a throttle valve for regulating the flow of nitrating acid when employing a centrifugal pump. Valve 23 becomes unnecessary when a metering pump or similar constant feed means is employed instead of a centrifugal pump

Valve 29 in line 14 is a quick opening by-pass valve which is normally closed. However, in case of an emergency shutdown, this valve can be instantly opened to shut off the supply of alcohol to the reaction zone and return the alcohol stream via line 31 to alcohol supply tank 11. Such a quick opening by-pass valve normally is not employed in the nitrating acid line, since in case of an emergency shutdown, nitrating acid is employed to sweep out the tubular reactor

It will be seen from the drawing that feed lines 14 and 24 converge and junction with tubular reactor 15 at one end thereof, and in the embodiment illustrated, the two feed lines and the tubular reactor form a simple T tube section, free of moving parts, obstruction, or constrictions, as illustrated in Fig 2. The separate streams of polyhydric alcohol and precooled nitrating acid thus converge and impinge upon each other at the point where the two feed lines junction with the tubular reactor"

The nitrating acid for this process contains 18–40% nitric acid, 45–70% sulfuric acid and 11–17% water. The preferred acid-to-glycerine (or glycerine-glycol mixture) ratio is 10 to 20 parts of acid per part of glycerine. Stow, in a later improvement patent (Ref 67) claims an improved mixing "tee" and a more automated continuous cyclic process. He specifies:

"In the preferred practice of this invention, the reaction mixture, upon completion of the nitration reaction and containing explosive liquid nitric acid ester dispersed in spent nitrating acid, is discharged into a centrifugal separating zone in which spent nitrating acid is continuously separated from acid-impure explosive liquid nitric acid ester. Centrifugal separation has a distinct advantage over separation by settling in that only a very small amount of explosive ester is present in concentrated form while in an impure unstable state. Also, during purification of the impure ester it is preferred to centrifugally separate explosive liquid nitric acid ester from washing liquid in order to minimize the quantity of explosive ester in concentrated form at any one time or point during purification"

A further benefit claimed for this process is:

"To achieve the maximum benefits from the present invention, it is preferred to centrifugally separate explosive liquid nitric acid ester from its emulsion in washing liquid in the one or more stages of purification employed in this invention, for by centrifugal separation the amount of explosive liquid nitric acid ester accumulated in concentrated form at any point in the system is reduced to the absolute minimum, particularly since it is preferred to employ the shortest practical lengths of transport pipes between the separators and the injection mixing zones, during which the explosive liquid nitric acid ester is in concentrated form. Since the explosive ester is in emulsified form in washing liquid during transport from the injection mixing zones to the separating zones, there is relatively no danger of detonation. This is because this invention contemplates the use of at least about 2 parts by weight of washing liquid per part of explosive liquid nitric acid ester, and preferably at least about 3 parts washing liquid per part of explosive ester. At 2 parts washing liquid per part of explosive ester, the emulsions of explosive ester in washing liquid are highly insensitive to shock,

and at ratios of 3:1 or more of washing liquid, such emulsions cannot be detonated."

The centrifugal separator used in conjunction with the tubular nitrator is described in two patents (Refs 53 & 64)

NC. Although the nitration of cellulose has been described quite extensively in Vol **2**, C100–119, certain aspects of the technical background for its manufacture need amplification

Commercial NC is not a single chemical entity. Indeed, as shown in Vol **2**, C103-L, there are a variety of grades of NC, usually characterized by their nitrogen content. The chemical species that constitute these grades are partially nitrated products and mixts of the following compounds:

cellulose trinitrate	$C_6H_7O_2(ONO_2)_3$	14.15%N
cellulose dinitrate	$C_6H_8O_3(ONO_2)_2$	11.11%N
cellulose mononitrate	$C_6H_9O_4(ONO_2)$	6.76%N

Thus every NC is composed of anhydroglucose rings with three nitrate groups attached (14.15% N) and of non-nitrated or partially nitrated anhydroglucose rings. Dalmon (Ref 22) succeeded in obtaining almost complete trinitration (14.12% N) by treating cellulose with gaseous N_2O_5

Many studies, primarily via X-ray patterns, have led to the following picture of NC of varying degree of nitration:

(1) Those containing less than 7.5% N show a fiber character and give no X-ray diffraction indicating nitration, but only the pattern of mercerized cellulose

(2) Those containing between 7.5 and 10.5% N are more or less disintegrated, yielding very diffuse diffractions, apparently due in part to very small crystalline elements of mercerized cellulose

(3) Those of more than 10.5% N give diagrams which indicate the crystalline character of the structure. Apparent crystallinity increases as the nitrogen content increases until eventually a critical point at 12.8% is reached when the sharply defined diagram characteristic of cellulose trinitrate makes its appearance. On the basis of these expts the following picture of cellulose nitration emerges. In first stage of nitration (stage I) the nitric acid penetrates the whole of the cellulose structure (otherwise it could not be mercerized), with nitration occurring only in the disordered amorphous regions (stage II). At the same time the micellar arrangement is almost entirely broken down

Swelling and breakdown of the micellar arrangement takes place in the final stage of nitration (stage III), but to a diminished extent as the acid concn increases. The number of nitrate groups increases with acid concn, but in a random manner, so that crystalline arrangement is at first hindered. It is facilitated as the nitrate groups accumulate, and when 12.8% N is reached there are so many ONO_2 groups that an orderly arrangement of chains becomes possible and there is a sudden appearance of the trinitrate structure

The amorphous part of cellulose is regarded as more reactive than the crystalline part. When the crystalline part enters into a reaction, as for instance in swelling or nitrating, its structure can undergo certain changes, as swelling causes the micelle chains to expand. An outline of the process suggested by Spurlin (Ref 24a) indicating how the micelles react with an esterifying agent is given in Fig 11, which suggests how the reagent attacks one end of the micelle and a gradual sliding apart of the chain ensues

The grades of NC that are important to the military and commercial explosives industry are *guncotton* (13.45% N) and *dynamite grade NC* (12.2% N). The former is primarily used in the manufacture of double-base and high energy propInts while the latter is an ingredient of gelatin and semi-gelatin Dynamites. As shown in Fig 12, the nitrogen content of NC can be controlled by the amount of water in the nitrating acid. However, note that guncotton can be obtained with mixed acids having a fairly wide range of water content (at the plateau in the curve). Also note that a "dry" (low water content) MA produces a low nitrogen-content NC

The above conclusions were also reached in an earlier study by Schiemann & Kühne (Ref 21). Their results, including spent acid compositions, are summarized in Table 7

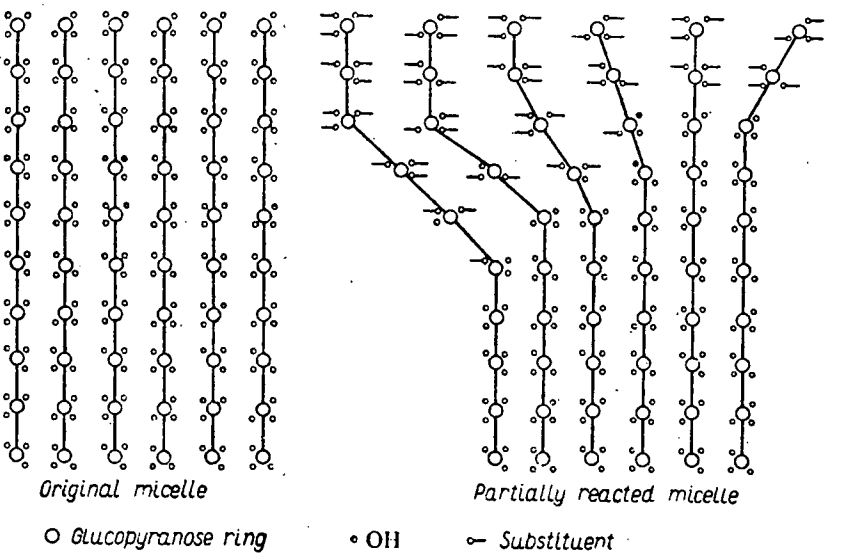


Fig 11 Diagram of esterification of cellulose (Spurlin, Ref 24a)

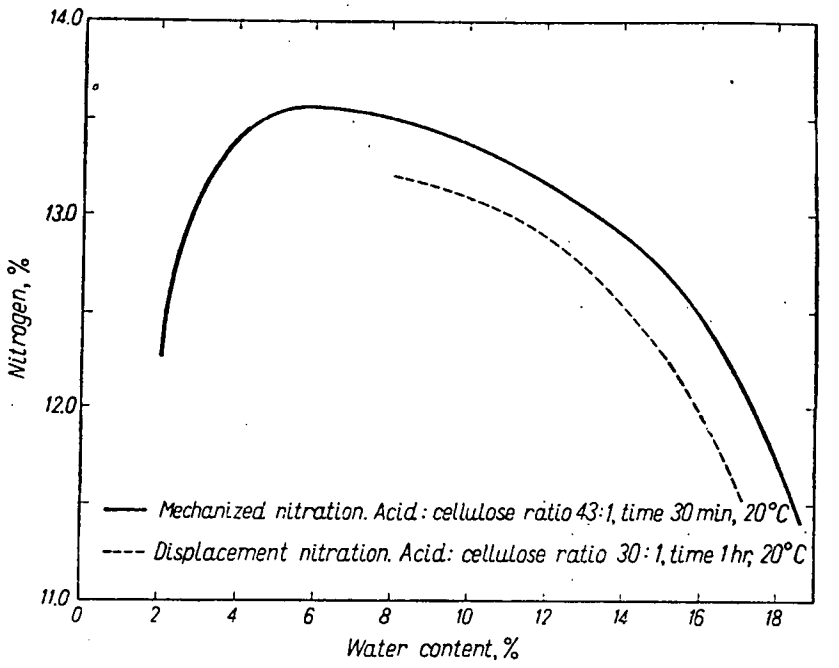


Fig 12 Change of nitrogen content in nitrocellulose as a function of water concentration in nitrating mixtures according to Miles (Ref 44)

Table 7

CHANGE IN THE MIXED ACID RATIO AFTER NITRATION

Composition of the nitrating mixture, %			Composition of the spent acid, %			Cellulose to acid ratio	Nitrogen content of nitrocellulose, %
HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4	H_2O		
24.78	70.82	5.40	20.69	71.29	8.02		
23.05	68.07	8.88	18.20	69.56	12.24	1:50	13.0–13.5
21.09	68.52	10.19	16.91	69.10	13.99		
22.65	76.50	0.85	21.80	76.71	1.49		
21.73	73.15	5.12	20.29	74.37	5.34	1:80	12.9–13.5
20.70	69.45	9.78	19.58	70.12	10.30		

A concise way of expressing the effect of MA compn on the nitrogen content of the product NC is the so-called Sapozhnikov diagram. Such a diagram, according to Miles & Milborn (Ref 16), is shown in Fig 13

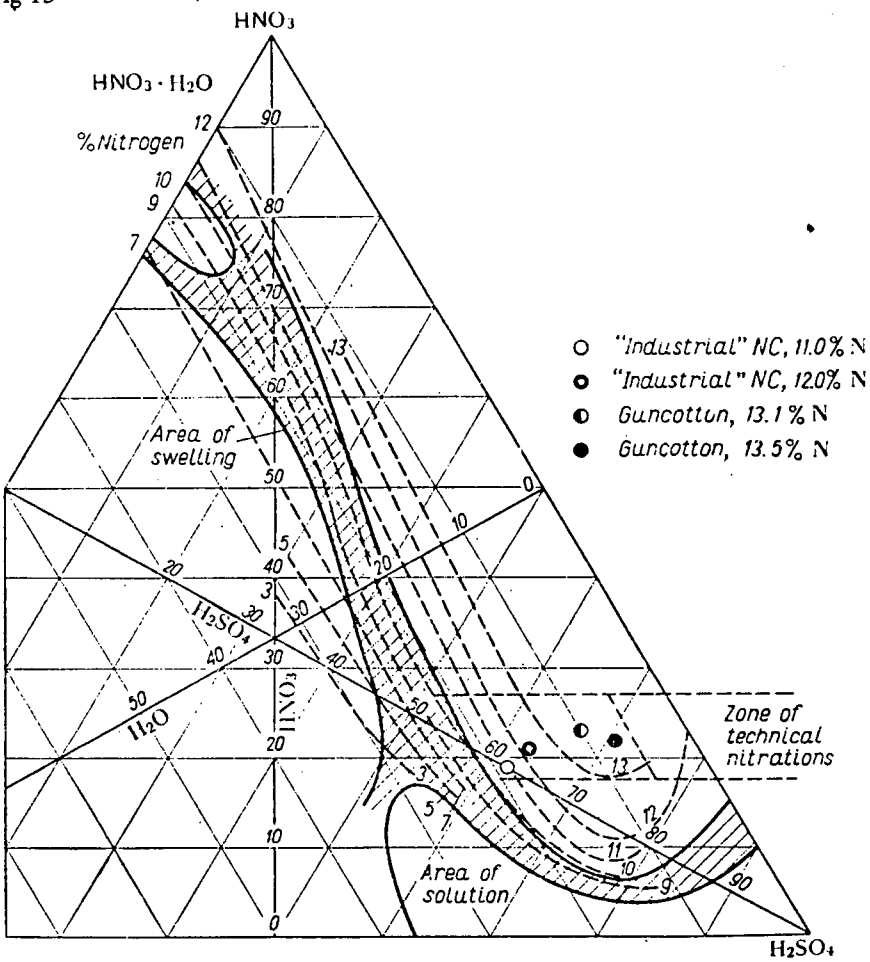


Fig 13 Sapozhnikov diagram modified by Miles and Milbourn. Composition of acid mixtures in weight %

Treating NC with a mixed acid capable of producing cellulose nitrate with a lower nitrogen value results in a partial denitration of the cellulose. On the other hand, NC immersed in a mixt of concd acids undergoes further nitration. Berl et al (Ref 18a) have reported that three samples of NC of different nitrogen content, 10.9, 12.7, and 13.5%, respectively, when drowned in two nitrating acids, and immersed for a sufficiently long time, showed the same percentage of nitrogen for each of the three samples of NC immersed in any one of the mixed acids

Extensive research has been carried out by Wilson and Miles (reported in Ref 44) on the denitration of NC by the mixed acid. They investigated the influence of acids that varied in chemical compn within wide limits (eg, the content of nitric acid varied from 10 to 70%). Several noteworthy rules were formulated. Thus, they found that the higher the proportion of nitric acid, the more rapid the rate of denitration. Sulfuric acid alone, or in a mixt containing a small amount of nitric acid (eg, 6% HNO_3 and 68% of H_2SO_4), has a very weak denitrating effect. The most rapid denitration occurs in the presence of acids able to cause cellulose to swell. The higher the nitrogen content of the substance undergoing denitration, the more rapidly denitrating proceeds. Raising the temp causes the rate of denitration to increase appreciably. The following example is given: nitrocotton of 12.2% N was denitrated down to 10.7% N at 20°C for 5hrs in acid composed of 69% HNO_3 and 19% H_2O, while at 60°C, denitration to 10.0% N was accomplished within 3 mins

Urbański (Ref 75, p 340) summarizes the nitration and denitration processes as follows:

"(1) A portion of the cellulose brought into contact with fresh mixed acid is nitrated to a high nitrogen content. The acid is diluted by water produced during the reaction

(2) Another portion of cellulose not nitrated so as to form a higher nitrated substance, reacts to give a product containing a lower percentage of nitrogen since the mixed acid has been diluted during stage (1). Gradually further dilution of the acid takes place

(3) Higher nitrated fractions suffer hydrolysis due to the presence of the more dilute acid

Process (3) may be slow, hence under industrial conditions it may be broken off before equilibrium is established. This means that chemical reaction (3) is not completed. As a final product, a not very homogeneous nitrocotton is obtained. The higher the nitrating temperature, the more rapid the denitration process, the sooner the reaction balance is established, and hence the more uniform the product"

Miles (Ref 44) suggests the following formulae for calculating MA compositions in equilibrium with NC:

$$D_n = \frac{100-n}{31.13\frac{R}{N} - R - 1} \qquad D_w = \frac{40+w}{31.13\frac{R}{N} - R - 1},$$

where: N nitrogen content of nitrocellulose as % N,
n the nitric acid concentration in the mixed acid as % HNO_3,
w the water concentration in the mixed acid as % H_2O,
R the weight ratio of mixed acid to cellulose,
D_n the difference in the nitric acid percentage of the mixed acid before and after the nitration,
D_w the difference in the water percentage in the mixed acid before and after the nitration.

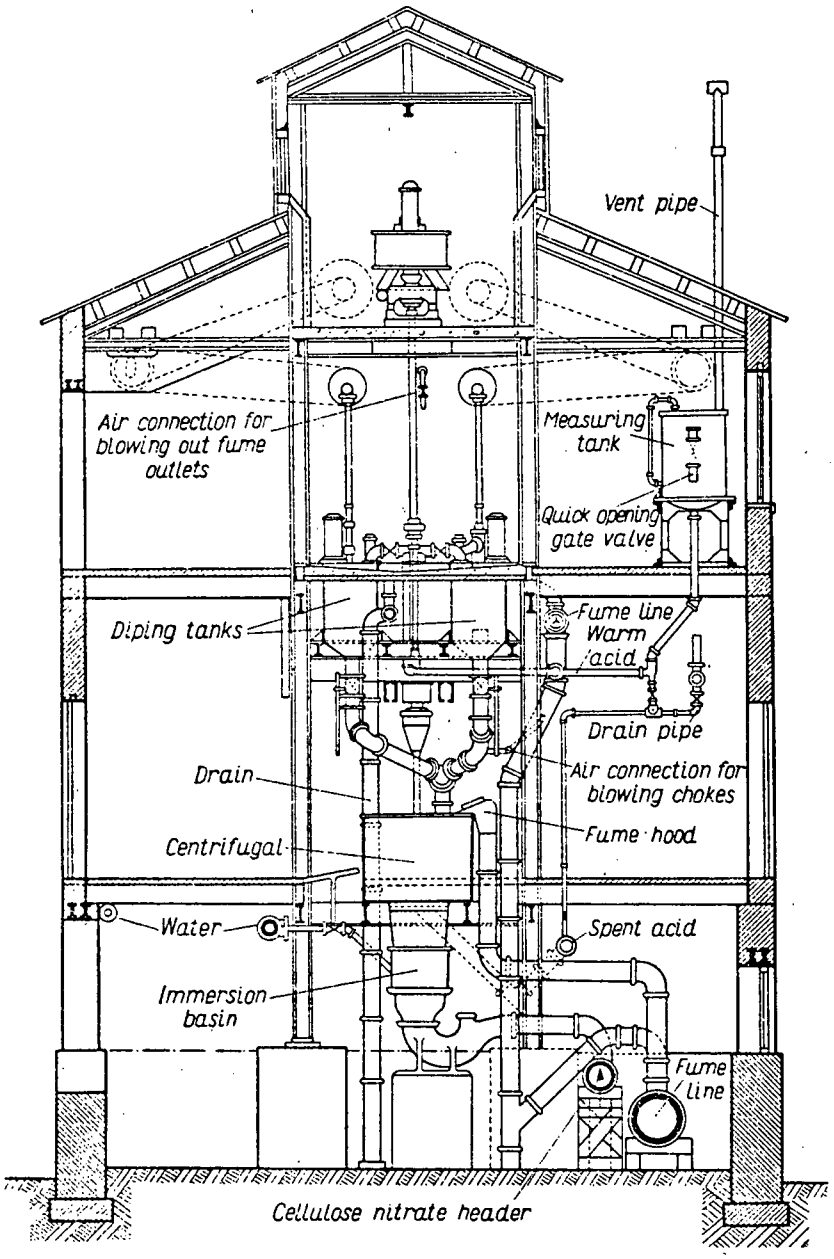


Fig 14 Diagram of a plant for nitration of cellulose in mechanical nitrators, du Pont system (according to du Pont de Nemours (Ref 13)

As already stated, the actual manufacture of NC is described in detail in Vol 2. A diagrammatic representation of the Dupont process (typical of US production practice), shown in Fig 14, complements the discussion presented in Vol 2

A continuous fully automatic nitrating process for producing NC was developed by Hercules, Inc (Ref 55a & Fig 14a)

Cellulose and mixed nitrating acid are fed continuously and simultaneously to a vessel where nitration of the cellulose takes place. After nitra-

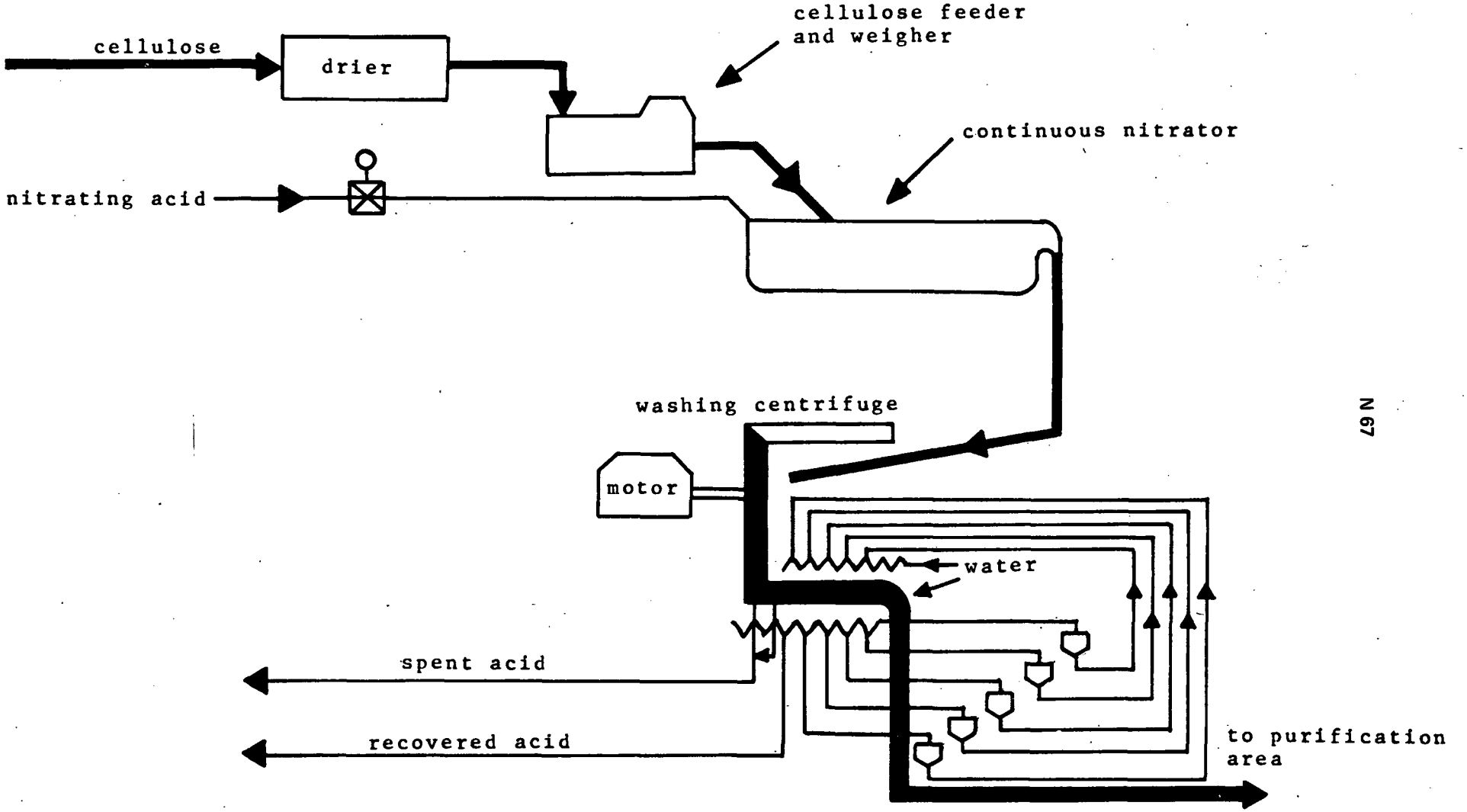
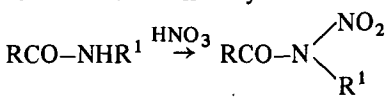


Fig 14a Flow diagram of nitration of cellulose by Hercules continuous process

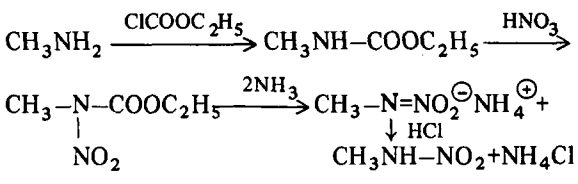
tion, the slurry of NC and spent acid is passed continuously into a centrifugal machine. This machine may be considered as divided into zones, and the NC is advanced intermittently from zone to zone. In the first zone most of the original acid from nitration is removed; in each succeeding zone the acid in the NC is displaced with weaker acid, and, finally, in the last zone with water. The operation in all zones proceeds simultaneously. The amt of water used in the final displacement, or wash, is just sufficient so that the effluent will have an acid concn suitable for the next preceding displacement, and so on until the recovered acid; ultimately leaving the system, approaches the strength of the spent acid from nitration

Hercules states that the change from batch to continuous nitration involves no change in raw materials, and no change in the nitration reaction. The product of the continuous process is identical with that of the older batch process, except that it is more uniform

Before proceeding to describe the manufacture of the *nitramines*, RDX and Tetryl, a few general remarks about the preparation of nitramines are appropriate. Nitramines can be prepared by direct nitration with anhydrous nitric acid, eg:



Where direct nitration results in degradation, a primary amine can be acylated, nitrated directly to form a secondary nitramine, which is then hydrolyzed to form the primary nitramine as exemplified in the following reaction sequence:





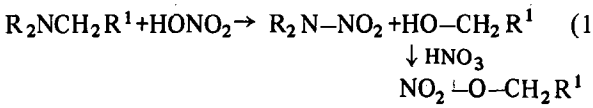
Another method of preparing nitramines is exemplified as follows:

$$RNHCl + AgNO_3 \rightarrow RNHNO_2 + AgCl$$

The formation of chloramine as an intermediate, followed by reaction with nitric acid to produce the corresponding nitramine and HOCl, may explain the catalytic action of HCl in the nitration of amines

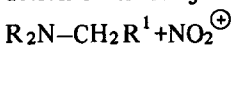
An important preparative method for nitramines is *nitrolysis* as described by Urbański (Ref 82, p 13):

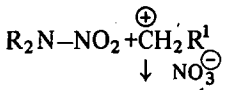
"The term 'nitrolysis' is usually applied to a nitrating mechanism in which both the rupture of the C–N bond and the formation of a nitramine occur simultaneously with the formation of an alcohol which subsequently undergoes esterification (1):



(1)

Nitrolysis may also proceed without giving rise to alcohol in accordance with Eq (2). Nevertheless, a nitric ester is formed by the possible action of the NO_3^- ion on a free alkyl cation:"

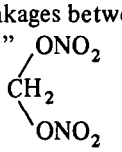




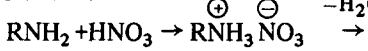
(2)

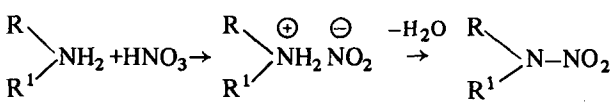
and:

"The nitration of hexamethylenetetramine, which contains the grouping $-CH_2N(NO_2)-CH_2-$ CH_2 to produce Cyclonite, is also a nitrolysis reaction. In addition to Cyclonite, a nitrate of methylene glycol is also formed as a result of the cleavage of one of the three linkages between each nitrogen and carbon atom:"



Although by our convention the following preparative method is not a nitration, we include it here for the sake of completeness, since it is used in the preparation of *Nitroguanidine* and *Nitrourea*



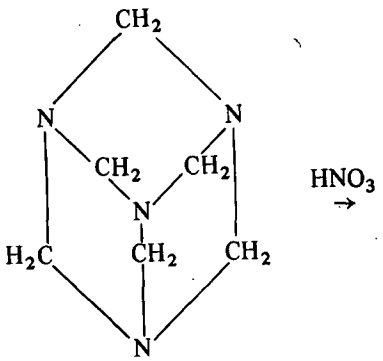


All of the above methods are described more fully in Urbański (Ref 82, pp 8–14)

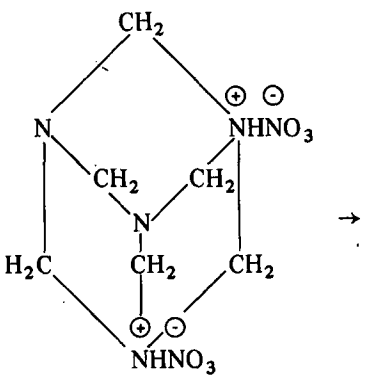
RDX (Cyclonite). The industrial prepn of RDX is discussed in Vol **3**, C612–615. As in the case of NC this discussion needs to be expanded,

particularly along the lines of presenting more details of the chemistry involved and the effects of process variables

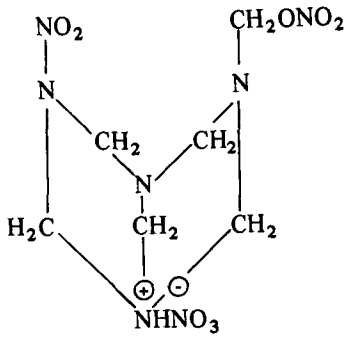
The chemistry of the prepn of RDX is highly complex and remains not fully understood. What follows is a synthesis of the views of British and Canadian investigators (Refs 37a & 41a) as summarized by Urbański (Ref 82, pp88–89). The following reactions presumably occur when hexamine is treated with nitric acid to produce RDX:



Hexamine



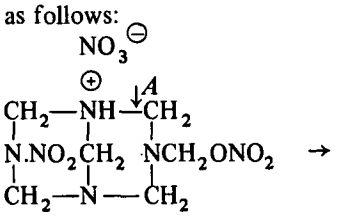
Hexamine Dinitrate



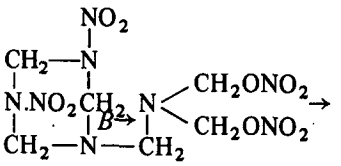
Compound I

Compound I is formed from Hexamine Dinitrate via *nitrolysis*

Further nitrolysis (with cleavage of bond A) forms a hypothetical compound (compound II) as follows:

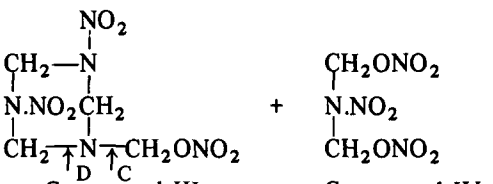


Compound I



Compound II (Hypothetical)

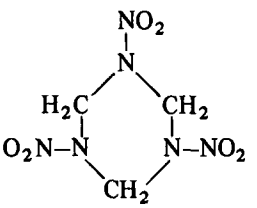
Compound II now undergoes further nitrolysis (with cleavage of bond B) to give another hypothetical material, Compound III, and a known material, Compound IV:



Compound III (Hypothetical)

Compound IV

Finally nitrolysis of bond C of compound III yields



which is RDX. Had bond D been nitrolyzed a chain compound would have been formed. Indeed the prepn of RDX is complicated by many side reactions resulting from the nitrolysis of bonds other than those shown in the above sequence (cf Ref 82, pp 89–93). For addnl discussion on the mechanism of nitrolysis of Hexamine, see this Vol under Nuclear Tracers in Explosive Chemistry

As suggested above, side reactions decrease the yield of RDX. The optimum RDX yield is

about 80% based on hexamine, and about 40% based on formaldehyde (used in making hexamine). Vroom and Winkler (Ref 36d) show that this optimum yield (based on formaldehyde) can be attained using 88 to 97% nitric acid, but the weaker acids require a large acid-to-hexamine ratio (cf fig 15)

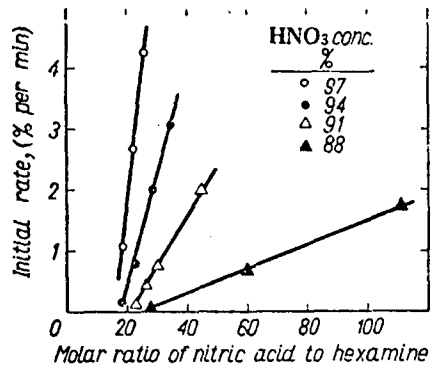


Fig 15 Effect of nitric acid–hexamine ratio on initial rate of cyclonite formation at 0°C, according to Vroom and Winkler (Ref 36d)

A faster nitration is also achieved when nearly anhydrous nitric acid is used (cf Fig 16)

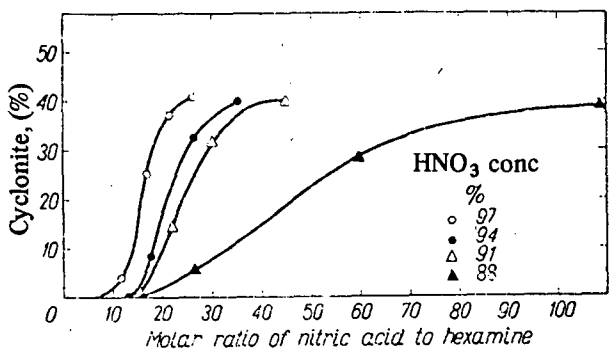


Fig 16 Effect of nitric acid–hexamine ratio on final yield of cyclonite, according to Vroom and Winkler (Ref 36d)

Similar results were obtained by Dunning et al (Ref 38a) as shown in Fig 17. Here the yield is based on Hexamine. Note that with 85% nitric acid, optimum RDX yield appears to be unachievable

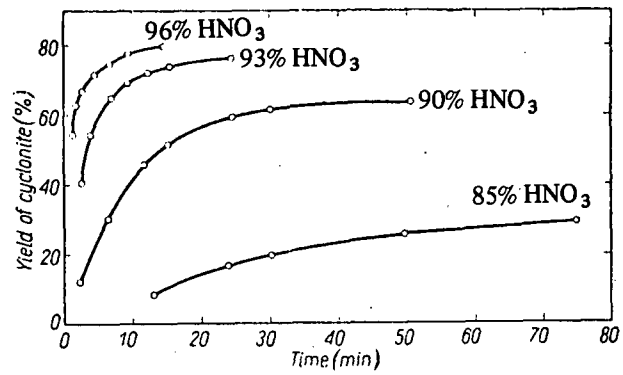


Fig 17 Rate of nitration of hexamine at 0°C with various concentrations of nitric acid, according to Dunning, Millard and Nutt (Ref 38a)

A description of the various RDX manufacturing processes is given in the Vol **3** ref cited above. Urbański (Ref 82, pp 104–113) gives the following material balances for these processes:

British process: To produce 1000kg of RDX, 833kg of Hexamine and 8779kg of HNO_3 are required: 3482kg of dil 55% HNO_3 are recovered plus 3429kg of HNO_3 from the absorption towers. Thus the net consumption of HNO_3 for nitration is 1868kg. In addition, 490kg of H_2SO_4 are used for the concn of HNO_3

SH process: To produce 1000kg of RDX, 880kg of Hexamine and 6800–7760kg of 99% nitric acid are required. The net consumption of nitric acid is 1720–1850kg; 5080–5850kg of 99% HNO_3 are recovered

K process: To produce 1000kg of RDX, 480–500kg of Hexamine, 8600kg of HNO_3, and 4800kg of AN are required. The consumption of HNO_3 and AN is 1400kg and 1200kg respectively. Recovery amounts to 7200kg of HNO_3 and 3600kg of AN

E process: To produce 1000kg of RDX, 630–635kg of paraformaldehyde, 1800kg AN, 5000–5100kg of acetic anhydride, containing 19kg of boron fluoride are required. The consumption of acetic anhydride amounts to about 800kg

KA process: To produce 1000kg of RDX, 400kg of Hexamine, 430kg of AN, 680kg of 99% HNO_3 and 2400kg of acetic anhydride are required. About 450kg of acetic anhydride are consumed

The material balance for the *Bachmann process* is similar to that of the KA process

Tetryl. In the manufacture of Tetryl, it is usual not to nitrate dimethylaniline directly, but to dissolve it first in concd sulfuric acid and then to nitrate the dimethylaniline sulfate so obtained. Direct nitration of dimethylaniline proceeds so violently that it can be carried out only under specialized conditions. Many years experience of Tetryl manufacture has shown that the ratio of sulfuric acid to dimethylaniline should not be lower than 3:1, since a smaller amount of sulfuric acid may be detrimental to the nitration process. However, the ratio of sulfuric acid to dimethylaniline must not be too high, otherwise Tetryl yield is decreased. Temp must be maintained between 20–45° to avoid sulfonation of the benzene ring. Care must be exercised not to leave any unreacted dimethylaniline prior to introduction of nitric acid, because of the potential violence of the dimethylaniline-nitric acid reaction. Consequently, continuous methods of prepn are to be preferred as they inherently minimize accumulation of unreacted dimethylaniline

A diagrammatic representation of a continuous process for the production of Tetryl is shown in Fig 18. According to Urbański (Ref 82, p 58):

"The nitrating acid is metered in the dosing tank (1) and the dimethylaniline soln in the dosing tank (2). Both liquids are introduced into the nitrator I, their rate of inflow being so regulated that 15.4 parts of the dimethylaniline soln in sulfuric acid mix with 9.2 parts of nitrating mixt composed of: HNO_3, 67%; H_2SO_4, 16%; and H_2O, 17%. The contents of the nitrator are heated to a temp of 68°, heating is then discontinued, and the temp in the nitrator

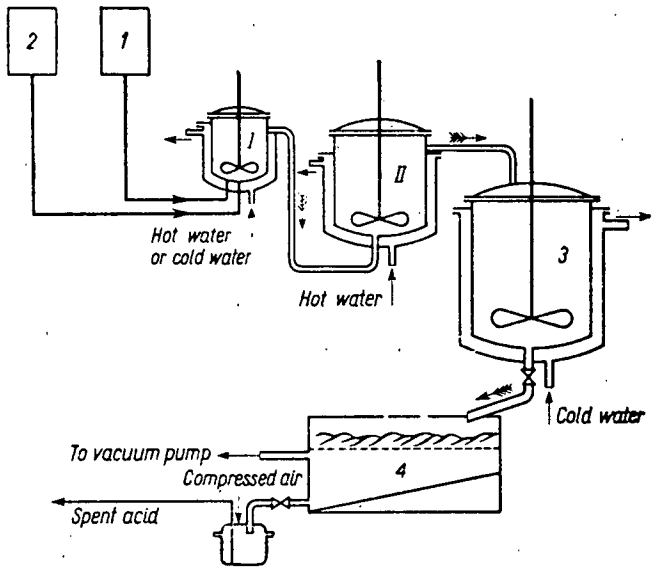


Fig 18 Flow diagram of plant for continuous nitration of dimethylaniline

maintained at 60–72°. The nitrator is cooled externally, if necessary. For safe and efficient nitration very vigorous stirring is essential to ensure that the reacting liquids are mixed almost instantaneously. Since the mixt is kept in nitrator I for a very short period, reaction may be incomplete. Its contents are discharged via an overfall to a larger reactor II, also provided with a stirrer. In reactor II the same temp (70°) is maintained by heating. Here the reaction is completed and the liq, together with the partly crystallized product, is allowed to run into crystallizer (3) in which the whole is cooled to 20° and afterwards discharged to the vacuum filter (4). Tetryl is collected on the filter and the spent acid is passed on to be denitrated"

The filtered product is then thoroughly washed with water and crystallized from a benz or acet soln. For details see Ref 82, pp 59–61

An alternate, two-stage method of producing Tetryl is used in Germany. In the first stage dinitromethylaniline is prepd by reacting chlorodinitrobenzene with methylamine in the presence of Na hydroxide. In the second stage the dinitromethylaniline is nitrated in a similar manner as above to produce Tetryl. The dinitromethylaniline is first dissolved in sulfuric acid (which is made from spent acid and contains some nitric acid, oxides of nitrogen, and 16%

water) and then poured into mixed acid consisting of 78/6/16 nitric acid/sulfuric/water

A lab study describes the formation of Tetryl from dimethylaniline proceeding in two main stages: (1) dimethylaniline → 2,4-dinitrodimethylaniline, and (2) 2,4-dinitromethylaniline →Tetryl, the latter stage proceeding largely via 2,4-dinitromonomethylaniline, but also via dimethylpicramide (Ref 36e)

VII. Thermochemistry of Nitration

Since nitrations are exothermic reactions it is necessary to provide some means of heat control to prevent run-aways. The simplest method is to use a large excess of nitrating agent and have it act as a heat sink. This is often impractical and precooling the reagents and/or heat removal during reaction are frequently employed. Thermochemical calcualtions are consequently most useful in determining how much heat is evolved in a particular nitration and how much heat must be removed to keep the reaction at an acceptable temp level

Sources of thermochemical data for such calculations are: Vol **7**, H38-Lff: "Heat Effects – Data for Common Explosives"; NBS Circular 500 (Ref 39a); Cox & Pilcher (Ref 89); and the studies of Rhodes & Nelson (Ref 24b) and McKinley & Brown (Ref 28a) on mixed acids

As an example of such a calculation we will compute the heat evolution and temp rise occurring during the mixed acid nitration of glycerol to NG. We will assume that a typical 50/50 nitric acid/sulfuric acid MA is used and that the MA/glycerol ratio is 5/1. Further assumptions are that all the glycerol is converted to NG, and that the heats of soln of NG in the spent acid, and of spent acid in the NG, are negligibly small (cf discussion of these effects by the writer in Ref 51). The net reaction is then:

$$C_3H_5(OH)_3 + \underbrace{3.65HNO_3 + 2.35H_2SO_4}_{\text{50/50 MA}} =$$

$$NG + \underbrace{0.65HNO_3 + 2.35H_2SO_4 + 3H_2O}_{\text{spent acid}}$$

The spent acid compn is 12.6/70.8/16.6 nitric acid/sulfuric acid/water, or 83.4% total acid and 15.1% nitric acid based on total acid. The total heat of reaction $\Delta H_t = \Delta H_n + \Delta H_d$ where ΔH_n is the heat of nitration, ie, the heat of reaction for:

$C_3H_5(OH)_3 + 3HNO_3 = NG + 3H_2O_{(liq)}$

and ΔH_d is the heat of dilution for the 50/50 MA being converted into the 12.6/70.8/16.6 spent acid. As shown in Vol **7**, H38-L, ΔH_n = −9.4kcal/mole for glycerol (negative ΔH's indicate exothermic reactions). According to Figs 19 and 20, taken from McKinley & Brown (Ref 28a), ΔH_d is obtained as follows: the enthalpy of 460g of 50/50 MA (the amount used per mole of glycerol) at 25° is

0.460 [−14.5+(25−0)0.405] = −2.03kcal

and the enthalpy of 325g of 12.6/70.8/16.6 spent acid is

0.325[−55.0+(25−0)0.45] = −14.25kcal.

The positive terms in these equations are the $c_p\Delta T$ terms to convert the enthalpies from 0° to 25° to make the ΔH_d consistent with ΔH_n which is for 25°. The difference in enthalpies of the spent acid and MA is ΔH_d = −12.2kcal. Then $\Delta H_t = \Delta H_n + \Delta H_d$ = −21.6kcal per mole of glycerol or −234kcal per kg of glycerol. Note that for NG the heat of dilution is greater than the heat of nitration. Urbański (Ref 74, p 146) gives ΔH_t = −252kcal per kg of glycerol without showing how this value was obtained. Fig 19 is not easy to use and it contains rather old but apparently reliable data. An *upper limit* estimate to check the validity of the above calculation is readily obtained by assuming that the total heat effect of dilution is due to the dilution of sulfuric acid by the water formed during the reaction. Using the accurately known heats of dilution of sulfuric acid (Ref 39a), ΔH_d = −18.7kcal for 2.35 moles of H_2SO_4 diluted by 3.00 moles of H_2O. Thus an upper limit estimate for ΔH_t = −28.1kcal/mole glycerol and a specific heat of 0.45cal/°g for the spent acid and 0.36cal/°g for the NG (from the above cited Vol **7** reference) the temp rise during nitration, if no cooling is provided, is:

$\Delta T = 21.6\times10^3 / (0.36\times227+0.45\times325) = 156°$

This is of course much higher than permissible (max nitration temps should be less than 50°) and means of heat removal or cooling must therefore be provided

Additional total heats of nitration quoted by Urbański (but without details of how they are obtained) are:

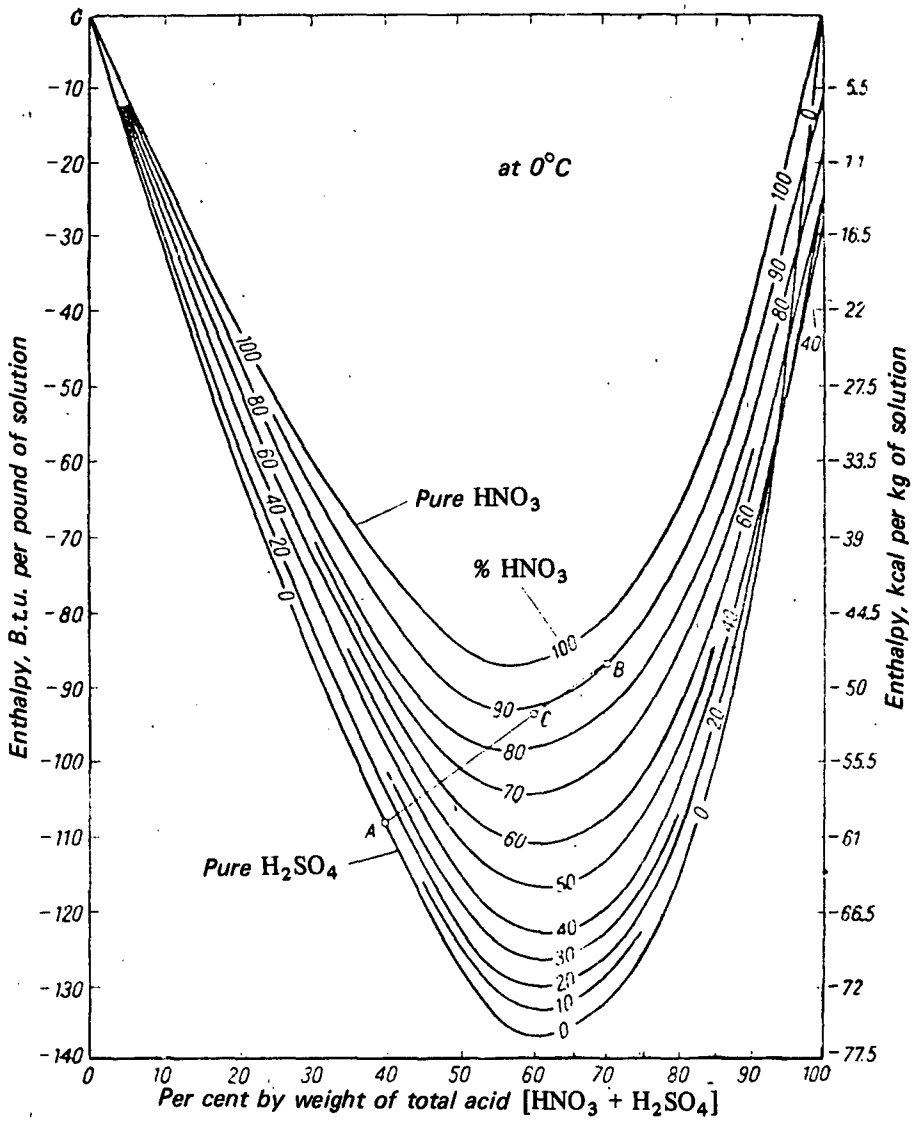


Fig 19 Enthalpy of nitric acid, sulfuric acid, and water mixtures
McKinley and Brown (Ref 28a)

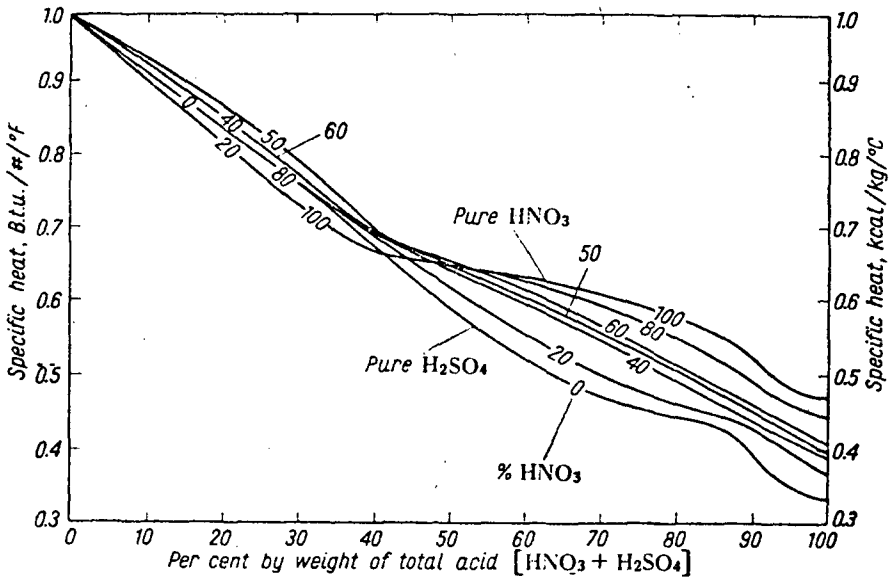


Fig 20 Specific heat of nitric acid, sulfuric acid, and water mixtures McKinley and Brown (Ref 28a)

Picric Acid: −917.4kcal/kg of phenol (Ref 74, p 146)

NC: 10.4 to 10.6% N; −6.9 to −7.8kcal/kg of cellulose; 13.3% N, −11.4kcal/kg of cellulose (Ref 75, p 358)

Several exptl studies are quoted for the heat of nitrating one OH group. On a per mole basis these range from 1.7 to 2.1kcal/mole. However, Miles (Ref 44) computes a lower value, 1.2kcal/mole, on the basis of accurately determined heats of combustion of NC

RDX. Gilpin & Winkler (Ref 38b) measured a heat of nitration of −88.0kcal/mole of hexamine for the reaction of hexamine with 97.5% nitric acid. They also obtained a value of −140kcal/mole of hexamine for the formation of RDX from hexamine and Bachmann reagents (acetic anhydride, acetic acid, ammonium nitrate and nitric acid). Incidentally, Gilpin & Winkler interpret their results to mean that hexamine dinitrate is an intermediate in the direct nitrolysis of hexamine to give RDX, while hexamine mononitrate is an intermediate in the Bachmann process of producing RDX

Dunning et al (Ref 38a) give the heat of reaction, per mole of hexamine, for the formation of RDX at several acid concns at 20° and at −35.5°. Their results are shown in Fig 21. Comparison of their data with those of Gilpin and Winkler shows that their heat effect is almost 10kcal/mole greater than that reported by Gilpin & Winkler (Ref 38b)

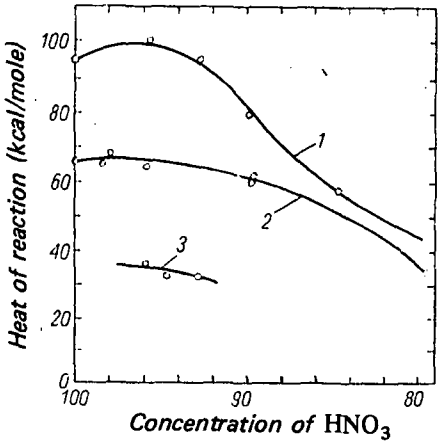


Fig 21 1−Nitration of hexamine at 20°C; 2− nitration of hexamine at −35.5°C, according to Dunning, Millard and Nutt (Ref 38a)

VIII. Nitration Mechanisms

Summary. Modern views of the mechanism of nitration are divided into two schools. Ingold and co-workers champion the concept that nitration is primarily *ionic* in character and its rate-determining step (at least in a concd nitrating acid medium) involves the *nitronium ion,* thus:

$$RH+NO_2^+ \xrightarrow{\text{slow}} R\begin{matrix}H^+\\ \diagdown NO_2\end{matrix} \xrightarrow[\text{fast}]{NO_3^-} RNO_2+HNO_3$$

for C-nitrations;

$$R_3COH+NO_2^+ \xrightarrow{\text{slow}} R_3CO\begin{matrix}H^+\\ \diagdown NO_2\end{matrix} \xrightarrow[\text{fast}]{NO_3^-} R_3CONO_2+HNO_3$$

for O-nitrations; and

$$R_3N\begin{matrix}H\\ \diagdown R'\end{matrix} +NO_2^+ \xrightarrow{\text{slow}} R_3N^+\begin{matrix}H\\ NO_2\\ \diagdown R'\end{matrix} \xrightarrow[\text{fast}]{NO_3^-} R_3N\begin{matrix}NO_2\\ \diagdown R'\end{matrix} +HNO_3$$

for N-nitrations

Titov and co-workers, although conceding the validity of the ionic nitration mechanism for liq phase nitrations with concd acids, believe that many nitrations occur via a *free-radical* mechanism involving the free radicals (at any rate molecules having an *unpaired* electron) $\dot{N}O_2$, $N\dot{O}_3$, and $\dot{N}O$. For vapor phase nitration of hydrocarbons, nitration of side chains of aromatic compds in solvents, and the nitration of olefins in nonpolar solvents, the Titov Mechanism is:

$$RH\begin{matrix}\diagup \dot{N}O_2 \rightarrow \dot{R}+HNO_3\\ \diagdown N\dot{O}_3 \rightarrow \dot{R}+HNO_3\end{matrix}$$

followed by $\dot{R}+\dot{N}O_2 \rightarrow RNO_2$. According to Titov the formation of the reactive $\dot{R}$ radicals explains the many side reactions (eg oxidations, nitrosations etc) observed in hydrocarbon nitrations

The main differences between the *ionic* and *free radical* schools are in their respective views of

a) Nitrations with moderately dil nitric acid

b) Vapor phase nitrations with nitric acid

c) The roles of NO and/or HNO_2 in nitrations

We will examine both schools of thought below, but before doing this we need to examine the compn (ie, the species present) in such nitrating mediums as mixed acid, nitric acid, and oxides of nitrogen

Composition of Nitrating Media

Early concepts of the composition of mixed acids were described in Section II. More recent concepts are best summarized by the following equilibria:

$$HNO_3 + H_2SO_4 = H_2NO_3^+ + HSO_4^- \quad (1)$$

$$H_2SO_4 = H_3O^+ + HSO_4^- \quad (2)$$

$$H_2NO_3^+ + H_2SO_4 = NO_2^+ + HSO_4^- + H_3O^+ \quad (3)$$

Steps (1) and (2) are fast while the production of nitronium ion in step (3) is "slow". A great mass of evidence exists in support of the formation of NO_2^+ in mixed acids of low water content, but there is some controversy about the presence of $H_2NO_3^+$ in MA. Hantzsch's cryometric studies (Refs 9 & 18) were interpreted to be in support of the existence of the nitracidium ion ($H_2NO_3^+$). These views were later supported by the studies of Hammet & coworkers (Refs 20 & 24). Furthermore, Hantzsch isolated crystalline nitracidium perchlorate ($H_2NO_3^+$)(ClO_4^-) (Refs 14a & 14b)

Euler was the first to suggest the presence of nitronium ions in mixed acids (Ref 12). This view was later supported by the conductometric studies of Walden (Ref 14). Titov (Ref 28) reinterpreted Hantzsch's data and suggested that the simplest way to explain them was:

$$HNO_3+2H_2SO_4 = NO_2^+ + 2HSO_4^- + H_3O^+ \quad (4)$$

ie, step (2) is eliminated and NO_2^+ is formed via step (4). Ingold et al isolated crystalline nitronium salts (Ref 36b). Raman spectra furnish convincing evidence of the presence of NO_2^+ in MA. Of particular value are the studies of Chedin et al (Ref 35) which show how NO_2^+ concn changes with water content of the MA

Water-free nitric acid is amphoteric, ie, it acts both as an acid and a base, or better as an electron donor or electron acceptor. This view, already suggested in the early Hantzsch papers, was supported by Walden (Ref 14) and later by Dalmon (Ref 30). Then Usanovich (Ref 25) demonstrated that nitric acid acts as a *base* with sulfuric acid and as an *acid* with water. Other strong acids (in the general Brönsted sense), such as perchloric acid, phosphoric acid (Ref 25), BF_3 (Ref 26), and HF (Ref 27) make HNO_3 behave as a base, eg

$$2HF+HNO_3 = NO_2^+ + H_3O^+ + 2NO_3^- \quad (5)$$

Concd nitric acid undergoes "self-ionization". According to Spasokukotskii (Ref 34):

$$3HNO_3 = NO_2^+ + H_3O^+ + 2NO_3^- \quad (6)$$

However, more recent investigators (Refs 36, 38 & 49) believe this to be a two stage process, similar to that shown in Eqns 1 & 3:

$2HNO_3 = H_2NO_3^+ + NO_3^-$ (7)

$H_2NO_3^+ = NO_2^+ + H_2O$ (8)

Ingold et al (Ref 36) indicate that step (7) is fast and step (8) is "slow"

The studies of Bunton et al (Ref 38) using heavy oxygen (18_O) are particularly noteworthy in elucidating the self-ionization process. With moderately "dilute" nitric acid they found that nitrations required presence of nitrous acid. Ingold and co-workers (Ref 36c) suggest that the action of nitrous acid is as follows:

$HNO_2 + HNO_3 = H_2NO_2^+ + NO_3^-$ (9)

$H_2NO_2^+ = NO^+ + H_2O$ (10)

$NO^+ + NO_3^- = N_2O_4$ (11)

Titov (Ref 65) claims that nitric acid also acts as a source of nitrogen oxides via

$NO + 2HNO_3 = 3NO_2 + H_2O$ (12)

According to Ingold et al (Ref 77) at high temps, in the gas phase:

$HONO_2 = \dot{O}H + \dot{N}O_2$ (13)

Nitrations can be carried out using N_2O_5 as the nitrating agent. According to Titov (Ref 28) and confirmed by Gillespie et al (Ref 36a):

$N_2O_5 = NO_2^+ + NO_3^-$ (14)

Moreover, as proved by Ogg (Ref 32a):

$N_2O_5 = \dot{N}O_2 + \dot{N}O_3$ (15)

Thus N_2O_5 can furnish both ionic and free radical species for nitrations

Nitrogen tetroxide disassociates according to:

$N_2O_4 = 2\dot{N}O_2$

and thus provides free radical nitrating species. With sulfuric acid:

$N_2O_4 + H_2SO_4 = NO^+ + HNO_3 + HSO_4^-$

and nitration can then proceed via reactions (1) and (3) to form NO_2^+, or via direct reaction with NO+ and subsequent oxidation of the nitroso compound. Alternatively,

$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$

provides both NO^+ and NO_2^+ (Ref 36)

An excellent review of the composition of MA, nitric acid and nitrogen oxides is given by Urbański (Ref 74, pp 12–52, 102–04)

Ionic Nitrations

We shall discuss ionic nitration mechanisms in terms of nitration by pure nitric acid and where appropriate comment on effects of such additives as sulfuric acid, water, nitrous acid etc. The nitration scheme now generally accepted for liq phase nitrations is an electrophilic substitution of the substituting agent on the conjugated 2p electrons of carbon, oxygen or nitrogen atoms. Nitronium ion is the substituting agent *par excellence* for C, O and N-nitrations. The best proofs of these nitration mechanisms come from studies of nitrations carried out in solvents – polar, non-polar, or even water. The reaction scheme is as follows:

$2HNO_3 = H_2NO_3^+ + NO_3^-$ fast (7)

$H_2NO_3^+ = NO_2^+ + H_2O$ slow (8)

$NO_2^+ + XH \rightarrow XHNO_2^+$ slow (16)

$XHNO_2^+ + NO_3^- \rightarrow XNO_2 + HNO_3$ fast (17)

where X is a benzenoid hydrocarbon, an alcohol or an amine, and NO_2^+ substitution occurs on a ring carbon, alcohol oxygen, or amine nitrogen respectively. Steps (8) or (16) are rate-controlling. Depending on which of these predominates the net reaction is either zero-order or first-order in XH

Thus, for a "reactive" XH in a not-too-aqueous medium, NO_2^+ will be primarily consumed by reaction (16), and the nitration rate will be independent of the concentration, or even the chemical nature, of XH, ie, zero-order in XH. In this case nitration rate will depend on the stationary concn of $H_2NO_3^+$ and thus in turn on the presence of additives that influence reaction (7), eg, addition of sulfuric acid will increase ($H_2NO_3^+$) via reaction (1), but NO_3^- addition will decrease ($H_2NO_3^+$) via the reverse of reaction (7)

Conversely, for an "unreactive" XH, or one present in small concn, or for a highly aq medium, the reverse of reaction (8) prevails over reaction (16), and the rate of nitration now depends on both the nature and concn of XH, ie, it is first-order in XH. The comments made above about H_2SO_4 or NO_3^- additives are also applicable to this situation

The above reaction scheme is largely based on the studies of Ingold's school (Refs 23, 36, 36a, 36b, 36c, 39, 49 & 49a). However, some previous and later investigators, Titov (Ref 28 & 52), Westheimer and Kharasch (Ref 32), Bennett et al (Ref 32b), Bunton et al (Ref 36c), Bonner & Frizel (Ref 48 & 55), Stromberg & Lel'chuk (Ref 72) and Chapman et al (Ref 93) also contributed to its elucidation

The following zero-order rate constants, from Refs 49 & 49a, were obtained in about

XH	Benzene	Toluene	Ethyl Benzene	Amine*	MeOH	Glycol	Glycerol
$k_0 \times 10^5$ (moles/1 sec)	1.72	1.70	1.66	1.40	1.69	0.83	0.88

* n-methyl-2,4,6-trinitroaniline

100-fold excess HNO_3 in nitromethane solutions at 25° (2.5M HNO_3 and 0.015 to 0.025M XH):

Note that all the zero-order rate constants are essentially equivalent except those for the polyhydric alcohols which are exactly half the value of the others. Ingold et al (Ref 49a) interpret this to mean that the rate of attack of nitronium is the same for both OH groups of the glycol molecule. Since there are two such groups the overall rate constant k_0 is ½ that for monohydric alcohols. The explanation for the observed k_0 for glycerol is more complex. In essence it consists of postulating that the two outside OH's are readily nitrated, ie, the 1-OH is nitrated at the same rate as the 3-OH, but the middle OH is nitrated much more slowly

As implied in the preceding discussion, deliberate introduction of water into the nitration medium should make step (8) competitive with step (16) even for a "reactive" XH, and the overall nitration rate changes from zero-order to first order. These phenomena have been observed (Refs 49 & 49a). Under nearly identical conditions (2.5M HNO_3, 1.09M H_2O, ca 0.02M XH in NM soln at 25°), the measured first-order rate constants are 2.5×10^{-4}, 2.0×10^{-4}, 1.2×10^{-5} sec^{-1} respectively for MeOH, toluene, and n-methyl-2,4,6-trinitroaniline. Combined with some earlier data, the "reactivities" (ratios of first-order rate constants) are: benzene 1.00, methyltrinitroaniline 1.4, toluene 24, MeOH 30 (Refs 49 & 49a)

In the nitration of amines there may be a competition between the formation of nitramines or acid salts. This is visualized by Lamberton (Ref 37a) as:

$$\underset{|}{\overset{}{>}}N + NO_2^+ \rightleftharpoons \underset{|}{\overset{+}{N}}-NO_2 \rightleftharpoons \underset{}{\overset{}{>}}N-NO_2 + H^+$$
$$H \qquad\qquad H$$

$$\underset{|}{\overset{}{>}}N + HNO_3 \rightleftharpoons N.....HONO_2 \rightleftharpoons \underset{}{\overset{+}{>}}NH_2 + NO_3^-$$
$$H \qquad\qquad H$$

A recent investigation (Ref 90) of the 2-stage mixed acid nitration of tetranitroethane (TNE) to hexanitroethane revealed that the ntiration was first-order in NO_2^+, TNE and "base" (either H_2O or HSO_4^-). The reaction was claimed to proceed via simultaneous attack of NO_2^+ on the C, and of base on the H of the TNE

As already mentioned, Bunton and Halevi (Ref 38) found that ca 60% nitric acid requires the presence of nitrous acid for it to be a nitrating agent. Ingold et al (Ref 36c) postulated the action of nitrous acid to proceed via reactions 9, 10 & 11. Now in competition with reaction 11, there may be a nitrosation reaction:

$$XH + NO^+ \rightarrow X\begin{matrix}H\\ \diagup\\ \diagdown\\ NO^+\end{matrix} \rightarrow XNO + H^+ \qquad (18)$$

followed by

$$XNO + HNO_3 \rightarrow XNO_2 + HNO_2 \qquad (18a)$$

which regenerates nitrous acid. The reaction sequence 9, 10, 11, 18 & 18a may thus explain the nitration mechanism in "dilute" nitric acid. An alternate scheme is proposed by Bonner & Frizel (Ref 55); if strong acids ($HClO_4$, H_2SO_4) are present:

$HNO_2 + 2HClO_4 = NO^+ + H_3^+O + 2ClO_4^-$,

presumably followed by reactions 18 & 18a

Several investigators report nitrations under conditions where NO_2^+ cannot be present. Amongst these are the studies of Lowen et al (Ref 37), Urbański et al (Ref 58) and Brennecke & Kobe (Ref 46), and in particular those of Titov (Refs 28 & 65). These studies suggest the necessity for a non-nitronium nitration mechanism and such a mechanism will be examined in the next subsection

Free Radical Nitration

Impure nitric acid can produce NO_2 via reaction (12). Titov (Refs 65 & 39b) also suggests the dehydration reaction for anhydrous nitric acid:

$$3HNO_3 = N_2O_5 + HNO_3.H_2O \qquad (19)$$

followed by reaction (15) to form $\dot{N}O_2$ and $N\dot{O}_3$

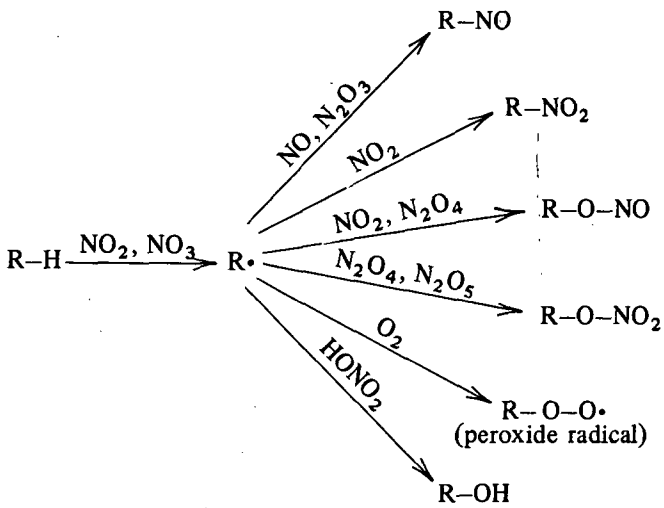
According to Titov, both $\dot{N}O_2$ and $N\dot{O}_3$ react with XH as follows:

$RH + \dot{N}O_2 \rightarrow R\cdot + HNO_2$ (20)

$RH + N\dot{O}_3 \rightarrow R\cdot + HNO_3$ (21)

and (21) is claimed to be much faster than (20). However, N_2O_5 also produces NO_2^+ via reaction (14)

Many reactions, nitration, nitrosation, oxidation, etc are then possible. Titov's generalized scheme is



Nitric oxide for the above sequence is formed via (12) and/or the decompn of nitrous acid produced in (20)

Of course most of the above reaction sequences are possible if one starts with either N_2O_4 or N_2O_5 as the nitrating agent

Titov claims that the free radical mechanism applies for nitration of aliphatic hydrocarbons, of aromatic side chains, of olefins, and of aromatic ring carbons, if in the latter case the nitrating agent is ca 60–70% nitric acid that is free of nitrous acid, or even more dil acid if oxides of nitrogen are present

Probably the main point of disagreement between the Ingold and Titov schools arises in the vapor phase nitration of hydrocarbons. Titov believes that this occurs via reaction (19), (20), (21), etc. Ingold et al (Ref 77), on the basis of some sound kinetics, propose the sequence:

$HNO_3 = H\dot{O} + \dot{N}O_2$

$H\dot{O} + R \rightarrow H_2O + \dot{R}$

$\dot{R} + HNO_3 \rightarrow RNO_2$ (or RONO) + $\dot{O}H$

$\dot{R} + HNO_3 \rightarrow ROH + NO_2$

Reaction Rates in Industrial Nitrations

It should be pointed out that most of the evidence presented above in support of the nitronium ion or free radical mechanisms of nitration was obtained with homogeneous solns under conditions that cannot be compared directly with the conditions prevailing in industrial nitrations

Since industrial nitration occurs, in most cases, in two-phase systems a number of workers have investigated the kinetics in both organic and acid phases (Refs 18b, 46 & 81). The consensus is that nitration occurs mainly in the acid phase. In what follows we will examine reaction rate effects in industrial-type nitrations for producing TNT, NG and EGDN

TNT: Reaction rate effects in the production of MNT and DNT were already examined in Section VI. Here we will examine reaction rate effects for the trinitration stage, ie, DNT → TNT

Orlova (Ref 62) made extensive studies of the conversion of DNT to TNT in mixed acid. Some of her results are shown in Figs 22 thru 25. All the data are for 90°. The mixed acid used in obtaining the results of Fig 23 consists of 16/81/3 nitric acid/sulfuric acid/water, the MA/DNT ratio of 1/5, and reaction time was 40 minutes. These results (Fig 23) should be compared with those shown in Figs 4 & 8

Orlova summarizes her studies of toluene nitration as follows: Nitration of toluene to MNT and of the latter to DNT under heterogeneous conditions should be considered mainly as a "surface" reaction. This is deduced from the fact that the rate of the reaction depends on the rate of stirring. The reaction of nitration of DNT to TNT in heterogeneous systems is not limited to the surface between the two phases. This is proved by the fact that the rate of nitration depends very little on the rate of stirring. DNT and nitric acid are distributed between two phases according to their coefficients of distribution and the ratio of the volumes of the two phases. Reaction occurs in both phases but the rate in the acid phase is much higher than in the organic oil phase. This is because the organic oil phase contains only HNO_3 with practically no H_2SO_4. The rate of nitration of DNT depends therefore largely on the solubility of DNT in the acid layer

To some extent the organic phase has a nega-

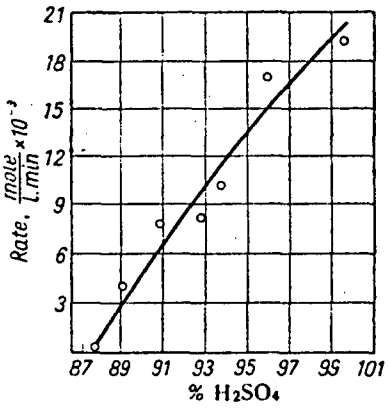


Fig 22 Influence of the concentration of sulfuric acid on the rate of nitration in homogeneous conditions (nitrating mixtures with a high content of HNO_3 (Orlova, Ref 62)

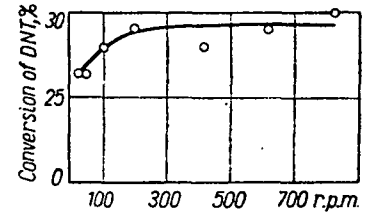
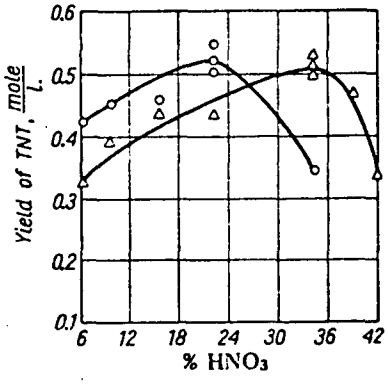
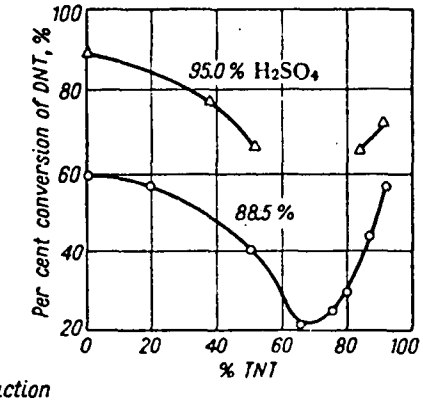


Fig 23 Influence of the rate of stirring on the rate of nitration of DNT (Orlova, Ref 62)





o – homogeneous reaction
Δ – heterogeneous reaction

Fig 24 Influence of the content of HNO_3 in nitrating mixtures on the rate of nitration of DNT to TNT (Orlova, Ref 62)

Fig 25 Change of the rate of nitration of DNT in the presence of TNT (Orlova, Ref 62)

tive action on nitration. It is a good solvent for HNO_3 and considerably reduces the concn of HNO_3 in the acid phase

The secondary reactions of oxidation occur in both the organic and acid layers. It is likely that oxidation occurs strongly in the organic layer because of the presence of HNO_3 free of H_2SO_4

The negative influence of the organic layer also consists in reducing the concn of DNT in the acid phase. This occurs when the organic phase is composed mainly of molten TNT.

The distribution coefficient of DNT between the two phases shifts the DNT towards the organic layer. This particular negative action of the TNT layer is less pronounced towards the end of the nitration when very little DNT is left unnitrated. Therefore the most favorable condition of heterogeneous nitration exists at the beginning of the reaction when the organic layer is composed only of DNT. Therefore at this stage of the reaction it is possible to use less concd nitrating mixts and a lower nitration temp

NG & EGDN

Oehman et al (Ref 56a) suggest that glycerol nitration to NG occurs to some extent on the surface between the acid and "oil" phases. They claim that stirring and/or atomization of the glycerol during its addition increase nitration rate. However, of primary importance is the ratio of H_2O/H_2SO_4 in the MA. Optimum rates are achieved for a mole ratio of 1:1 (or somewhat less) corresponding to formation of the hydrate $H_2SO_4.H_2O$. According to Oehman nitration becomes slow at a water content corresponding to more than 1.2 moles H_2O/mole H_2SO_4. Optimum nitration temp is around 20°

Roth, Stow & Kouba (Ref 51) investigated the nitration of ethylene glycol in a tubular nitrator (cf Section VI). Reaction rate was followed by measuring temp rise along the flow path. This furnished data in the form of ΔT vs time curves such as the one shown in Fig 26

Since mixing of glycol and MA was very thorough and rapid this ΔT mirrors the progress of the exothermic nitration reaction. Note the strong influence of mixed acid water content on the nitration rate. This agrees with Oehman et al (Ref 56a), except that Roth et al observed

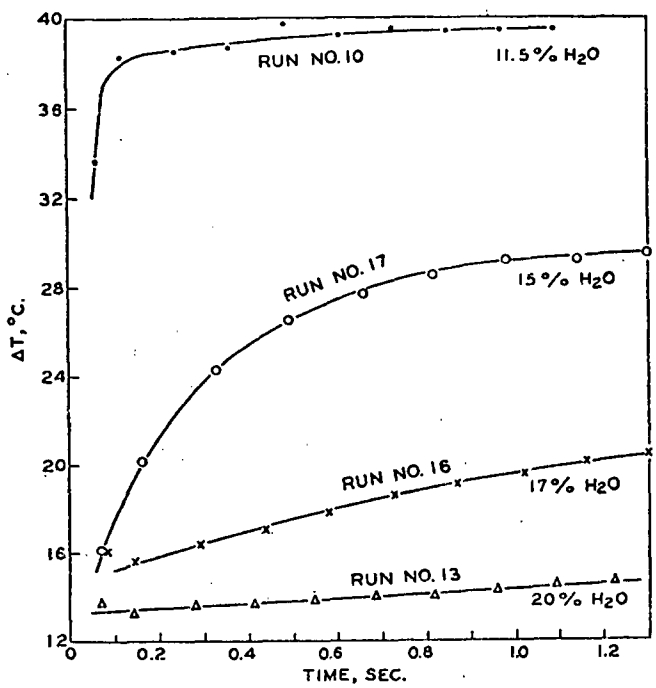


Fig 26 Temperature rise in the tubular nitration of ethylene glycol

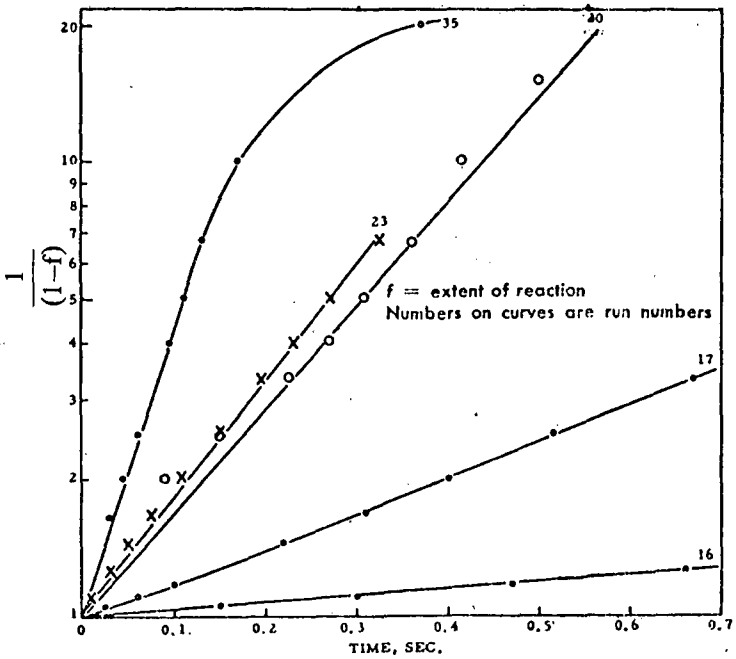


Fig 27 Extent of EGDN formation as a function of time

quite rapid nitration at mole ratios of greater than 1.2/1 H_2O/H_2SO_4 where Oehman et al claim slow nitration

The data of Fig 26 can be converted into the extent of reaction plot of Fig 27. Fig 27 is a typical first-order plot and this and other data were interpreted to mean that the reaction is pseudo first-order in glycol and nitration proceeded via a NO_2^+ mechanism

IX. Recent Literature on Nitration

In recent years there has appeared a considerable volume of literature dealing with nitrations. The expl-oriented publications on nitrations can be divided, albeit somewhat arbitrarily, into three general headings: *nitration mechanisms; TNT production;* and *miscellaneous nitrations,* ie, production and prepn of expls other than TNT. Studies of nitration mechanisms were summarized in the preceding section. Recent investigations on expl production and prepn via nitration will be presented below in chronological order

TNT Production

An interesting study by Holahan, Castorina,

Autera & Helf (Ref 63) used carbon-14 tracers to determine the origin of tetranitromethane (TNM) formed during nitration of nitrotoluenes. They found that over 50% of the TNM is derived from the ring carbon attached to the CH_3 group, and over 80% of the TNM comes from m-nitrotoluene. These observations are interpreted in terms of competitive reactions, namely nitrations leading to the formation of TNT and oxidations producing TNM. Since nitration is slowest in the trinitration step it is likely that most of the TNM is formed at this stage. A mechanism is postulated based on the formation of dinitrobenzoic acid from DNT, followed by hydrolysis and nitration to form TNM. Presumably the nitration of either 2,4 or 2,6 DNT m-nitrotoluene is faster than the nitration of m-nitrotoluene-derived DNT, thus permitting more extensive oxidation of the latter

Nitration vs side-chain oxidation of toluene in dilute MA was investigated by Namba et al (Ref 69). They found that addition of sulfuric acid accelerated both reactions but nitration more than oxidation. Addition of water to the MA favors oxidation as does an increase in reaction temp

The effects of reactant feeding methods on toluene nitrations were studied by Yamasue et al (Ref 70) in a 15 liter nitrator with a 500rpm agitator. Production of pure MNT or DNT was favored by addition of acid to the toluene or MNT, while in the production of TNT the addition of "oil" to acid is to be preferred, provided sufficient cooling and agitation is available. Purest TNT was produced when the MA contained free SO_3

R.C. Hauze patented a method of preparing DNT containing a high proportion of the 2,4 isomer (Ref 76). A cycling method using separate moving streams of toluene and mixed acid (eg 20–28% nitric acid, 6–65% sulfuric acid and 8–12% water) is claimed to give consistently high yields of DNT. Product and spent acid are separated by conventional means

According to Wright et al (Ref 78), nitration of toluene, using a dehydrated, sulfonic acid ion-exchange resin instead of H_2SO_4, with HNO_3 gave decreased ortho/para ratios, which indicated that this type of nitrating agent has a large steric effect. In addition to the normal products, 25–30% of $PhCH_2NO_2$ was sometimes produced. Ortho/para ratios obtained were 0.68–1.40 depending upon reaction conditions such as: temp, solvent, the stoichiometry (ie, resin/HNO_3 ratio), and the amount H_2O present. In addition to the three nitrotoluenes, BzH, $PhCH_2OH$ and $PhCH_2NO_2$ were identified

Picard et al (Ref 80) patented a method of nitrating toluene with HNO_3 and BF_3 to form DNT and TNT. Thus, 18g toluene was added to 200g acid containing 50% BF_3 and 40% HNO_3 (98.6%). The mixt was stirred vigorously during addition and maintained at 30–50° with cooling. The mixture was then refluxed (90–5°) for one hour, cooled to 70° and separated. The organic layer was poured into ice water and filtered. The residue was washed and dried. Some product was isolated similarly from the lower layer. The total yield of crude TNT, purity 65.6%, was 79.3%. Increasing the reflux time increased the yield and purity of the product. The spent acid was used to form DNT from toluene. The DNT was then nitrated in fresh acid to give TNT. This process eliminated the use of large quantities of H_2SO_4 in the manufacture of TNT

A patent granted V. Vonasek claims an improved method of washing TNT and its mixts with DNT (Ref 83). Passing CO_2 thru the wash water prevents formation of brown side products and reduces the volume of washing liq. Thus TNT containing 30% dinitrotoluene of 0.1–0.5% total acidity (expressed as H_2SO_4) was fed at 85° at the top of a 120 liter washing column, while a 0.5–1% $NaHCO_3$ soln and 300 liter/hr of CO_2 were fed at the bottom. The product was pumped in a CO_2 atm into a 10 liter separator, H_2O was recycled and the product washed with H_2O in a 60 liter column with passing of CO_2 to an acidity of 0.001–0.005% H_2SO_4. The earlier process without CO_2 yielded a dark-red to brown product of 0.03–0.05% acidity

A three-step nitration process of toluene is described. The advantages of the modified process are reduced waste, less hazardous operation, reduced oleum requirement, partial replacement of concd HNO_3 with dil HNO_3, and higher rate of toluene flow into the reactor (Ref 86)

The continuous process of H.C. Prime (Ref 73) for preparing TNT was studied by thin-layer chromatography on silica gel with a starch binder and a fluorescent indicator. The nitration

products at various stages of nitration and the oxidation products from the nitration are identified. The purification process is improved by eliminating the use of soda ash and by lowering the pH (Ref 87)

TNT is claimed to be prepd continuously from toluene by subsequent mono-, d-, and trinitration. Spent acid of the last step was passed thru the second step, extracted with $O_2NC_6H_4Me$ (I) prepd in the first step, and centrifuged to give (I), which was passed back into the second step, and spent acid which was recycled to the first step (Ref 88)

Miscellaneous Nitrations

Nakajima (Ref 71) gives a review of aromatic nitrations

An app for continuous nitration of organic compds is described, comprising a circulation loop into which the organic compd, solvent, and nitrating agent are introduced continuously, with a heat exchanger for the desired reaction temp. Means are provided for recirculating the mixt, while withdrawing a portion into an acid separator and crystallizer. Nitration of 2,4-dinitromethylaniline with MA in dichloroethane solvent to give Tetryl is claimed (Ref 68)

The irreversible conversion of a primary aliphatic amine RNH_2 (R = Me, Me_2CH, Bu, EtMeCH, Me_3C_3, $C_{10}H_{21}$) (I, II, III, IV, V, VI) to its conjugate base with BuLi, subsequent nitration using $EtONO_2$ and acidification gave the corresponding nitramines, $RN(NO_2)H$ (VII) (nitramine, solvent, % yield and bp/mm are given): I, Et_2O, 35, 80–5°/10; II, 2:1 Et_2O–C_6H_{14}, 58, 87–8°/10; III, C_6H_{14}, 49, 92°/0.5; IV, C_6H_{14}, 45, 110°/10; V, C_6H_{14}, 37, 86–7°/10; VI, 2:1 Et_2O_2–C_6H_{14}, 46, –[mp 38.0–0.8° (C_6H_{14})]. Details of the procedure were given. The main disadvantage of the procedure is that amines bearing functional groups reactive with BuLi do not form nitramines (Ref 79)

A patent granted C.W. Plummer (Ref 84) describes the prepn of polynitrohydrocarbons (I). These are saturated hydrocarbons having terminal polynitro groups, and may be prepd by treating saturated hydrocarbons, having at least one terminal nitro group substituted in one terminal Me group, with tetranitromethane (II) in an alkaline soln of a base (NaOMe, NaOH, KOH, or $NaHCO_3$). Thus, to a chilled, stirred soln of 7.5g nitroethane in 150ml MeOH is added dropwise 77.5ml 2.58N methanolic NaOMe, and to the clear colorless soln (in an ice bath) is added 39.2g (II) at such a rate that the temp does not rise above 10°. The orange soln is kept four days at room temp, the volume reduced to about 125ml in vacuo, and the residual soln poured into 400ml of water. Extraction of the colorless heavy oil with CH_2Cl_2 gives 7.7g crude orange liq, which distills at 34°/1 mm to afford 6.80g colorless distillate, which crystallizes in the dry-ice chilled receiver. Most of the distillate liquefies at 10°, the liq is decanted, and the solid is recrystallized from 2.5ml BuOH to yield 8.5% 1,1,1-trinitroethane (III), mp 53–5°. The liq product (crude wt 5.4g, 45%) is mostly dinitroethane (IV). To a stirred and chilled soln containing 2.4g (V) and 14ml MeOH is added 4ml 0.02M NaOH and the resulting yellow soln (pH 8) stirred 15 minutes; 3.92g (II) is added rapidly, whereupon the color changes immediately to orange-red and the pH drops to ∿7. The soln is kept at room temp 18 hours, after which the pH has dropped to about 5, then diluted with 200ml water and the turbid oil which separates is extracted with three 10ml portions CH_2Cl_2. The extract is washed with water, dried over Na_2SO_4, and the solvent removed at 20mm to give 2.7g yellow oil having a very strong odor of (II). The crude product is recrystallized from 2ml BuOH to afford 35% (III), mp 49–52°. The following compounds are similarly prepd (bp/mm, mp, d/temp, and RI/temp given): 1,1,1-trinitropropane, 23°/2, –57.7°, 1.3988/22°, 1.4432/22°; 1,1,1-trinitrobutane, –, –23°, 1.3253/23°, 1.4424/23°; 2-methyl-1,1,1-trinitropropane, 33°/0.35, 9.5, 1.3452/23°, 1.4436/23°; 1,1,1-trinitropentane, 50°/0.7, –, 1.2740/25.5°, 1.4443/25.5°; 2,2-dimethyl-1,1,1-trinitropropane, –, 139–41°, –, –; 1,1,1-trinitrohexane, – (liq), –, –, –; 1,1,1-trinitro-3-phenylpropane, –, 35.5–36.5°, –, –. (I) are high expls which are much less sensitive than NG and may be used as substitutes for an equal amount of the latter in the manuf of blasting gelatins and Dynamites. When three parts by weight of these compds is absorbed in one part by weight of kieselguhr, Dynamites are produced which can be exploded by an engineer special blasting cap and fuse, and are superior to those made with NG because

they are less sensitive to shock, there is less danger of freezing, and they have a longer storage life. (I) may also be used in pure form for shooting oil wells, and because they contain large proportions of O and N are useful as ingredients in proplnt compns, to increase the burning rate and gas volume. Incorporation of 30–40% by weight of (I) into NC produces a double-base proplnt of considerably improved power over that prepd from guncotton alone. In addition, (I) are useful additives for hydrocarbon fuels to increase ignitability, and when mixed with Al may be employed as underwater expls

Nitrohydrocarbons are produced by contacting atomized nitric acid with a molar excess of a hydrocarbon containing 1–10 C atoms in the gas phase in a reaction zone under superatmospheric press, and at a temp of at least 300° for a time ≦350 msec, and immediately quenching the resulting mixt to freeze the equilibrium of the reaction by expanding the reaction products thru an exhaust nozzle with simultaneous water cooling. A rocket engine with a reaction chamber, a fluid injection system for atomizing, mixing, and injecting fluids into the chamber, and an expansion nozzle, is a preferred reactor. Thus, a 35:1 mixt of CH_4 (natural gas) and HNO_3 (as 66% HNO_3) was heated 45msec at 571° and 150psig to give a 9.6% conversion to $MeNO_2$. Using a mole ratio of 11.6:1 at 510° and 150psig with a residence time of 225msec, a conversion of 10% was obtained (Ref 85)

Nitration of mononitrocarbanions, nitroform, and halodinitromethane by nitryl fluoride is described by Fedorov et al (Ref 92). $XC(NO_2)_2$ and $NH_4{}^+C^-(NO_2)_2X$ (X = NO_2, F, Br) were nitrated by FNO_2 to give the respective $XC(NO_2)_2$ in 39.1–90% yield. FNO_2 also converted C^-HRNO_2 (R = Me, Et) and $C^-Me_2NO_2$ to mixts containing AcOH and the corresponding $RCH(NO_2)_2$ and $RC(NO_2)_2$:NOH and $Me_2C(NO_2)_2$, $Me_2C(NO_2)NO$, and Me_2CO, respectively

X. Safety in Nitrations

Since the nitrations of interest to us are exothermic reactions that produce expl substances it is obvious that safety is an important consideration in any laboratory nitration and even more so in an industrial nitration process. In the context of the discussion that follows, *safety* is taken to mean not only the accident-free production of expls but also the production of *stable* expls. Furthermore, some aspects of preventing pollution of the environment by nitration wastes will be included in this discussion

The use of frictionless, spark-proof equipment and the necessity of good housekeeping in expls plants is too well-known to require further elaboration. Temp control during nitration has already been discussed in Sections V, VI, and VII. Here we will focus our attention on potentially hazardous impurities formed during nitrations and on potential incompatibility of the nitration mixts with their surroundings and/or accidentally introduced impurities. We will confine our discussion to safety considerations in the manufacture of TNT and NG

The manufacture of TNT is one of the safest operations in the explosive industry. Nevertheless, disregard of safety procedures may have disastrous consequences

The most hazardous operations in TNT manufacture are the mono- and tri-nitration stages. In mononitration the hazard is due to the extremely violent reaction of the unreacted hydrocarbon with the MA, and to the fact that nitro derivatives of cresols are formed in the process, along with nitrotoluenes. The last stage – trinitration – is dangerous due to the drastic conditions of the reaction which requires concd acids and a high temp. The earlier method of trinitration at which temps up to 120° were applied was particularly hazardous. If the mononitrotoluene has not been freed from nitrocresols, trinitration is still more dangerous, due to the high reactivity of nitrocresols, and their liability to undergo oxidation

According to Urbański (Ref 74, p 391):

"The spent acid from trinitration has also been the cause of several disasters, although it had been considered safe to handle. The most noteworthy example of this occurred in the Reinsdorf factory in Germany in 1935. The hot spent acid flowed down to open iron tanks, where, as the liquid cooled, a mixture of di- and tri-nitrotoluenes rose to the surface. It was skimmed off from time to time and transferred to a washing tank, where it was washed with water. On skimming, a rubber glove and a shelf left on the brim of the tank with some

cotton wool on it, fell into the tank. The reaction between the spent acid and the rubber and cotton wool initiated violent decomposition and fire. An attempt to extinguish the flames failed, and soon the nitro compounds on the surface of the spent acid exploded. The explosion and fire spread over several nearby tanks, then to the nitro compounds in the washing tank. As a result the whole plant for the recovery of nitro compounds was destroyed. In addition to this the expl tore away the roofs of some nearby buildings, among them drier buildings located at a distance of about 660m. Parts of the tank thrown off by the explosion into one of the driers detonated the TNT present, and in another they caused the ignition of the load. Similar explosions or fires spread over further buildings of the TNT factory. Moreover, a neighboring nitroglycerine plant also exploded. This disastrous explosion cost 82 human lives and in addition 104 people were seriously and 700 lightly injured"

It is known that alkalis react with TNT to form sensitive expls. Urbański (Ref 74, p 392) gives an example of a disastrous accidental expln in a French TNT plant which could have resulted from the interaction of TNT and alkaline Na carbonate: "Investigations showed that the explosion occurred after about 2000kg of TNT in a drying tank had caught fire. The TNT in question was that recovered from the spent acid from trinitration. It is known that such a product contains various impurities, among them the isomers of α-trinitrotoluene, nitrocresols, etc. It had first been washed with water at 90°C, then with a 6% solution of Na carbonate, and again with water. The drying was effected at 85–90°C by passing air for 8 hours. In the case described, as the drying TNT still contained some acid, 7kg of Na carbonate (ie, 0.35% in relation to TNT weight) were added to the tank with the drying TNT which at the time contained only a very small quantity of water. This must have led to the formation of typical decomposition products of TNT brought about by reaction with alkalis. It is highly probable that these compounds were the first to ignite, whereupon the flames spread over the whole drier"

Kovache & Thibon (Ref 10) describe a number of explns that occurred in French TNT plants during 1917–18. These were ascribed to the formation of reaction products of TNT with lead or iron in the presence of dil nitric acid. These products were found to be very sensitive to impact, friction, and contact with concd acids. Such products were found at the expln sites

The most recent major expln in a US TNT plant occurred in May 1974 at the Radford Army Ammunition Plant. The accident completely destroyed one of the three continuous nitration lines at the plant. According to the AMC News, Sept 1974, the investigation board reported that an operator inadvertently introduced a 5 to 6-foot rubber hose "to clean out unwanted material that had collected in a transfer line leading to the nitrator, when the hose was pulled from his hands into the nitrator. This resulted in a rapid temp rise and subsequent explosion. The hose was commonly used in this manner". The material causing the blockage in the transfer line was believed to be an oxidation product of TNT, 2,2′-dicarboxy-3,3′,5,5′-tetranitroazoxybenzene, also referred to as *White Compound*. The introduction of the rubber hose caused a rapid, exothermic oxidation reaction between the hose material and the mixed acid present. The heat generated by this reaction caused a local acceleration of the normal nitration/oxidation reactions which occur in the nitrator until a critical temp was reached, at which point rapid oxidation of DNT/TNT proceeded as a runaway reaction, igniting the material present in the vessel.

According to the AMC News article "authorities summed up the report by pointing out that the incident was not the direct result of normal operations, but rather was the result of an unusual condition, and that the design and operating procedures were not unsafe when considered in the context of the total hazardous environment. The process in the nitration and purification building was operating normally when the rubber hose was introduced into the system.

In all, the board submitted 32 recommendations as a result of its investigation. They include additional training for personnel in nitration and purification areas to enable them to cope with such emergency situations. The board also recommended the development of sensing equipment to uncover possible hazardous conditions earlier in the TNT manufacturing process".

Although damage to the plant was extensive, there was no loss of life. There were 15 disabling and 102 non-disabling injuries. Slight damage and minor injuries also resulted beyond the plant boundary from the blast and flying debris

NG, unlike TNT, can become very unstable on prolonged contact with acid. Explns of NG in contact with spent acid have occurred. Studies by Oehman et al (Ref 56) have demonstrated which spent acid compns are "safe" and which are dangerous in contact with NG or EGDN. Their results are summarized in Fig 28

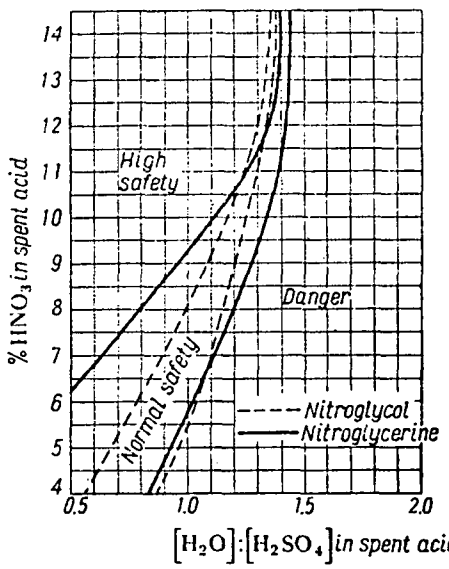


Fig 28 Safety diagram of acidic nitroglycerine, according to Oehman et al (Ref 56). For comparison, nitroglycol is also indicated

Accidents have also occurred while NG was being transported around manufacturing facilities via gravity flow in gutters. To increase the safety of such transport, "detonation breakers" can be introduced along its flow path. An example of a detonation breaker is shown in Fig 29 which consists of a lead tank half-filled with water. NG flows into the tank, collects on the bottom and runs on from below thru the siphon. This arrangement interrupts the NG stream. Detonation cannot be transferred readily thru the water barrier

Further increase in safety can be achieved by

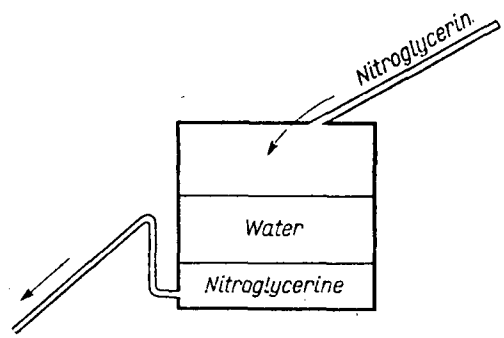


Fig 29 Diagram of a detonation breaker

flowing NG as water emulsions. These should consist of no less than 3 parts of water per part of NG, since 1.5:1 or even 2:1 emulsions can be detonated (Ref 41)

Some recent publications on nitration safety are listed below:

S. Raczynski, Przemysl Chem **42**(9), 470 (1963) & CA **59**, 15114 (1963) (A discussion of technological difficulties in attempting to reduce explosion hazards during nitrations)

S.V. Egorov et al, Otkrytiya, Izobret, Prom Obraztsy, Tovarnye Znaki **46** (34), 199 (1969) & CA **72**, 91696 (1970) (Describes an automatic safety system for nitration processes based on the generation of warning signals by press inside the nitrator)

L. Albright & C. Hanson, Loss Prevention **3**, 26 (1969) & CA **72**, 99685 (1970) (Kinetics and mechanism of aromatic nitrations are reviewed in terms of safety considerations)

T.A. Ventrone, Ibid **38** & CA **72**, 113375 (1970) (a number of explosions during batch nitration are described. The effects of temp, rate of addition, and ratio of reactant on the explns are shown. It is suggested that safety standards be determined and enforced)

E.J. Fritz, Ibid **41** & CA **72**, 113380 (1970) (A detailed investigation was made of a nitration expln, including lab simulation of the event. The expln took place in production of dinitrobenzene in a batch nitrator. The problems of avoiding this sort of expln are detailed)

An interesting survey of pollution abatement in munition plants was recently published by I. Forsten of PicArsn (Ref 91). This article

focuses on pollution abatement in TNT manufacture and describes *air pollution* and *water pollution* as separate facets of the overall pollution problem. Air pollutants in TNT production are primarily oxides of nitrogen, MNT and TeNMe. The main water-pollutant is "red water" produced during the Na_2SO_4 (sellite) purification of TNT. To a lesser degree "Pink water" is also a problem in munition loading plants. This is formed during washing of TNT loading bays, particularly when the wash waters are of elevated pH and the TNT dissolved in them undergoes photochemical reaction

Air pollutant control is still in the pilot plant stage. Two methods appear promising for controlling oxides of nitrogen. These are molecular sieve absorption and acid scrubbing. Both are described in the Forsten article. Scrubbing with sellite is being evaluated as a means of removing TeNMe from the exhaust gases

Water pollution can be mitigated by aeration of the wash streams formed in the sellite treatment of TNT. Further control can be achieved by incineration of the "red water". However, the oxides of nitrogen and the Na_2SO_4 ash thus formed can be troublesome. A recently developed scheme of converting this ash to Na_2CO_3 and H_2S, which can then be recycled to form sellite, looks promising

Activated carbon can be used to preclude the formation of "pink water". Methods of reactivating the carbon are still under investigation

Written by **J. ROTH**

Refs: 1) J.S. Muspratt & A.W. Hoffmann, Ann **57**, 201 (1846) 2) J. Willbrand, Ann **128**, 178 (1863) 3) F.K. Beilstein & A. Kuhlberg, Ann **155**, 1 (1870) 4) P. Spindler, Ber **16**, 1252 (1883) 5) Rheinisch-Westfälische Sprengstoff AG, GerP 81664 (1894) 6) G. Henning, GerP 104289 (1899) 7) V. Markovnikov, Ber **32**, 1441 (1899) 8) V. Sapozhnikov, ZPhysikChem **49**, 697 (1904); **51**, 609 (1905); **53**, 225 (1905) 9) A. Hantzsch, ZPhysikChem **61**, 257 (1907); **62**, 178, 626 (1907); **65**, 41 (1908); **68**, 204 (1909); CA **2**, 930 (1908), CA **2**, 1773, 1775 (1908), CA **3**, 604 (1909), CA **4**, 533 (1910) respectively 10) A. Kovache & H. Thibon, written in 1918, published MP **34**, 369 (1952) & CA **49**, 4293 (1955) 11) E. von Herz, BritP 145791 (1920) & CA **14**, 3533 (1920) 12) H. Euler, AngChem **35**, 580 (1922); not found in CA 13) J.R. Dupont de Nemours, Chem&MetEng **26**, 11 (1922) & CA **16**, 647 (1922) 14) P. Walden, AngChem **37**, 390 (1924), not found in CA 14a) A. Hantsch, Ber **58B**, 941 (1925) & CA **19**, 2312 (1925) 14b) A. Hantzsch & K. Berger, Ber **61B**, 1328 (1928) & CA **22**, 4318 (1928) 15) A. Stettbacher, AngChem **41**, 716 (1928) & CA **22**, 3991, (1928) 16) F.D. Miles & M. Milbourn, JPhysChem **34**, 2598 (1930) 17) T. Urbański, PolP 19858 (1931); not found in CA 18) A. Hantzsch & W. Langbein, ZAnorgChem **204**, 193 (1932) & CA **26**, 2106 (1932) 18a) E. Berl & O. Hefter, Cellulosechem **14**, 65 (1933), & CA **27**, 5183 (1933) 18b) J.A. Hetherington & I. Mason, JCS **1933**, 105 19) M.S. Belenkii, "Spravochnik po proizvodstvu vzryvchatykh veshchestv", GozKhimIzdat, Moscow (1934); not found in CA 20) L.P. Hammet & F.A. Lowenheim, JACS **56**, 2620 (1924) 21) G. Schiemann & S. Kühne, Cellulosechem **15**, 78 (1934) & CA **29**, 4169 (1935) 22) R. Dalmon, CR **201**, 1123 (1935) & CA **30**, 854 (1936) 23) C.K. Ingold et al, JCS **1936**, 1637 24) L.P. Hammet & H.P. Treffers, JACS **59**, 1708 (1937) 24a) H.M. Spurlin, TransElectrochemSoc **73**, 95 (1938) & CA **32**, 3953 (1938) 24b) F.E. Rhodes & C.C. Nelson, IEC **30**, 648 (1938) 25) M. Usanovich & coworkers, ZhObshchKhim **10**, 224, 227, 230 (1940) & CA **34**, 7285 (1940) 26) R.J. Thomas et al, IEC **32**, 408 (1940) 27) J.H. Simons et al, JCS **1941**, 63, 608 28) A.I. Titov, ZhObshchKhim **11**, 1125 (1941) & CA **37**, 3752 (1943; **18**, 455, 465, 473, 534, 1313 (1948) & CA **43**, 5012 (1948); **24**, 78 (1954) & CA **49**, 14659 (1955) 28a) C.M. McKinley & G.G. Brown, ChemMetEng **49**, 142 (1942) & CA **36**, 4754 (1942) 29) T.L. Davis, "The Chemistry of Powder and Explosives", John Wiley & Sons, London (1943) 30) R. Dalmon, MemServChiml'Etat **30**, 191 (1943); **31**, 58 (1944); not found in CA 31) A. Quilico & M. Simonetta, Gass **76**, 200, 255 (1946) & CA **41**, 963 (1947) 32) F.H. Westheimer & M.S. Karasch, JACS **68**, 871 (1946) 32a) R.A. Ogg, JChemPhys **15**, 337 (1947) 32b) G.M. Bennet et al, JCS **1947**, 474, 1185 33) R.J. Gillespie & D.J. Miller, QuartRevs **2**, 277 (1948) & CA **43**, 3799 (1949) 34) N.J. Spasokukotskii, Us-

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Nitrato. Prefix indicating an organic compound containing the radical $-O.NO_2$

Nitratodimercuriacetaldehyde.
$OHC.C(:Hg).Hg.O.NO_2$, mw 504.20, N 2.77%, colorless prisms, puffs off on heating, practically insol in w. Can be prepd by passing acetylene, or by the gradual addition of an alc soln of acetaldehyde, into a soln of mercuric nitrate in dil nitric acid

Refs: 1) Beil **3**, 606 (listed under Oxidimercuriacetaldehyd) 2) K.A. Hofmann, Ber **31**, 2213 & 2784 (1898) and **38**, 2002 (1905)

Nitratotrimercuriacetaldehyde.
$OHC.C\begin{pmatrix}.Hg\\.Hg\end{pmatrix}:O.Hg.O.NO_2$, mw 720.79, N 1.94%, light grey powd, puffs off on heating. Can be prepd by passing a stream of acetylene for 2 hours thru a mercuric oxide soln in 30% nitric acid

Refs: 1) Beil **3**, 607 2) K.A. Hofmann, Ber **31**, 2787 (1898) and **38**, 2004 (1905)

NITRATOPHOSPHITES

Several salts of a hypothetical nitratophosphorous acid, $HNO_3.H_3PO_2$, are known which are explosive

Lead Nitratophosphite (LNP).
$Pb(NO_3)_2.Pb(H_2PO_2)_2$ or $[Pb(NO_3)(H_2PO_2)]$, mw 668.43, N 4.19%, heavy white granular crysts; mp, starts to decomp above 100°, puffs off at about 180°. Was prepd by von Herz (Ref 2) by adding a hot satd soln of Pb nitrate (331g) to a boiling satd soln of Ca hypophosphite (170g), cooling the mixt rapidly with efficient stirring, upon which Pb hypophosphite separates. After filtering, 250g of the ppt are added with stirring to a boiling soln of Pb nitrate (500g) in 1500ml of w, and rapidly cooled. The LNP ppt is filtered and dried at 40–50°

Its rate of deton is comparable to that of LA and its thermal stability is quite good (no weight loss at 80° for several days). It burns in air, producing a hot flame

The relatively small volume of gas liberated on its decompn, $2[Pb(NO_3)_2.Pb(H_2PO_2)_2] \rightarrow 2Pb_2P_2O_7 + 4H_2O + 2N_2 + O_2$ (117ℓ/kg, as contrasted with 314ℓ/kg for MF or 230ℓ/kg for LA), inhibits its use as an initial expl by itself, but does not prevent its use in mixts such as LNP 30–60%, Sb sulfide & Ba nitrate, 70–40%

Its suitable sensitivity to friction and impact (comparable to that of MF), its stability and high flame temp, render it very suitable for percussion-fuze use. An additional asset is that LNP functions in a practically smokeless manner, leaving little residue or slag

Refs: 1) Mellor **8** (1928), 887 2) E.R. von Herz, SS **11**, 365 & 388 (1916)

Mercurous Nitratophosphite.
$HgNO_3.Hg(H_2PO_2).H_2O$, mw 546.24, N 2.56%, white powd; mp, turns grey at 90°, explds at 100°. It was prepd by Hada (Ref 2) by adding a fairly concd soln of K hypophosphite to a

soln of mercurous nitrate, avoiding an excess of hypophosphite. [The soln of mercurous nitrate, free from nitrous acid, can be prepd by dissolving mercuric oxide to saturation in nitric acid, and then shaking the soln violently with metallic Hg for a few minutes.] As the Mercurous Nitratophosphite ppt decomps when left in contact with the mother liquor, it must be filtered and dried immediately on a porous plate without washing. It is sl sol in w, in which it decomps with the separation of Hg

Mercurous Nitratophosphite explds on being heated to about 100°, or on being touched with a hot wire. When left in a vacuum desiccator, it eventually loses its w of crystn, but undergoes no decompn

Refs: 1) Mellor **8** (1928), 885 2) S. Hada, JCS **67**, 225 (1895)

Nitre. Same as Saltpeter. See as K nitrate under List of Nitrate Compounds in this Vol

Nitrérythrite. Fr for Erythritol Tetranitrate. See in Vol **5**, E124-L to E125-L

NITRIC ACID

HNO_3, mw 63.02, N 22.23%, colorless liq when free of dissolved NO_2, otherwise sl yel. Possesses a pungent odor; vapors toxic when inhaled. Mp –41 to –42°; bp 86° (decompn, 21.5° at 24mm, d 1.502g/cc at 25/4°; RI 1.397 at 16.4°. Sol in eth & w. The following varieties are commercially available in the USA:

1) Nitric acid c.p., d 1.42g/cc, which corresponds to about 70% HNO_3

2) Nitric acid, tech 40°Be, which corresponds to about 62% HNO_3

3) Nitric acid, c.p., Fuming, d 1.50g/cc, which corresponds to about 95% HNO_3

4) Nitric acid, tech, "Fuming", d 1.49–1.50 g/cc, which corresponds to about 90% HNO_3

5) Nitric acid, c.p., "Red Fuming", d 1.59–1.60g/cc, which corresponds to 100% HNO_3 containing about 25% dissolved NO_2

6) Nitric acid, tech, "Red Fuming", d 1.59–1.60g/cc – same as above

7) Nitric acid, c.p. absolute (100% HNO_3), d about 1.513g/cc (Refs 33, 34, 37, 39 & 40)

Historical. A deposit of metallic Ag as part of the markings on ancient Egyptian mummy cases has led to the conclusion that since Ag nitrate was used to form these markings, a knowledge of the manuf & use of nitric acid to prepare the Ag nitrate must certainly have been available (Ref 30). However, the first written description of the prepn of nitric acid, known as "aqua dissolutiva", appeared in the 17th century Latin work, "De Inventione Veritates", wherein it was claimed that the method was discovered by the Arabian alchemist Geber in the 8th century (Refs 9, 13 & 30). The described acid was capable of dissolving Ag or S, and, when mixed with sal-ammoniac, of dissolving Au. The method of prepn consisted of distg saltpeter with vitriol, perhaps in the form of sulfates such as those of Cu, and Al. A similar method was used by Albert Magnus in the 12th century, whereas the Frenchman R. Lully (Lullins), in the 13th century, heated saltpeter with either Fe sulfate or clay. G. Agricola, in the 16th century, described all the previous methods employed, and J. Kunckel, in the 17th century, prepared it by heating saltpeter with white As. In the same century (about 1648), J.R. Glauber prepared nitric acid by heating saltpeter with sulfuric acid, a method that was used thereafter until recently replaced by the ammonium oxidation method. Glauber proved that his product was the same as the acids previously obtained by heating saltpeter with substances other than sulfuric acid. He called his acid "aqua fortis" & "spiritus acidus nitri", but it later became known as "spiritus nitri fumans Glauberi". The French at first called it "eau de depart", then "l'esprit de nitre" & finally "l'acide nitrique" or "l'acide azotie". The Germans at first called it "scheidwasser" (by Basil Valentinus in 1624) & later, "stickstoffsäure"

In about 1750, a Frenchman, G.F. Rouelle, devised a method for concg the acid by distg the weak nitric acid with concd sulfuric acid. This method is used even at the present time (Ref 30)

The chemical nature of the acid remained unknown for a long time, further investigation being obscured thruout the late 17th & early

18th century by the Phlogiston Theory. In 1776, A.L. Lavoisier demonstrated the presence of oxygen in nitric acid, and in 1785, H Cavendish showed that nitric acid was produced when humid air was submitted to electric sparking, conclusively proving it contained both nitrogen & oxygen. In 1816, J.L. Gay-Lussac & C.L. Berthelot established its exact compn (Ref 30)

The application of nitric acid to the arts & crafts seems to have followed shortly after sulfuric acid became an article of commerce. With the invention of the distn process by Glauber in 1648, the acid seems to have been in demand by jewellers, gilders & brass-finishers, because of its effect on most of the non-ferrous metals, especially Cu. It was used for the "parting" of Au from Ag and for Au & Pt refining. However, for centuries the principal object for the collection or manufacture of nitric acid has been the prepn of gunpowder, expls & proplnts (Ref 30)

Nitric acid occurs naturally, in traces, in the atmosphere & in rain w from the electrical discharge of lightning and from nuclear explns. Indeed, the natural nitrates of the world have probably been formed by the action of naturally occurring nitric acid to the extent of 4–6 lbs of combined nitrogen per acre (Ref 30)

For many years nitric acid was prepd by the method of Glauber which involves heating saltpeter with concd sulfuric acid. In 1798, I. Milner experimentally oxidized NH_3 vapor over heated Mn dioxide; the resulting nitric acid fumes were led into w. In 1824, W. Henry almost duplicated the present commercial method of manuf when he showed that ammonia could be oxygen oxidized in the presence of a Pt sponge catalyst. Until 1900, commercial prodn of nitric acid used K nitrate & sulfuric acid. However, with the opening of Chilean saltpeter deposits, K nitrate was replaced by Na nitrate. Birkeland & Eyde developed their electric arc process in Norway in 1903, replacing the distn process. In 1908 the first commercial ammonia oxidation plant was built in Germany with a 3-ton per day capacity. An economical source of NH_3 was assured with the development of the Haber-Bosch ammonia synthesis process in 1913. The very heavy demands for electrical power made the electric arc process economically unfeasible when compared with the NH_3 oxidation process (Refs 30, 34 & 36)

Uses. Since 1947, 70 to 85% of the annual USA production of nitric acid has gone into the production of NH_4 nitrate fertilizer, initially in the form of solid prills; currently, increasing amounts have been supplied mixed with excess ammonia and/or urea as aqueous "nitrogen solution" for direct application to the soil. Some 15% is used in expls (nitrates & nitro compds), and about 10% is consumed by the chemical industry. As the red fuming acid or as nitrogen tetroxide, nitric acid is used extensively as the oxidizer in proplnts for rocketry. It is estimated that current USA capacity for nitric acid is in excess of 10 million tons (Refs 30, 34, 36 & 37)

Processes for Nitric Acid Manufacture

All processes for the manuf of concd nitric acid have the following four stages in common:

(a) Formation of nitric oxide, NO

(b) Oxidation of nitric oxide to nitrogen peroxide, which is a mixt of NO_2 and N_2O_4

(c) Absorption of peroxide in w to form a weak soln of nitric acid

(d) Concn of the weak acid to the required grade of acid

There is only one exception to this scheme, a process in which highly concd nitric acid is directly produced by absorption of the nitrogen oxides in perchloric acid (Ref 36)

Nitric Acid from Saltpeter. In the manuf of nitric acid from Chile saltpeter, 85 parts of saltpeter and 98p of concd sulfuric acid (both calculated on 100% basis) were heated together in large iron retorts, often capable of holding 5 tons or more of ingredients. The following reaction took place:

$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$. The reaction should be conducted below 150° to avoid loss by decompn of the HNO_3. The resulting "bisulfate" residue is obtained in an easily fusible mass, which could be withdrawn in a fluid condition merely by opening a plug at the bottom of the retort. However, in actual practice, it was preferred to raise the temp toward the end of the reaction so that part of the w would be driven off: $2NaHSO_4 = Na_2S_2O_7 + H_2O$. The resulting pyrosulfate was run off in a fluid condition into iron pans, where it solidified and was called "**nitre cake**". This cake could be con-

verted either into Na_2SO_4, by heating with NaCl, or into Na_2S (Refs 7, 8, 9, 12, 16 & 30). If weak nitric acid is distd without being previously mixed with sulfuric acid, the highest concn obtainable in the distillate is about 68%, because nitric acid forms a constant boiling mixt with w at that concn

In addition to systems using distn at atm press in the prepn of nitric acid, there was also the so-called Valentiner's Vacuum Process. This method was more expensive to install, but it gave whiter acid because distn was conducted at low temp, thus avoiding decompn of HNO_3 with consequent formation of NO and NO_2. The Valentiner process was modified so as to obtain the best results with the press reduced to 15–25 mm of Hg

A continuous process for the manuf of nitric acid from saltpeter and sulfuric acid was introduced in 1894 by Prentice (Ref 9, p 147)

Nitric Acid by the Oxidation of Ammonia. Here, the catalytic oxidation of ammonia under press using a Pt catalyst maintained at a temp of 900–1000° is the process used. The reaction press is the rate determining step, being directly proportional to the product nitric acid concn (Refs 6, 22, 26, 30, 34, 36, 37 & 41).

Direct Production of Concentrated Nitric Acid. The concept of "direct production" of nitric acid covers many processes. In one, aq nitric acid is agitated with an excess of liq nitrogen dioxide (N_2O_4) until two layers are formed. The lower layer consists of a soln of N_2O_4 in nitric acid of about 75% strength, while the upper layer consists of liq N_2O_4 in which is dissolved strong (98–99%) nitric acid. The upper layer is removed and the N_2O_4 driven off by distn

Manning (Refs 18 & 19) describes a method of direct prepn of strong nitric acid in which a mixt of dil (60–65%) nitric acid and liq N_2O_4 is treated with oxygen under high press

Atroschenko and Kargin (Ref 26, pp 223–268) describes several methods of prepn of concd nitric acid directly from oxides of nitrogen

Instead of using air for the oxidation of ammonia, some investigators, for instance Cze and Chi Wu (Ref 21), advise using oxygen, especially in cases where oxygen is available cheaply. According to Thorpe (Ref 22, p 571), the use of oxygen was first recommended by Partington and Prince in 1924

Many variations in nitric acid processes are operated, and are distinguished by the characteristic conditions of the oxidation of ammonia and absorption of the oxides to produce nitric acid, and by the concn or strength of the nitric acid which is produced. These processes are known by such titles as atmospheric process, pressure process, Montecatini process, Bamag-Meguin process, etc. Pressure process plants are those in which both oxidation of ammonia and absorption of oxides are carried out under superatmospheric press, generally in the range of 50 to 125psig. These plants comprise over 62% of the installed capacity of the USA (Ref 36). Most of these plants as well as pressure process plants constructed more recently, produce nitric acid of a concn not greater than about 62% and generally in the range of about 50 to 60% strength. In recent years, considerable progress has been made in increasing the size and in proving both the thermal and the economic efficiency of pressure process nitric acid plants, so that plants of recent construction are thermally self-sufficient; on balance they may even be net producers of energy, usually in the form of steam, which can be utilized in other nearby operations outside the nitric acid manufg plant. But the standard product of these more economical, larger, modern, thermally self-sufficient, pressure process nitric acid plants has continued to be nitric acid of strengths up to but not exceeding about 62% concentration, by wt (Ref 36)

Much nitric acid is used at concns of 95% by weight, or more, Acids of this concn can be produced directly by more costly processes, but generally are produced most economically by a separate nitric acid concentrating operation on feed of dil nitric acid from a pressure nitric acid plant. Such concn requires extractive distn of weak nitric acid in the presence of a third component, such as sulfuric acid or magnesium nitrate, which acts as a dehydrating agent. Obviously, less of the dehydrating agent will be required if the nitric acid feed to the process is stronger than 63% by weight (Ref 36)

Absorption of Nitrogen Oxides in Water to Form Nitric Acid Solution. The production of nitric acid from nitrous gases such as are obtained in

the catalytic combustion of ammonia, requires an oxidation of these gases and their absorption in w or an aq soln already containing nitrogen oxides. In this process, the nitric oxide has to be converted into nitrogen dioxide. By absorption of the nitrogen dioxide in w, nitric oxide is formed, besides the nitric acid, and this nitric oxide has to be subjected once more to oxidation. In the large scale manuf of nitric acid, the oxidation and absorption of the nitrous gases has hitherto been carried out in acid towers or columns, in which the absorbing liq, which is w or a dil acid soln, starting at the top of the tower, uniformly trickles thru several layers of packing material, being collected at the bottom of the tower in a collecting vessel, from which it is lifted by a pump, after having been duly cooled, back to the top of the tower (Ref 36)

Nitric Acid Production in a Nuclear Reactor. While this process is widely applicable, it has been found to be highly advantageous in the fixation of nitrogen. Thus, it is possible to directly produce nitrogen dioxide from the normal constituents of air thru the utilization of the energy of recoil fragments from atomic fission. One possible highly useful product of such a reaction is nitric acid, which can be processed from nitrogen dioxide by the addition of w and oxygen after sepn of the nitrogen dioxide from unreacted gases and admixed radioactive fragments. Particularly advantages of this process include the following: the only raw materials required are air and w; a low operating temp is combined with a high effective processing temp; the process has an inherent ultrafast built-in quench; and the process achieves the direct conversion of nuclear energy into chemical energy (Refs 34 & 36)

Nitric Acid Production by Detonation Incurred Shock Wave. J.F. Haller (Ref 36) found that passing a detonation or shock waves thru a gaseous mixt comprising nitrogen and oxygen produces nitrogen oxides. According to this process, a make charge of a gaseous mixt comprising nitrogen and oxygen is introduced into a portion of a reaction space, and a detonatable material is introduced into the remaining portion. The detonatable material is detonated and the detonation wave impinges on the make charge, causing reaction between the nitrogen and oxygen and formation of nitrogen oxides. The nitrogen oxides produced are suitable for use in making the corresponding acids

Nitric Acid Production using Pebble Bed Regenerators (Wisconsin Thermal Process). When air or similar mixts of nitrogen and oxygen are subjected to temps of the order of 2000°C, part of the nitrogen and oxygen react with one another to form nitric oxide, this reaction being generally termed "nitrogen fixation". The reaction is reversible, however, and the newly formed nitric oxide will quickly decomp into its constituents, unless the temp is rapidly reduced to materially lower levels at and below which the rate of decompn is so slow as to be negligible. Thus, to recover nitrogen oxide for practical use, the reaction gases must be rapidly chilled to a sufficiently low temp to stabilize the nitric oxides

In his US Patent 2422081, Frederick G. Cottrell (Ref 36) discloses methods and apparatus to meet this requirement while at the same time providing such rapid chilling rates for the newly formed nitric oxide as will reduce its decompn to a tolerable minimum. According to this patent, the hot reaction gases produced in the combustion zone of a furnace are passed thru a bed of heat-absorbing pebbles of a refractory material that chill the bases and are themselves heated in the process; after the pebbles in the bed have become heated to a sufficiently high extent, the direction of the process is reversed; that is, the fresh air is delivered to the combustion zone thru the newly heated pebble bed, while the reaction gases are discharged thru another pebble bed located at the opposite side of the combustion zone (Ref 36). The process is not considered to be economically feasible (Ref 34)

Laboratory Preparation of Absolute Nitric Acid. Strong nitric acid, 99%+, free from oxides (white) is used for many nitrations. Since nitric acid of this quality is not generally commercially available, it is usually prepd in small quantities in the laboratory as needed. The customary procedure is to mix one p of concd nitric acid (d 1.42g/cc) with 2p of sulfuric acid (d 1.84g/cc) and to distill the nitric acid from this mixt under reduced press, using an all glass system

Distillation under reduced press is necessary to minimize the decompn of pure nitric acid,

which decomps while being distd according to the equation: $4HNO_3 \rightarrow 4NO_2+2H_2O+O_2$ (Refs 13 & 32)

The vacuum distn of a mixt of Na nitrate and concd sulfuric acid, with condensation of the liq just above its fr p, results in a colorless liq with a fr p of -41.5° (Refs 32 & 34)

Properties of Nitric Acid

Physical Properties. According to Lagowski (Ref 32), X-ray analysis of a single crystal of nitric acid shows a monoclinic unit cell (symmetry $P2_1/a-C_{2h}^5$) with the following dimensions: a=16.23, b=8.57, and c=6.31Å, and $\beta=90^\circ$. The unit cell contains 16 molecules, and the calc d is 1.895g/cc at -41.6°

The Raman spectrum of the monohydrate, $HNO_3.H_2O$, shows it to exist as the hydroxonium salt, $H_3O^+NO_3^-$[13]. Also, according to analyses of the Raman spectrum, nitric acid exists in aq solns either as a **pseudo-acid**, $NO_2.OH$ or as a **true acid**, $NO_3^-.H^+$. In 10 molar aq soln, both acids are present in equal amounts, being caused by the self-dissociation of nitrogen pentoxide (N_2O_5), while in a 6 molar soln, the pseudo acid is present only to the extent of 2%, and the more dilute the soln, the less pseudo acid is present. In very concd solns, the true acid is present only in small quantities (Refs 32 & 33)

The liq acid has a mw greater than that expressed by the formula HNO_3, probably $H_2N_2O_6$ or $H_3N_3O_9$

Pure abs nitric acid exists only below its fr p as a white crystalline mass. The moment it becomes liq, some slight decompn occurs and the acid assumes a light coloration due to the formation of nitrogen dioxide

The nitrate ion $(NO_3)^-$ is one of the most electronegative ions and its absolute velocity at 18° under a potential gradient of 1 volt per cm is 6.4×10^{-4}cm per second (Ref 9, p 340)

It can be seen from Fig 1 (Ref 30, p 13), that when an aq soln of nitric acid is boiled under atm press, mostly w at first evaporates with only a small amount of HNO_3. This lasts until the concn of the distillate reaches 68.18% HNO_3 and the bp climbs to 121.70°. Further boiling would neither increase nor decrease the concn of the distillate and it may be said that the 68.18% acid is a constant boiling mixt. If the press is reduced to 735mm, the bp drops to

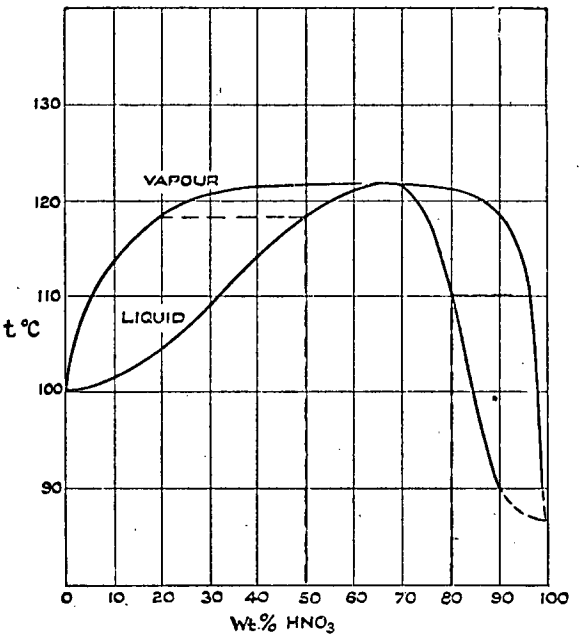


FIG 1 – Boiling-Points and Vapour Compositions of Nitric Acid–Water Mixtures (from Ref 30, p 13)

120.5° and the compn of the distillate is reduced to 68% HNO_3

According to Kirk & Othmer (Ref 34), nitric acid is completely miscible with w and is generally known and used as an aq soln, sometimes with the addition of dissolved nitrogen oxides at high concns. Two hydrates may be crystallized from acid solns: a monohydrate ($HNO_3.H_2O$), corresponding to 77.77% acid by wt, with a mp of -37.62°, and a trihydrate ($HNO_3.3H_2O$), corresponding to 53.83% by wt, melting at -18.48° With local maxima at the freezing points of the four crystal forms, the freezing point curve for nitric acid solns is quite irregular. Local minima are found at concns of about 32, 71, and 91% acid, as shown in Table 1 (Ref 34, p 798)

The heat capacities of liq & gaseous nitric acid may be expressed as functions of the absolute temp, T, by Eqs 1 & 2 (according to Lagowski, Ref 32, p 153)

$Cp\ (liq) = 28.64-(8\times10^{-3}T)$,
$T = 232-305^\circ K$ (1)

$Cp\ (gas) = 6.57+(18.75\times10^{-3}T)$,
$T = 275-500^\circ K$ (2)

Table 1
Physical Properties of Nitric Acid Solutions

Percent HNO_3 by wt	Density at 20°C, g/ml	Freezing point, °C	Boiling point, °C	Specific heat at 20°C, cal/(g)(°C)	Partial pressures at 20°C, mm Hg		Viscosity at 20°C, cP	Thermal conductivity at 20°C, Btu/(hr)(ft²)-(°F/ft)
					HNO_3	H_2O		
0.0	0.99823	0	100.0	1.00		17.5	1.0	0.35
10.0	1.0543	−7	101.2	0.89		17.0	1.1	0.33
20.0	1.1150	−17	103.4	0.81		15.2	1.2	0.31
30.0	1.1800	−36	107.0	0.76		13.2	1.4	0.29
40.0	1.2463	−30	112.0	0.72		10.8	1.6	0.27
50.0	1.3100	−20	116.4	0.68	0.2	7.9	1.9	0.25
60.0	1.3667	−22	120.4	0.63	0.9	4.9	2.0	0.23
70.0	1.4134	−41	121.6	0.58	2.9	2.6	2.0	0.21
80.0	1.4521	−39	116.6	0.53	10.5	0.9	1.9	0.20
90.0	1.4826	−60	102.0	0.47	27.0	0.2	1.4	0.18
100.0	1.5129	−42	86.0	0.42	45	0	0.9	0.16

The thermodynamic properties of nitric acid and its hydrates are given in Table 2 (Refs 32 & 34)

Table 2
Thermodynamic Properties of Nitric Acid and Its Hydrates

	HNO_3	$HNO_3.H_2O$	$HNO_3.3H_2O$
nitric acid, wt %	100.0	77.77	53.83
freezing point, °C	−41.59	−37.62	−18.47
heat of formation at 25°C, kcal/mole	−41.404	−112.966	−212.203
free energy of formation at 25°C, kcal/mole	−19.100	−78.410	−193.701
entropy at 25°C, kcal/(mole)(°K)	37.19	51.83	82.92
heat of fusion, kcal/mole	2.503	4.184	6.954
heat of vaporization at 20°C, kcal/mole	9.43		
heat of dilution to infinite dilution, kcal/mole	−7.97	−4.73	−2.12
gaseous entropy, cal/mole (°K)	63.62		

The thermodynamics for aq dilution of nitric acid is expressed by Eq 3 and the heat of dilution can be found in Fig 2 (Ref 30, p 15)

HNO_3 (liq)+xH_2 ⇌ $HNO_3.xH_2O$(s) (3)

when x	=	1	3
$\Delta G_{343.1°K}$ (cal/mole)	=	−2523	−4404

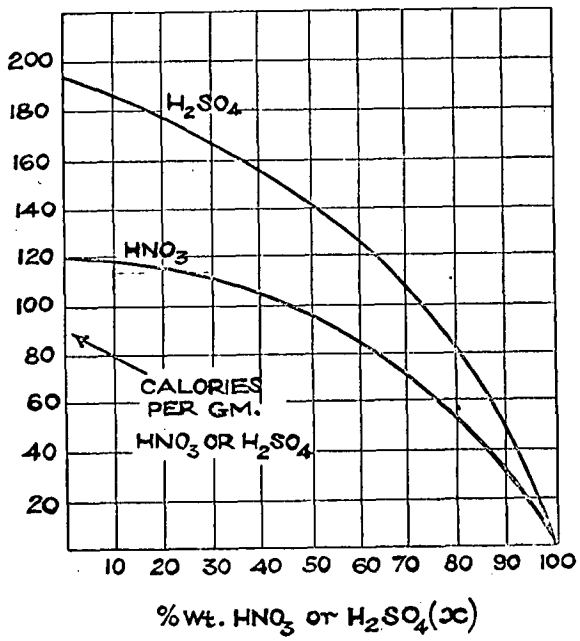


FIG 2 – Heat of Diluting 1 gm HNO_3 or H_2SO_4 to X% (Calories) (from Ref 30, p 15)

The formation of nitric acid in various states results in the following thermodynamic quantities (Ref 32)

$$1/2N_{2(g)} + 3/2O_{2(g)} + 1/2H_{2(g)} \rightarrow HNO_3 \quad (4)$$

	Liquid	Gas	Aq, a=1
ΔH (kcal/mole	–41.35	–31.99	–49.32
ΔG (kcal/mole)	–19.03	–17.55	–26.35

The absorption of nitric acid vapor at 1.4μ has been measured so that the equilibrium represented by Eq 5 could be studied

$$H_2O_{(g)} + 2NO_{2(g)} + 1/2O_{2(g)} \rightleftharpoons 2HNO_{3(g)} \quad (5)$$

The equilibrium constant, K_p, varies with temp in the following manner:

T°, K	343	363	391	393
$\log_e K_p$	4.6	2.9	0.25	0.15

The values for surface tension, γ, are (Ref 32):

t, °C	0	20	25
γ, dynes/cm	43.56	41.15	40.00

The Eq for the free energy of vaporization of nitric acid for the temp range 275–305°K has been obtained from vapor pressure measurements (Ref 30)

$$\Delta G = 14744+22.07T(\log_e T)-13.38x10^{-3}T^2-166.26T \text{ (cal/mole)} \quad (6)$$

The bp calcn using Eq 6 is 84°

The electrical properties of nitric acid are presented in Table 3 (Ref 30):

Chemical Properties

The action of nitric acid on various metals as well as on constructional materials is described in Perry's Handbook, 3rd ed (Ref 28, p 1502); in the book by Atroschenko and Kargin (Ref 26), pp 366–369 and in Refs 23, 24 & 25

According to Kirk & Othmer (Ref 34), the reactions of nitric acid may be classified conveniently into three groups: (1) reactions as an acid (formation of inorganic nitrates); (2) reactions as an oxidizing agent; and (3) organic reactions

Nitric acid is a strong, monobasic acid. It reacts readily with alkalies, oxides, and basic materials, forming salts. The reaction with ammonia, forming ammonium nitrate, for use as a fertilizer, is by far the largest single industrial outlet for nitric acid

Nitric acid is a strong oxidant. Organic materials such as turpentine, charcoal, & charred sawdust are violently oxidized, while alc may

Table 3
Electrical Properties of Nitric Acid

T, °C	–20	–10	0	5	10	14	15	24	25	35
Dielectric Constant, ε	–	–	–	–	–	50±10	–	–	–	–
Dipole moment, μ, Debye	–	–	–	–	–	–	2.16	–	–	–
RI, n_D	–	–	–	1.4030	–	–	–	1.3970	–	1.3910
Specific Conductance, $Kx10^2$	3.40	3.67	3.77	–	3.65	–	3.68	–	3.72	–

react explosively with concd nitric acid. In addition, furfuryl alcohol, aniline, etc are used with nitric acid in rocket fuels. Most metals, with the exception of the Pt metals and Au, are attacked by nitric acid, some are converted into oxides (As, Sb & Sn), but most are converted to nitrates. Metals which are not attacked are Al and Cr steel; these become passivated by the acid. Concd nitric acid will rapidly oxidize to a higher oxidation level the oxides, sulfides, etc of the lower oxidation states of most elements (Ref 34)

Again, according to Kirk & Othmer (Ref 34), the activity of nitric acid as an oxidizing agent is apparently dependent upon the presence of free oxides of nitrogen. Pure nitric acid does not attack Cu, for example, but when oxides of nitrogen are introduced, the reaction is at first slow and then proceeds with great rapidity and violence. The reduction products of nitric acid vary with the concn of the acid and the strength of the reducing agent with which it reacts. A mixt of oxides is generally produced; dil nitric acid tends to give a predominance of nitric oxide while concd acid produces a mixt richer in nitrogen dioxide. Very dil acid reacting with a storng reducing agent such as metallic Zn produces a mixt of ammonia and hydroxylamine

Nitric acid also undergoes reactions with organic compounds wherein the acid serves neither as an oxidizing agent nor as a source of hydrogen ions. The formation of organic nitrates by esterification (O-nitration) involves reaction with the hydroxyl group:

$$ROH + HONO_2 \rightarrow RONO_2 + H_2O$$

Esterification with nitric acid includes the industrially important reactions with glycerol to form glyceryl trinitrate (nitroglycerin), and with cellulose to form cellulose nitrate (nitrocellulose)

C-Nitration does not involve the hydroxyl group but is a reaction with an aliphatic or aromatic hydrocarbon or a substituted derivative to produce such compounds as the nitroparaffins and the nitrotoluenes:

$$R{-}H + HONO_2 \rightarrow RNO_2 + H_2O$$

These reactions are conceived to be with the positive "nitronium" ion NO_2^+, which is formed in nitric acid when free of w. These reactions therefore normally take place with a mixt of concd nitric and sulfuric acid, the sulfuric acid serving to remove the water formed

In both the liq & the vapor phase, nitric acid decomps as $2HNO_3 \rightleftharpoons 2NO_2+H_2O+\frac{1}{2}O_2$ with a second equil with NO_2; $2NO_2 \rightleftharpoons 2NO+O_2$. The rate determining step is the dehydration of HNO_3;

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

for the low-press vapor phase decompn within the 260–475° temp range (Ref 30)

Other techniques for decompng nitric acid are photochemical & flash photolysis. The photochemical decompn of nitric acid is not solely a gas-phase reaction; X-rays have caused the evolution of O_2 from nitric acid crystals. The use of flash photolysis has shown the nitrate radical to be an intermediate in the decompn (Ref 30)

See also under **Nitration** in this Vol

Nitric Acid Explosives. According to Stettbacker (Ref 20), solns of aromatic nitrocompds in fuming nitric acid are very powerful expls, which are inexpensive and simple to prepare. Such solns can be kept for several months in Fe or Al containers, even in sunlight, without decompg. These mixts can be transported in closed containers without danger of press rise

When placed in air-tight Fe or Al containers, they can be used for underwater work. In such cases it is not necessary to insert the blasting cap into the acid charge, but merely to press it against the outside of the sheet metal with an insulating band. Since fuzes burn underwater, it can be lighted in the air, and the entire assembly then placed at the required depth

When, for example, a mixt of NB is mixed in proper proportion with nitric acid, the resulting expl is as powerful as the corresponding amt of PA. This type of expl is known as a *Sprengel type*, ie, in which strong nitric acid is mixed with some combustible material or an expl. The expls *Hellhofite* and *Dithekite* consist of nitric acid and NB, and *Oxonite* contains nitric acid and PA

An interesting plastic expl contg nitric acid was patented in 1887 by M. Jeschek & J. Jaresch of Vienna. It was prepd by adding 20 to 40% cellulose (cotton, straw, hemp, flax, etc) to a liq consisting of an aromatic nitrocompd and an amt of nitric acid sufficient to nitrate all the cellulose to NC, and to give a favorable OB to the mixt (Ref 4)

Also see under **Liquid Explosives** in Vol **7**, L26-R

Other Uses of Nitric Acid. As mentioned earlier, fuming nitric acid (FNA) when mixed with alc, toluene or acet anhydr will cause an expln. However, there are many other uses for FNA in energetic materials technology. As either red fuming nitric acid (RFNA) or as nitrogen tetroxide, it is used extensively as the oxidizer in proplnt systems for ram-jets, jet motors, space rockets and other missiles (Refs 37, 38 & 39). See also under **Liquid Propellants** in Vol **7**, L24-Rff

Another extremely important application area for FNA and RFNA is to either directly nitrate or be used in mixed acids to nitrate raw materials to yield widely used expls and proplnt ingredients (Refs 29, 31, 33, 38 & 39). Also see under **Nitration** in this Vol

Analytical. Analysis and assay procedures for nitric acid may be found in Refs 1, 2, 10, 11, 15, 17, 27, 29, 34, 35, and in this Vol under **Nitrogen Determinations in Energetic Materials.** For mfg plant electronic control systems see Ref 36; for plant chemical control procedures see Refs 3, 5, 14 & 26. USA Mil Specs are listed in Refs 29 & 35

Written by **H. L. HERMAN**

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Nitric Ether. See under Ethane Nitrate in Vol **6**, E143-R

Nitric Oxides. See under Nitrogen Oxides in this Vol

NITRIDES

Antimony Nitride. SbN, mw 135.76, N 10.32%, org cryst, mp 550–750° (decomps exply), bp 750° (subl, decomps). Prepd by heating Sb to a dull redness in a current of N_2. Decomps explosively when heated or upon addition of cold w
Refs: 1) Gmelin, Syst Nr **18**, Teil B (1927), 391–2 2) Mellor **8** (1928), 124

Bismuth Nitride. BiN, mw 223.01, N 6.28%, blk cryst, d 7.8g/cc. Prepd from Bi tribromide or trioxide by reaction with potassamide in liq ammonia. The dry nitride explds when treated with w or dil acids; sl decompn with w vapor. Explds when shaken, yielding Bi
Refs: 1) Gmelin, Syst Nr **19** (1927), 124; (1947), 648 2) Mellor **8** (1928), 124

Bromine Nitride (Nitrogen bromide or Nitrogen tribromide). NBr_3 (probably), mw 253.74, N 5.52%, dark red volatile oil, strong smelling, which attacks the eyes. Prepd by action of NCl_3 on KBr (Refs 1 to 4). Bromine Nitride is very unstable and a powerful expl. It explds violently when brought into contact with P or As
Refs: 1) Gmelin, Syst Nr **7** (1925), 333 2) Mellor **8** (1928), 605 3) N.A. Millon, AnnChimPhys (2) **69**, 75 (1938) 4) Partington (1949), 556 5) W.L. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, NY (1964), 54–55

Cadmium Nitride. Cd_3N_2, mw 365.22, N 7.67%, or cryst (turns blk), bp subl over 100°, d 7.67g/cc. Prepd by heating the amide, $Cd(NH_2)_2$ under vac for 36 hrs at 180°. Compd is decompd by w and oxidized by air. Reacts explosively with dil acids and bases, and upon strong heating. Q_f 38.6 ± 0.4Kcal/mole
Refs: 1) Gmelin, Syst Nr **33** (1925), 75 2) Mellor **8** (1928), 107 3) Ibid **8** (1) (1964), 161

Cerium Nitride. CeN, mw 154.13, N 9.09%, bronze-blk cryst, mp 320–762° (decompn). Prepd by heating Ce to 850° and reacting with N_2. Reaction is sudden and violent, accompanied by a brilliant incandescence. It reacts violently with w, dil acids and moist air
Refs: 1) Gmelin, Syst Nr **25** (1938), 115 2) Mellor **8** (1928), 120–1

Chlorine Nitride. (Nitrogen Trichloride, Trichloramine, or Stickstofftrichlorid in Ger). NCl_3, mw 120.38, N 11.64%; yel, vol, pungent-smelling oil, mp <–40° (Porret in 1813 reported –27°), bp about 71° (explds at 93–95°), d 1.653g/cc. Sol in cold w (decompd by hot w), alc, eth, chlf, bz, CCl_4, CS_2 & phosphorous oxychloride. Prepd (with great care) by the action of sodium hypochlorite on amm chloride. The compd also forms at the anode in the electrolysis of concd amm chloride soln. Another prepn consists of bubbling chlorine into a cooled aq soln of amm sulfate & di-n-butyl ether (Refs 1, 6 & 10)

Explds at 60° after 13 sec in a sealed glass tube (Ref 4). Explds spontaneously when frozen and then thawed. Compd is a violent expl, extremely sensitive to impact or friction. It also explds on exposure to strong light (sunlight or diffused), or when in contact with P, As, ozone, fused alkalies, and organic matter such as turpentine & rubber, but not with sugar or resins. Metals & strong acids do not cause it to expld. Q_f 55kcal/mole (Ref 9)

It is very poisonous & attacks the eyes & mucous membranes

Use. Too sensitive to be used as an expl. The bz soln has been used for chlorinating org subs

Analytical. Evolves N_2 quant when reacted with amm chloride

Refs: 1) Gmelin, Syst Nr **6** (1927), 410–17 2) C.T. Dowell & W.C. Bray, JACS **39**, 896–905 (1917) & CA **11**, 1611 (1917) 3) Mellor **8** (1928), 598–605 4) A.Ya. Apin, KhimReferatZhur(Rus) No **8**, 17 (1939) & CA **34**, 5009 (1940) 5) Ibid, JPhysChem(Rus) **13**, 405–22 (1939) & CA **14**, 494–504 (1940) & CA **35**, 2325 (1941); Acta Physico-chem(Rus) **13**, 405–22 (1940) & CA **35**, 7715 (1941) 6) Thorpe **8** (1947), 511–13 7) Partington (1949), 555–6 8) Sidgwick, ChemElems **1** (1950), 705–06 9) W. Jolly, "The Inorganic Chemistry of Nitrogen", Benjamin, NY (1964), 52 10) Anon, C&EN **44**, 46 (1966)

Copper Nitride (Cuprous Nitride). Cu_3N, mw 204.63, N 6.85%, v dk grn powd, mp 300° (decompn), d 5.84g/cc at 25/4°. Sol in concd HCl. Prepd by reaction of ammonia with Cu fluoride at 280°, and is stable at RT

The compd burns explosively at 470° and produces a flaming expln when heated quickly to 500° in air. It is not decompd by percussion or friction. Cu_3N is violently decompd on reaction with w, alc, concd nitric & sulfuric acids. Decomps with dil mineral acids, no reaction with dil or concd alkalies. Q_f −17.8kcal/mole; sp ht 0.1059cal/g/°C

Refs: 1) Gmelin, Syst Nr **60**, Teil B (1958), 139–42 2) Mellor **8** (1946–47), 99–100 & **8** (1964), 154 3) Anon, "Manual of Hazardous Chemical Reactions, 1971", 4th Ed, NFPA **No 491M**, Boston (1971), 87 4) ChemRubHdbk (1975), B-89

Fluorine Nitride (Nitrogen Fluoride or Nitrogen Trifluoride). NF_3, mw 71.01, N 19.73%, colorless gas having a moldy odor or mobile liq, mp −208.5°, fr p > −216.6°, bp −128.8°, d (liq) 1.537g/cc at 129° & (gas) 0.1864lbs/cu ft at 70°F. V sl sol in w. Prepd by electrolysis of fused amm acid fluoride (Refs 2, 3, 4 & 5)

NF_3 explds when mixed with hydrogen and kindled according to the equation: $2NF_3 + 3H_2 \rightarrow N_2 + 6HF$. It is a severe expln hazard, extremely sensitive to shock & blast. Reacts violently with reducing agents, grease & oil, etc. Highly toxic & corrosive to tissue. Q_f −29.7 ± 1.8kcal/mole (Ref 6)

Use. Oxidizer for high energy fuels and in chemical synthesis (Ref 9)

Analysis. NF_3 can be quant anal by reaction with hot hydriodic acid; $NF_3 + 7HI \rightarrow NH_4I + 3HF + 3I_2$; the iodine being titrated, or by reaction with sodium; $2NF_3 + 6Na \rightarrow N_2 + 6NaF$; the nitrogen being measured (Ref 3)

Refs: 1) Gmelin, Syst Nr **5** (1928), 50 2) O. Ruff et al, ZAnorgChem **172**, 417 (1928); **197**, 273 & 395 (1931); **198**, 32 (1931) & **217**, 3 (1934) 3) Thorpe **8** (1947), 511 4) Partington (1949), 555 5) Sidgwick, ChemElems **1** (1950), 704 6) S. Morentz, "Heat of Formation of Nitrogen Trifluoride", **NBSR 6363** (1959) 7) Kirk & Othmer **13**, 815 (1967) 8) Sax (1968), 969 9) CondChemDict (1971), 623 10) Anon, "Manual of Hazardous Chemical Reactions 1971", NFPA **No 491M**, Boston (1971), 178 11) Hackh's (1972), 459

Iodine Nitrides. There are two compds of interest, the triiodide & the triiodide monamine, both of which are very sensitive expls:

Nitrogen Triiodide. NI_3, mw 394.77, N 3.55%, blk powd, mp (explds), bp (subl in vac). Insol in cold w, decomps in hot w; sol in aq $Na_2S_2O_3$ and KCNS. Prepd by the action of gaseous NH_3 on solid $KIBr_2$, followed by rapid w washing (Refs 1, 4, 10 & 11). NI_3 must be kept ether wet. When dry, the slightest shock, vibration, temp rise, air draft, etc, will cause it to detonate (Refs 14 & 15). Under vac, dry NI_3 detonates at pressures under 2×10^{-3}cm. Over this press simple decompn occurs with the evolution of I_2 (Refs 7–9)

Nitrogen Triiodide Monoamine. (Nitrogen Iodoazoimide). $I_3N{:}NH_3$, mw 411.75, N 6.81%, dark red rhombic cryst, mp > 20° (decompn or explds), bp (explds), d 3.5g/cc. Sol in HCl, aq $Na_2S_2O_3$ and KCNS, decompd by w to NI_3. Prepd by adding an iodine chloride soln in HCl to an ammonia soln (Ref 10)

$I_3N{:}NH_3$ detonates according to the equation: $8I_3N{:}NH_3 \rightarrow 5N_2 + 9I_2 + 6NH_4I$. When dry, the compd can expld without apparent external cause (Refs 10–15). It will expld in contact with concd acids, bromine, chlorine, ozone and hydrogen sulfide (Ref 16). The initiation or activation energy is 19.0±1.3kg-cal. Q_f 35.0 kg-cal (Refs 8 & 9)

Analytical. $I_3N{:}NH_3$ can be quant analyzed by reaction with Zn ethyl: $I_3N{:}NH_3 + 3Zn(C_2H_5)_2 \rightarrow 3ZnIC_2H_5 + NH_3 + N(C_2H_5)_3$ & $2NH_3 + Zn(C_2H_5)_2 \rightarrow Zn(NH_2)_2 + 2C_2H_5$. The liberated ethane is measured

Refs: 1) Gmelin, Syst Nr **8** (1927), 593–99 2) O. Silberrad, JCS **87**, 55 (1905) 3) Mellor **8** (1928), 606–7 4) H.W. Cremer & D.R. Duncan, JCS **2750** (1930) 5) W.E. Garner & D.R. Duncan, Nature **135**, 832 (1935) & TrFaradSoc **32**, 567–9 (1936) & CA **30**, 3737 (1936) 6) E. Roederer, ZAnorgChem **226**, 145 (1936) 7) F.R. Meldrum, TrFaradSoc **34**, 947 (1938) 8) F.R. Meldrum, PrRoySoc **174**, 410 (1940) & CA **34**, 3568–9 (1940) 9) Ibid, 425–32 (1940) & CA **34**, 3577–8 (1940) 10) Thorpe **8** (1947), 513 11) Partington (1949), 556–7 12) Sidgwick, ChemElems **1** (1950), 707 13) Kirk & Othmer **13**, 816 (1967) 14) Sax (1968), 969 15) CondChemDict (1971), 623 16) Anon, "Manual of Hazardous Chemical Reactions, 1971", NFPA **No 491M**, Boston (1971), 46 & 178 17) ChemRubHdbk (1975), B-115

Mercury Nitride. Hg_3N_2, mw 629.78, N 4.45%, brown powd, mp (explds). Sol in amm hydroxide, dil acids, concd nitric acid and amm salts. Prepd by adding a soln of mercuric iodide or bromide to an excess of a soln of K amide in liq ammonia (Refs 1–3)

The compd is v expl & requires great care in handling. It will expld on heating, when struck with a hammer, or when rubbed. It explds when brought in contact with sulfuric acid

Hg_3N_2 can be used as a dehydrogenating agent, viz, in liq ammonia soln it reacts with hydrazobenzene yielding azobenzene

Refs: 1) Gmelin, Syst Nr **34**, Teil B (1965), 76 2) Mellor **8** (1928), 107–8 3) Partington (1949), 543 4) Sax (1968), 904 5) Anon, "Manual of Hazardous Chemical Reactions, 1971", NFPA **No 491M**, Boston (1971), 158 6) ChemRubHdbk (1975), B-110

Potassium Nitride. K_3N, mw 131.31, N 10.67%, grn-blk cryst, mp 343°, ignites spontaneously in air. Effervesces violently with w quantitatively evolving ammonia. Prepd by heating K amide to redness in a closed vessel or by striking an arc between a Pt cathode and a K anode under liq nitrogen (Refs 1–3)

K_3N puffs into flaming decompn when heated to 355°. It also unites with P or S when heated, forming a highly inflammable mixt

Refs: 1) Gmelin, Syst Nr **22** (1937), 247 2) Mellor **8** (1928), 99 3) Partington (1949), 543 4) Sax (1968), 1047 5) Anon, "Manual of Hazardous Chemical Reactions, 1971", NFPA **No 491M** (1971), 203 & 219 6) ChemRubHdbk (1975), B-125

Selenium Nitride (Nitrogen Selenide). Se_4N_4, mw 371.87, N 15.07%, yel-brick red hygr amorph powd, mp (expl 160–200°), bp (decompn). Sl sol in hot w (decompn); v sl sol in acet, acet ac, bz & CS_2. Methods of prepn include passing dry ammonia into a dil soln of selenyl chloride in bz, or into a cooled soln of selenium chloride in CS_2 (Refs 1–5 & 7–10)

Se_4N_4 explodes violently on heating or when brought into contact with a drop of concd sulfuric acid. It is very sensitive to friction and impact. Q_f −169.2kcal/mole

Refs: 1) Gmelin, Syst Nr **10** (1949), 108–110 2) R. Espenscheid, Ann **113**, 101 (1860) 3) A. Vernenil, BullFr (2), **38**, 548 (1882) & JCS (Abs) **44**, 423 (1883) 4) M. Berthelot, MP **13**, 153 (1905–1906) 5) V. Lenher & E. Wolesensky, JACS **20**, 215 & CA **1**, 968 (1907) 6) H.B. Van Vankelburgh & J.C. Bailer, Jr, JACS **47**, 2134–37 (1925) 7) Mellor **10** (1928), 788 8) Davis (1943), 438 9) Thorpe **8** (1947), 514 10) Partington (1949), 733 11) Sax (1968), 1086 12) ChemRubHdbk (1975), B-132

Silver Nitride. (Fulminating Silver). Ag_3N, mw 337.65, N 4.15%, blk-grey powd, mp 25° (start of decompn), d 9.0 ± 1g/cc at 19°. Sol in weak acids, sl sol in aq ammonia & sol in aq solns of Na chloride and K cyanide. Prepd by treating aq Ag oxide with aq ammonia soln, or by heating concd ammoniacal Ag chloride with solid KOH until evolution of ammonia ceases. The thoroughly washed product must be stored under w and, even so, is sensitive to touch (Refs 1–7)

Ag_3N explodes readily but is not very brisant. It explds when illuminated with an electronic flash after receiving 0.2watts/sq cm of energy, and is unusually sensitive to mechanical action of any kind. Spontaneous expln occurs on heating from 100 to 165°. Contact with concd sulfuric acid will cause expl. Q_f −61.0kcal/mole (Refs 1, 2 & 5–9)

Refs: 1) Gmelin, Syst Nr **61**, Teil B (1971), 143–46 2) Mellor **8** (1928), 101 3) W. Latimer & J. Hildebrand, "Reference Book of Inorganic Chemistry", Macmillan, NY (1947), 115 4) Partington (1949), 347 5) H. Hahn, ZAnorgChem **258**, 58–68 (1949) & CA **43**, 5690–91 (1949) 6) Mellor **8** (1) (1964), 155 7) Sax (1968), 1093–94 8) CondChemDict (1971), 787 9) Hackh's (1972), 613

Sodium Nitride. Na_3N, mw 82.98, N 16.88%, drk grey powd, mp 300° (at 275° decompn), d 1.7g/cc at RT. Sol in w with quantitative evolution of ammonia. Prepd by passing an electric arc between a Pt cathode and a Na anode under liq nitrogen (Refs 1–4)

Na_3N decomps appreciably at 150°, at 200° in about one hour, and at 350° in a few minutes. When heated rapidly nitrogen is evolved with expl violence (Refs 1, 2, 5 & 6)

Refs: 1) Gmelin, Syst Nr **21** (1928), 248 & (1966), 897 2) Mellor **8** (1928), 98–99 & **8** (1) (1964), 154 3) Thorpe **8** (1947), 509 4) Partington (1949), 543–4 5) Sax (1968), 1109 6) Hackh's (1972), 620 7) ChemRubHdbk (1975), B-139

Sulfur Nitride (Nitrogen Sulfide, Nitrogen Tetrasulfide). N_4S_4, mw 184.27, N 30.41%, golden-yellow to orange-red monoclinic cryst, mp 178° (subl beginning at 135°), bp 185° (decompn), d 2.22g/cc at 15°, RI 2.046 at 4/20°. V sl sol in bz or CS_2; sl sol in alc, ether, turpentine, toluene, CCl_4, chlf or liq ammonia (Refs 1 & 9)

Preparation. By the action of liq ammonia on S in the presence of Ag iodide. The N_4S_4 is isolated by filtn of the Ag sulfide ppt, evapn of the filtrate and recrystn from CS_2. Also, by passing dry ammonia through S mono- or dichloride, dissolved in a non-aq solvent such as bz, CCl_4, etc; or by the interaction of vapors of ammonia and S dichloride (Refs 2, 3, 4, 5, 7, 8, 9, 16, 17 & 18)

Brisance. Sand Test. 15.0g of sand were crushed by 0.4g of N_4S_4 (Ref 13). The press developed by the expl is comparable to, and sometimes exceeds that of MF, but the brisance is lower

Detonability. Loading d of 2.119g/cc at a loading press of 2000kg/sq cm is required for consistent ignition (Ref 5). Muraour (Ref 14a) reported it "dead pressed" at the above loading press, with failure to detonate

Explosion Temperature. At 190° it explds in about 20sec (Ref 5). Temps between 160° and 207° have been reported in the literature. The discrepancies may be attributed to the various degrees of purity of the materials tested, as well as the methods of testing, rates of heating, etc

Heat of Combustion. Q_c^v is 700cal/g at 25°

Heat of Formation. Q_f is −138.8kcal/mole (Ref 18)

Heat Tests. International heat test at 75° resulted in a 0.05% wt loss. It is not appreciably affected by storage after one year at 50° (Refs 14, 19 & 20). Vacuum stability test at 120° yields 1.57cc of gas from an 11g sample after 40 hours (Ref 13)

Impact Sensitivity. 20cm on a PicArsn app using a 2kg wt versus 5cm for MF

Lead Block Test. A 2g sample pressed at 2000 kg/sq cm to a d of 2.119g/cc caused a 37.2cc expansion versus 25.6cc for MF at a d of 3.349 g/cc

Uses. The use of N_4S_4 as a primer and detonator ingredient has been suggested (Refs 5 & 6), but Hopper (Refs 13 & 14) found that in mixts with K chlorate it was not stable in storage at 50°. It has been used to some extent as an ignition promotor for Diesel fuels, in insecticides, fungicides, as an accelerator in rubber vulcanization, and as an indicator in acid titrations (Refs 10 & 11)

Refs: 1) Gmelin, Syst Nr **9**, Teil B (1964), 1537 2) M. Berthelot, "Sur la Force des Matières Explosifs", Paris, 3rd ed, Vol **1**, 387 (1883) 3) O. Ruff & F. Geisel, Ber **37**, 1573 (1904) 4) Ibid **38**, 2659–67 (1905) 5) L. Wöhler & O. Matter, SS **2**, 203–6 & 265–69 (1907) 6) L. Wöhler, ZAngChem **24**, 2089–99 (1911) 7) C. Claessen, BritP 6057 (1913) & CA **8**, 2949 (1914) 8) H.B. Van Valkenburg & J.C. Bailar, Jr, JACS **47**, 2134–37 (1925) 9) Mellor **8**, 624–32 (1928) 10) S.A. Voznessenskii, JRussPhysChemSoc **61**, 1317, 1323 (1929) & CA **24**, 1308 (1930) 11) V.N. Skvortzov, JGenChem(Russ) **2**, 569–75 (1932) & CA **27**, 2366 (1933) 12) L.R. Carl, USP 2127106 (1938) & CA **32**, 8147 (1938) 13) J.D. Hopper, "Study Explosive Properties of Nitrogen Sulphide and Compositions Containing It", PATR **919** (1938) 14) Ibid, PATR **978** (1939) 14a) H. Muraour, MAF **18**, 895–7 (1939) 15) L.R. Carl, USP 2337798 (1943) & CA **38**, 3428 (1944) 16) Thorpe **8** (1947), 513 17) Partington (1949), 587 18) Urbański **3** (1967), 229 19) Sax (1968), 969 20) Hackh's (1972), 459

Tellurium Nitride. Te_3N_4, mw 438.87, N 9.58%, yellow amorph powd, mp (explds above 200° or when quickly heated). Decompd by w (under vac the heat of soln causes deton). Insol in aq ammonia & dil acet ac. Prepd by reacting gaseous ammonia with $TeCl_4$ at −15°

Te_3N_4 is unaffected by heating to 150°. Expl temp is 320°, flaming deton occurs. Impact sensitivity is 1 cm using a 20g weight on a g equiv wt of compd. Expln occurs on contact with either dil hydrochloric or nitric acids or concd sulfuric acid

Refs: 1) Gmelin, Syst Nr **11** (1940), 311 2) Sax (1968), 1137

Thallium Nitride. Tl_3N, mw 627.18, N 2.23%, blk needles, mp not reported. Hydrolyzed by steam. Sol in K amide-ammonia soln. Prepd by reacting K amide in liq ammonia with Tl nitrate. Tl_3N explds when shocked and on contact with w or weak acids

Ref: 1) Gmelin, Syst Nr **38** (1940), 234

NITRILES

Nitriles are organic derivatives of hydrocyanic acid in which the substituting group is attached to carbon. Their formula is R.C:N. Because most nitriles can be derived from corresponding acid amides, $R.CO.NH_2$, by removal of w, they are called nitriles. For instance, the compd $CH_3.CN$ is called acetonitrile because it is derived from acetamide. It can also be called methyl cyanide. The compd $C_2H_5.CN$ is called either propionitrile or ethyl cyanide, etc

The first nitrile to be prepared was propionitrile which J. Pelouze obtained in 1834 by distg Ba ethyl sulfate with K cyanide

Some nitriles are expl, especially if they contain several –CN groups or a combination of –CN and $-NO_2$ groups. Other nitriles have been considered for use in double-base proplnts as they cool the flame and provide longer burning times; a variety of alkyl nitriles have been investigated as plasticizers (Ref 7)

Refs: 1) Houben **4** (1941) 2) J.W. Teter, USP 2385745 (1945) and CA **40**, 590 (1946) 3) J.F. Olin, USP 2388218 (1945) & CA **40**, 591 (1946) 4) Thorpe **8** (1947), 484 5) Hickinbottom (1948), 281–85, 290–91 & 415 6) Sidgwick (1950), 310–17 7) M.H. Kaufman et al, "Nitriles as Plasticizers for Double Base Propellants", **NOTS 1299** (NAVORD 4973) (1956) 8) D.N. Lapedes, Ed, "Encyclopedia of Science and Technology", McGraw-Hill, NY (1970)

LIST OF NITRILES

Acetonitrile and Derivatives. See Vol **1**, A45-L to A46-R

Acrylonitrile and Derivatives. See Vol **1**, A97-R to A98-L

Benzonitrile and Derivatives. See Vol **2**, B76-R to B77-L

Cyanamide and Derivatives. See Vol **3**, C580-L to C582-L

Cyanocompounds. See Vol **3**, C583-L to C591-L

Diazoacetonitrile. $(N_2)CH.CN$, mw 67.06, N 62.68%, OB to CO_2 −107.37%, orange-yel liq, fr p −18°, bp 46.5° at 14–15mm Hg. Sol in w and eth. Prepd from the reaction of an aq soln of Na nitrite and aminoacetonitrile hydrochloride

The compd burns with a luminous flame. Explds violently on contact with Cu oxide and is friction sensitive. Its Hg salt is also an expl

Refs: 1) Beil **25**, 114 2) D.D. Phillips & W.C. Champion, JACS **78**, 5452 (1957) & CA **51**, 718 (1957)

1,2 Dicyanoethane (Butandinitril in Ger, Succinonitrile, Ethylenecyanide or Ethylenedicyanide). $NC.CH_2CH_2.CN$, mw 80.09, N 34.98%, OB to CO_2 −199.8%, colorl waxy substance which can either be cryst or amorph, mp 53.7–54.5°, bp 265–7°, d 0.989g/cc at 58.7/4°, 0.9800g/cc at 70/4°, 0.9642g/cc at 90/4° and 0.950g/cc at 107.8/4°, RI 1.4165 at 63°. V sol in w, alc & chlf; sl sol in eth. Prepd by adding dropwise a satd aq soln of KCN to a boiling soln of ethylene bromide in ethanol (Ref 2)

Dicyanoethane is an expl which is less powerful and brisant than PA. Q_c 546.1kcal/mole. Viscosity 0.0276g/cm-sec at 58.7° and 0.0181 at 83° (Ref 4). *The compd is very poisonous*

Refs: 1) Beil **2**, 615 & (265) 2) Fauconnier, BullFr [2], **50**, 214 3) CondChemDict (1956), 276 4) A.E. Dunstan, T.P. Hilditch & F.B. Thole, JCS **103**, 138 (1913)

Dicyanomethane (Methylenedicyanide, Malononitrile or Propanedinitrile). $NC.CH_2.CN$, mw 66.07, N 42.41%, OB to CO_2 −169.52%, colorl cryst, mp 31°, bp 223–24°, d 1.0506g/cc at 32.7/4°, 1.0338g/cc at 50/4° and 0.9794g/cc at 107/4°, RI 1.4146 at 34.2°. Sol, w 13.4p/100p, alc 40, eth 20, chlf 10, ac acid 10, bz 6.7 (Ref 1). Prepd by heating cyanoacetamide with PCl_5 under vac at 100° & then distg the product (Ref 2)

Dicyanomethane is an expl substance, less powerful and less brisant than PA. Q_c^p 395.1 kcal/mole, Viscosity is 0.0285g/cm-sec at 32.7° and 0.0215g/cm-sec at 50°. *The compd is very poisonous*

Refs: 1) Beil **2**, 589, (256) & [615] 2) B.B. Carson, R.W. Scott & C.E. Vose, "Organic Synthesis", J. Wiley, NY, **10**, 66 (1930)

Nitrilo Triacetic Azide (Triglykolamidsäuretriazid in Ger). $N(CH_2.CO.N_3)_3$, mw 266.22, N 52.63%, OB to CO_2 −72.12%, mp not found, leaflets. Sol in eth. Prepd from an aq soln of Na nitrite and nitrilotriacetic azide in eth. *Very expl compd*

Refs: 1) Beil **4**, (483) 2) T. Curtius & O. Hoffmann, JPraktChem **96**, 202–35; JCS **114**, I, 293–5 (1918) & CA **12**, 2317–18 (1918)

Analytical Tests for Nitriles (Ref 6). 1) Redn to the corresponding amines with Na & alc & identifying the amines by the usual methods; 2) Hydrolysis with aq KOH to ammonia, distn of the liberated NH_3 into w & titration of the resulting NH_4OH with H_2SO_4 (Ref 3); 3) Hydrolysis to amides with KOH in diethyleneglycol or glycerin solns (Refs 4 & 5); 4) Treatment of nitriles with Grignard reagent to give ketones which form characteristic derivatives (Ref 1); and 5) Condensation with phloroglucinol by the Houben-Hoesch synthesis to give readily characterized phlorophenones (Ref 2)

Refs: 1) R.L. Schriner & T.A. Turner, JACS **52**, 1267 (1930) 2) H.P. Howells & J.G. Little, JACS **54**, 2451 (1932) 3) L. Palfrey, S. Sabetay & S. Revira, CR **209**, 483–5 (1939) & CA **34**, 345 (1940) 4) H.B. Cutter & M. Taras, IEC (Anal Ed) **13**, 830 (1941) 5) S. Revira & C.B. Palfrey, CR **211**, 396–8 (1940) & CA **36**, 368 (1942) 6) Thorpe **8** (1947), 487

ISONITRILES. This designation includes isocyanides (see Vol **3**, C582-L to C583-L and Vol **7**, I135-R for Cyanicic Acid and Derivatives) and Carbylamines, R.N:C. The first isonitriles were prepd in 1886 by Gautier, by the action of Ag cyanide on alkyl iodides. Later, Hofmann prepd them by the action of chlf & alc KOH on primary amines:

$R.NH_2 + CHCl_3 = R.N{:}C + 3HCl$

These compds are also formed during the prepn of nitriles, by heating aryl or arylalkyl halides, or alkyl sulfuric or phosphoric esters, or arylsulfonic esters with K or Na cyanide in alc

The isonitriles are reactive, volatile liqs with an extremely repulsive odor. Their formation is often used as a method for the detection of primary amines

Refs: 1) Thorpe **8** (1947), 487 2) D.-

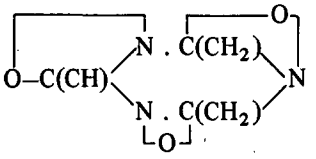
Hammick, R.C. New, N.V. Sidgwick & L.E. Sutton, JCS **1930**, 1886 3) N.P. Gambaryan, "Progress in Isonitrile Chemistry", Journal of All-Union Chemical Society in Mendeleyev (12), USSR (1967), 65–75, Technical Trans **FSTC-HT-23-257-68** by ACSI, AD 843104

NITRILE OXIDES. Nitrile oxides are a well known class of compds represented by R.C:N→O, and are usually prepd by treating hydroxamic acid chlorides with a mild alkali, thus eliminating HCl (Ref 2). Wieland (Refs 1 & 3) was responsible for the first isolation of free nitrile oxides. These compds are somewhat unstable, showing a marked tendency to dimerize to the corresponding furoxanes (1,3-dipolar addition) (Refs 2 & 3). The nitrile oxides add to a considerable number of carbenes, as benzonitrile oxide (for example) to a large number of olefins in ether at 20° (Ref 3)

As shown below, several of the nitrile oxides are expls

Refs: 1) H.Wieland, Ber **42**, 803–816 (1909) 2) R.C. Fuson, "Reactions of Organic Compounds", J. Wiley, NY (1962), 242 3) S. Patai, "The Chemistry of Alkenes", Interscience Pub Co, J. Wiley, NY (1964), 822–26

Triacetonitrile Oxide.

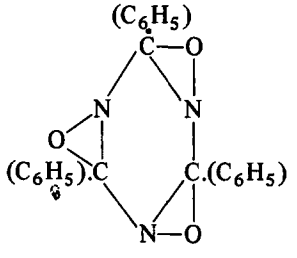


mw 167.14, N 25.15%, OB to CO_2 −110.04%; vitreous, brittle mass; mp 95° (decompn). Dissociated by boiling acids & toluene. Prep by reacting ethyl nitrolic acid & Na carbonate

Triacetonitrile oxide explds when heated on a spatula

Refs: 1) Beil, not found 2) H. Wieland, Ber **42**, 816–20 & CA **3**, 1271 (1909)

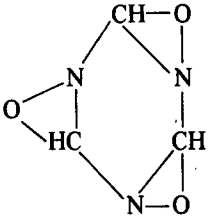
Tribenzonitrile Oxide (2,4,6-Triphenyl-1,3,5-Triazine-Trioxide or Trimer Benzonitriloxide).



mw 357.39, N 11.76%, OB to CO_2 −208.18%, colorl cryst, mp 125–30° (decompn). Dissociated by alc, HCl, boiling toluene, acet ac, me alc, PCl_5 and bz chloride. Prepn from phenylnitrolic acid and Na carbonate in 50% yield. It explds very readily when heated or in contact with concd sulfuric acid

Refs: 1) Beil **26**, 97 2) H. Wieland, Ber **42**, 803–16 & CA **3**, 1270–1 (1909)

Trifulmin (1,3,5-Triazine-Trioxide, Trimery Formonitriloxide or Tris-Formonitriloxide).



mw 129.09, N 32.56%, OB to CO_2 −92.96%, colorl powd, mp not available. Dissoc by w into formhydroxamic acid. Prepd from an aq soln of methylnitrolic acid when reacted with ammonia or Na carbonate. Yield is 85%. It explds in contact with either concd sulfuric or concd hydrochloric acids

Refs: 1) Beil **26**, 34 2) H. Wieland, Ber **42**, 803–16 & CA **3**, 1270–1 (1909)

NITRIMINES

Compds of the general formula $R_2C{=}N{-}NO_2$. The first compd of this kind was prepd in 1895 by Angeli et al upon treating camphoroxime with nitrous acid. Similar compds were obtained from a number of terpenoid ketones. Angeli called the resulting substances "pernitroso" derivatives and assigned to them structures of either $R_2C{=}N{-}O{-}NO$ or $R_2C{=}(NO)_2$ (Refs 1 & 2)

Scholl et al (Refs 3 & 4) prepared the same compds by treating ketoximes (such as pinacolone) with nitrogen tetroxide, but he assigned them the structure $R_2C{=}N{-}NO_2$ and called them *nitrimines.* One of the compds described by him in Ref 4, p 27 is a weak expl. It is the Ag salt of pinacolone-nitraminic acid which puffs off on rapid heating (this compd described below under "List of Nitrimines"). Further work on

nitrimines was done by Harries et al (Refs 5 & 6), Fusco et al (Ref 10), Hantzch (Ref 7), Ponzio (Ref 8), and Saccardi and Latini (Ref 9). Suggitt et al gave a brief general review on nitrimines and described the prepn and properties of many of these compds (Ref 11)

Nitrimines seem to exist in several isomeric forms and their structures have *not* been definitely established. For instance, four different structures for mesityl nitrimine are given by Suggitt et al in Ref 11

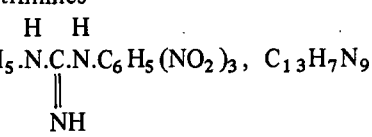
A discussion of nitrimines usage as energetic materials is part of the article entitled "Amines Nitrated and Nitrited" in Vol **1**, A174-R to A178-R

Refs: 1) A. Angeli & E. Rimini, Ber **28**, 1077–8 (1895) 2) Ibid, Gazz **26**, II, 29, 517 (1896) 3) R. Scholl et al, Ber **28**, 1361–63 (1895) 4) Ibid, Ann **338**, 1–35 (1905) 5) Harries et al, Ber **32**, 1330 (1899) 6) Ibid, Ann **319**, 230 (1901) 7) D. Hantzch, Ber **35**, 226 (1902) 8) G. Ponzio, Gazz **36**, II, 287 (1906) 9) Saccardi & Latini, AnnChim(Rome) **22**, 88 (1932) 10) Fusco et al, AltiAcadItaliaRend-ClasseSciFisMatNat [7] **2**, 618 & 751 (1941) & Ibid [7] **3**, 113 (1941) 11) J.W. Suggitt, G.S. Myers & G.W. Wright, JOrgChem **12**, 372–78 (1947)

LIST OF NITRIMINES

Dicyandiamidine & Derivatives. See Vol **5**, D1217-L to D1218-L

Hexanitrodiphenylguanidine. *Note:* guanidines are included here, although A.F. McKay et al (Ref 4) states ". . . these compds should *not* be classed as nitrimines"

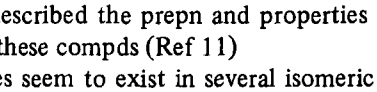


$(NO_2)_3C_6H_5.N.C.N.C_6H_5(NO_2)_3$, $C_{13}H_7N_9O_{12}$, mw 481.29, N 26.20%, OB to CO_2 −58.18%. Prepn not found. Hexanitrodiphenylguanidine is an expl claimed to be less sensitive and 1/3 more powerful than Tetryl (Ref 2)

Refs: 1) Beil – not found 2) D.M. Jackman & F. Olsen, USP 1547815 (1925) & CA **19**, 3021 (1925) 3) Blatt, OSRD **1085** (1942) 4) A.F. McKay et al, CanJChem **29**, 746–58 (1951) & CA **46**, 2501–02 (1952)

Nitroguanidine and Derivatives. See Vol **6**, G154-Rff

3-Nitro-5-Imino-1-Benzoyl-Cyclopentene-1.



$C_{12}H_{10}N_2O_3$, mw 230.24, N 12.17%, OB to CO_2 −180.68%, brn-yel amorph mass, mp 127–132° (decompn). V sol in chlf, acet, et acet, glac acet ac; sl sol in alc and benz; insol in eth, ligr and w. Prepd by the reaction between 4-nitro-2-phenacyl-pyrol with the hydrochloride of β-amino-propiophenon in aq alc soln of NaOH at 50°

Ref: 1) Beil **7**, (386); *Note:* Beil does not differentiate between a *nitrimine* and a *nitroimine*. Both compd types are listed under "Nitroimines" by Beil and are so presented here. Perhaps this method of presentation is because of the lack of a nitrimine structural definition

Alpha'-Nitro-Alpha-Imino-Dibenzyl-Carbonic acid-2. $C_{15}H_{12}N_2O_4$, $C_6H_5.CH(NO_2).C(:NH).C_6H_4.CO_2H$, mw 284.29, N 9.86%, OB to CO_2 −180.10%, sulfur-yel cryst, mp 147–150° (decompn). Prepd by warming alpha-nitro-benzal-phthalimidin with dil aq NaOH

Ref: 1) Beil **10**, 757

[N-Nitro-Iminodiacetic Acid]-bis-[2,4-Dinitro Anilide]. $C_{16}H_{12}N_8O_{12}$, $[(O_2N)_2C_6H_3.NH.CO.CH_2]_2N.NO_2$, mw 508.36, N 22.04%, OB to CO_2 −119.60%, sulfur-yel leaflets, mp 214–15° (decompn). Sol in nitrobenz and dil KOH. Prepd by reacting iminodiacetic acid-dianilide with anhydr nitric acid at the fr p of the reactants

Ref: 1) Beil **12**, (364)

Nitroiminodiacetic Acid (Nitrodiglycolamidic Acid). $C_4H_6N_2O_6$, $O_2N.N(CH_2.CO_2H)_2$, mw 178.12, N 15.73%, OB to CO_2 −44.91%, cryst, mp 148–155° (decompn). Sol in w, methanol, et alc, acet and et acet; insol in chlf and benz. Prepd by briefly heating iminodiacetic acid with anhydr nitric acid

Nitroiminodiacetic acid forms expl metallic salts; viz,

Copper Nitroiminodiacetic Acid, $CuC_4H_4N_2O_6$, is a greenish microcryst powd which explds on heating

Dipotassium Nitroiminodiacetic Acid, $K_2C_4H_4N_2O_6$, cryst plates whose expln temp is 195°

Silver Nitroiminodiacetic Acid, $Ag_2C_4H_4N_2O_6$, a wh ppt which explds on heating

Zinc Nitroiminodiacetic Acid, $ZnC_4H_4N_2O_6$, cryst which explds on heating

Ref: 1) Beil **4**, (488)

Nitroiminodiacetic Acid Diamide (Nitrodiglycolamidic Acid). $C_4H_8N_4O_4$, $O_2N.N(CH_2.CO.NH_2)_2$, mw 176.16, N 31.81%, OB to CO_2 −72.66%, clear platelets, mp 190–218° (decompn). Prepd by nitration of iminodiacetic acid amide with anhydrous nitric acid at RT

Ref: 1) Beil **4**, (488)

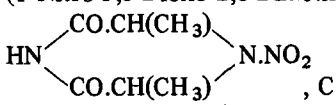
Nitroiminodiacetic Acid Dinitrile (Nitrodiglycolamidic Acid Dinitrile). $C_4H_4N_4O_2$, $O_2N.N(CH_2.CN)_2$, mw 140.12, N 39.99%, OB to CO_2 −91.35%, colorl ndls, mp 98° (softens); 104–5° (decompn). Sparingly sol in benz, eth, alc and et acet; sl sol in w and chlf; insol in petr eth. Prepd by nitrating iminodiacetic acid dinitrile with anhydr nitric acid at RT

Ref: 1) Beil **4**, (488)

N-Nitro-[Alpha, Alpha′-Imino Dipropionic Acid]. $C_6H_{10}N_2O_6$, $O_2N.N[CH(CH_3).CO_2H]_2$, mw 206.18, N 13.59%, OB to CO_2 −85.36%, cryst, mp 175–80° (decompn). V sol in alc, methanol, acet; sol in et acet, chlf, benz and cold w; also sol in cold concd HCl. Prepd by warming alpha, alpha′-imino-dipropionic acid with anhydr nitric acid

Ref: 1) Beil **4**, (498)

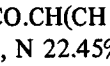
N-Nitro-Alpha,Alpha′-Imino Dipropionic Acid. (1-Nitro-3,5-Dioxo-2,6-Dimethyl Piperazine).



, $C_6H_9N_3O_4$, mw 187.18, N 22.45%, OB to CO_2 −106.85%, ndls, mp 136–38 (decompn). Sparingly sol in cold w. Prepd by nitration of alpha, alpha′-iminodipropionic acid imide with anhydr nitric acid

Ref: 1) Beil **24**, (309)

Pinacoline Nitraminic Acid. $C_5H_{11}N_2O_2$, $(CH_3)_3.C.N.N.O_2$, mw 131.18, N 21.36%, OB to CO_2 −164.66%, oil, bp 80–83°/11mm. Sol in eth. Prepd by reacting pinacolonoxime in dry eth with fresh liq N_2O_4 at −10° (Ref 3)



The Ag salt of pinacoline nitraminic acid, or

Silver Pinacoline Nitraminic Acid, $AgC_5H_{11}N_2O_2$, is a weak expl which puffs off on rapid heating (Ref 2)

Refs: 1) Beil – not found 2) R. Scholl et al, Ann **338**, 27 (1905) 3) J.W. Suggitt et al, JOC **12**, 373–78 (1947) & CA **41**, 5505–06 (1947)

NITRITES

Nitrites are the salts of nitrous acid, discovered by Scheele in 1774. The inorganic nitrites, with the general formula $M.NO_2$, where M is a metal, are well known. They are all insol in w with the exception of the alkali nitrites. Nitrites may be prepd either by thermal decompn of alkali nitrates; $2KNO_3 \rightarrow 2KNO_2 + O_2$; or by reduction of nitrates by C or Pb; $2KNO_3 + C \rightarrow 2KNO_2 + CO_2$. The lone pair of electrons in the nitrite ion is sterically significant; consequently, the nitrite ion is bent:



The N–O bond distance has been reported as 1.24Å with a bond angle of 115° (Ref 3). The salts as well as the acids act both as oxidizing and reducing acids. The principle use of the inorganic nitrites is in organic synthesis, including diazotization. *When heated with thiosulfates or cyanides, nitrites detonate violently* (Ref 4)

The so-called nitrite compds, having the same formula as nitro compds, RNO_2, are not identical with them, and should be represented by the formula R.O.N:O

Refs: 1) Thorpe **8** (1947), 529 2) Ephraim (1954), 721–23 3) W.L. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, Inc, NY (1964), 79 4) Anon, "Manual of Hazardous Chemical Reactions", 5th Ed, Natl Fire Protection Assoc, Boston, Mass (1973), **491M**, 173

LIST OF NITRITES

Ammonium Nitrite. See Vol **1**, A380
Addnl Ref: Ephraim (1954), 723

Amyl Nitrite. See Vol **1**, A397-R

Barium Nitrite. $Ba(NO_2)_2$, mw 229.38, N 12.21%, mp 217°, d 3.19g/cc at 23°; and $Ba(NO_2)_2.H_2O$, mw 247.38, N 11.32%, mp decomps 115°, d 3.17g/cc at 29°. Both salts are colorl to yel cryst compds, and are v sol in w, sl sol in abs alc and insol in eth. Prepn given in Refs 1 & 2. *Highly toxic by ingestion.* Used in diazotization reactions, prevention of corrosion of steel bars, and in expls
Refs: 1) Gmelin, Syst Nr **30** (1932), 149–64 & Supplement (1960), 178–79, 305–16 2) Mellor **8** (1946), 485–88 3) Partington (1950), 551 4) Merck (1968), 121-R 5) CondChemDict (1971), 93-R 6) Hackh's (1972), 79-L

Copper Diamminonitriles. See under Ammines in Vol **1**, A275ff

Ethyl Nitrite. See under Ethane Nitrite in Vol **6**, E145-L

Hydrazine Nitrite. See in Vol **7**, H196-R

Methyl Nitrite. See under Methyl Nitrite in this Vol

Potassium Nitrite. KNO_2, mw 85.10, N 16.46%, white or slightly yel, deliq crysts or granules, mp 441° (decompn starts at 350°), bp explds at 1000°F, d 1.915g/cc. Sol in 0.35p water, sl sol in alc. Prepn is described in Refs 1 & 2. It is decompd even by weak acids with evolution of brown fumes of nitrous anhydride (Ref 1)

KNO_2 detonates violently when heated in the presence of thiosulfates or cyanides. Ref 1 states that when mixed with K cyanide, the mixt burns, and at 450°, it explds violently. Ref 6 details instances of molten KNO_2 being violently decompd by boron, and of a vigorous reaction attended by flame caused by the addition of a little amm sulfate to fused KNO_2

Its primary uses have been in analytical chemistry (testing for amino acids, Co, I_2 and urea), in medicine, and in org synthesis
Refs: 1) Mellor **8** (1946), 473–4 & 478 2) Partington (1950), 551 3) Merck (1968), 856-L 4) CondChemDict (1971), 723-R 5) Hackh's (1972), 540-R 6) Anon, "Manual of Hazardous Chemical Reactions", 5th Ed, Natl Fire Protection Assoc, Boston, Mass (1973), **491M**, 219

Propyl Nitrite. See Propyl Nitrite under P

Sodium Nitrite. $NaNO_2$, mw 69.01, wh or sl yel hygr granules, rods or powd, mp 271°; bp explds at 1000°F, decomps at 320°; d 2.157 g/cc. Oxidizes slowly to nitrate in air. Sol in 1.5p cold w, 0.6p boiling w; sl sol in alc. Prepn is described in Refs 1 & 2. Decompd by even weak acids with evolution of brown fumes of N_2O_3

When mixed with Na thiosulfate or cyanide salts and heated, violent explns occur. A similar reaction occurs if an ammonium salt is melted with a nitrite salt. $NaNO_2$ at 460°F in contact with the fiber drums in which it is shipped undergoes a vigorous decompn reaction producing a proplnt-type burning until the carton is consumed (Ref 6)

$NaNO_2$ is used for diazotizing in dyestuff manuf, in org synthesis, rubber accelerators, prepn of nitric oxide, pharmaceuticals, photographic reag, curing meats, dyeing and printing textile fabrics, etc
Refs: 1) Mellor **8** (1946), 473–4 & 478 2) Partington (1950), 551 3) Merck (1968), 963-L 4) CondChemDict (1971), 806-L 5) Hackh's (1972), 620-L 6) Anon, "Manual of Dangerous Chemical Reactions", 5th Ed, Natl Fire Protection Assoc, Boston, Mass (1973), **491M**, 246–7

Nitrito- Compounds. Organic compds containing one or several –O.N:O groups which are called *oxynitroso* radicals. These compds are also known as *organic nitrites.* Some are expl, as, for example, Methyl Nitrite, $CH_3.O.NO$ (see in this Vol). They are not as stable as the corresponding nitrates and nitrocompds
Ref: Hackh's (1972), 457

Nitritodimercuriacetaldehyde. OHC.C(:Hg).Hg.O.NO, mw 488.26, N 2.87%, OB to CO_2 & HgO −11.5%, golden yel powd. Prepd by passing acetylene thru a soln of mercuric nitrate in 1% nitric acid in the presence of an excess of K nitrite. The dry compd explds on heating or by friction
Refs: 1) Beil **3**, 606 2) K.A. Hofmann, Ber **38**, 2004 (1905)

Nitroacetaldoxime. See Methazonic Acid in Vol **1**, A16-L, listed as Mononitroacetaldoxime under Acetaldoxime

Nitroacetic Acid. See Vol **1**, A27-R under Acetic Acid and Derivatives. Its *dipotassium salt*, which is expl is briefly described, whereas its other expl salts, such as Pb, Ag and Hg are only mentioned. All of these salts are described by W. Steinkopf in Ber **42**, 2026–31 (1909) & CA **3**, 1438 (1909)

Nitroacetin. Same as Glycerin Acetate Dinitrate. See Dinitroacetin in Vol **1**, 33-L, and as Glycerol Dinitrate Monoacetate in Blatt, OSRD **2014** (1944)

Nitroacetonitrile. See under Acetonitrile and Derivatives in Vol **1**, A45-R

Nitroacid. A compd containing both the radicals −COOH and $-NO_2$. Some of these are expl, eg, Nitroacetic Acid, $O_2N.CH_2.COOH$; Dinitrobenzoic acid, $(O_2N)_2.C_6H_3.COOH$; Trinitrobenzoic acid, $(O_2N)_3.C_6H_2.COOH$; etc
Ref: Hackh's (1972), 457-R

Nitroagave. See under Agave in Vol **1**, A110-L

Nitroalbuminoids. Albuminoid products usually include glue, bones, hair, feathers, etc. The nitration of these materials with mixed nitric-sulfuric acids, in two stages, for the prepn of expls, is detailed in the Ref
Ref: V. Gallarati, BritP 358116 (1930) & CA **26**, 6141 (1931)

Nitroalkanols, $R.CH(OH)CH_2.NO_2$; **Nitroalkanol Nitrates,** $R.CH(O.NO_2).CH_2.NO_2$; and **Dinitroalkanes,** $R.CH(NO_2).CH_2(NO_2)$. These compds, suitable for use in expl compns, may be prepd by treating olefins with 3 to 6 atoms with an ethereal soln of N_2O_4 in the presence or absence of O_2. For example, when propylene, $CH_3CH:CH_2$, is bubbled thru a soln of N_2O_4 in methylated ether in the presence of O_2, a mixt of (1) 1-Nitropropanol-2, $CH_3.CH(OH).CH_2(NO_2)$; (2) 1-Nitropropanol-2-nitrate, $CH_3.CH(O.NO_2).CH_2(NO_2)$ (bp 71°); and (3) 1,2-Dinitropropane, $CH_3.CH(NO_2).CH_2(NO_2)$ (bp 88°), is obtained. For the best yields of compd (1), the O_2/olefin ratio should be less than 0.15/1; for high yields of (2), more than 0.25/1; and for (3), the reaction should be conducted in the absence of O_2
Ref: A.E. Wilder Smith, C.W. Scaife & H. H. Baldeck, USP 2472550 (1949) & CA **43**, 6647–8 (1949)

Nitroaminocompounds or Nitroamines. Compds containing both $-NO_2$ and $-NH_2$ radicals attached to different C atoms, eg, nitroaniline, $O_2N.C_6H_4.NH_2$, etc. Nitroamines can be prepd either by the nitration of amines, or by partial reduction of nitrocompounds contg several $-NO_2$ groups. Another method is to treat a chloronitrocompound with ammonia, as in the prepn of dinitroaniline

Nitroamines differ from *Nitramines* in that the latter contain either $-NH.NO_2$ or $=N.NO_2$ radicals, each attached to one C atom

Some nitroamines are expl. The following are examples:

2,4-Dinitroaniline, $(O_2N)_2.C_6H_3.NH_2$. See in Vol **1**, A408-R

2,4,6-Trinitroaniline, $(O_2N)_3.C_6H_3.NH_2$. See in Vol **1**, A409-R

2,4,6-Trinitro-3-aminoanisole, $(O_2N)_3.C_6H(OCH_3).NH_2$. See in Vol **1**, A182-L

2,4,6-Trinitro-3-aminophenetole, $(O_2N)_3.C_6H(OC_2H_5).NH_2$. See in Vol **1**, A240-R

4,6-Dinitro-2-aminophenol, $(O_2N)_2.C_6H_2(OH).NH_2$. See in Vol **1**, A241-R

Refs: 1) Sidgwick (1937), 73–4 2) Houben **4** (1941) 3) Hickinbottom (1948), 320–21

Nitroaminoguanidine. See in Vol **1**, A210-Rff

Nitroamyleneglycol (Nitro-iso-amylglycol, 2-Nitro-2-methylol-butanol-(1), Nitropentanediol). $(O_2N).C(C_2H_5):(CH_2OH)_2$ or $CH_3.CH_2.C(NO_2):(CH_2OH)_2$, mw 149.15, N 9.39%, OB to CO_2 −123.4%, white needles from w, mp 58.8°, bp decomps. Prepd either by treating 1 mol of secondary nitro-normal butylic alc, $(O_2N).CH(C_2H_5)(CH_2OH)$, with 1 mol of formaldehyde in the presence of a small amt of anhydr K carbonate, or by treating 1 mol of primary nitropropane with 2 mols of formaldehyde in the presence of K carbonate

Nitroamyleneglycol is v sol in w, sol in alc and eth. On nitration it yields an expl dinitrate (see below)

Refs: 1) Beil **1**, 483 2) J. Pauwels, JCS (Abs) **74** (1), 506–7 (1898)

Nitroamyleneglycol Dinitrate (Nitro-iso-amylglycol Dinitrate). $(O_2N).C(C_2H_5):(CH_2.O.NO_2)_2$ or $CH_3.CH_2.C(NO_2):(CH_2.O.NO_2)_2$, mw 239.15, N 17.57%, OB to CO_2 −43.5%, yel viscous oil. Prepd by Bergeim (Ref 2) by the nitration of nitroamyleneglycol with mixed acid containing 40% nitric and 60% sulfuric

It is an expl with properties resembling those of Nitro-iso-butylglycol Dinitrate, and was proposed for use in Dynamites as either a substitute for, or in conjunction with NG. It may also be used in double-base proplnts

Refs: 1) Beil – not listed 2) F.H. Bergeim, USP 1691955 (1928) & CA **23**, 708 (1929)

Nitroanilines. See under Aniline in Vol **1**, A406ff

Nitroanisoles. See under Anisole and Derivatives in Vol **1**, A448ff

Nitroarabinose. See under Arabinose and Derivatives in Vol **1**, A476

Nitroazido Compounds. See under corresponding Azido compound

Nitrobaronit. An early type of aluminized expl. Two formulations which were tested by the Commission des Substances Explosif are shown below:

	Nitrobaronit	
	A	B
Amm Nitrate	82	69
Al	5	2
NG	5	22
NC (12% N)	–	0.75
Liq DNT	5	3
Wood flour	1.5	1.25
Petr pitch	5	3
C.U.P.	124% of PA	125.5% of PA

C.U.P. (Coefficient d'utilisation practique) is the same as power by Pb block expansion, as compared with PA (100%)

Ref: L. Mĕdard, MAF **22**, 596 (1948)

Nitrobellite. Same as Bellite, see Vol **2**, B32-R

Nitrobenzaldehyde. See under Benzaldehyde and Derivatives in Vol **2**, B35

Nitrobenzamide. See under Benzamide and Derivatives in Vol **2**, B38-R

Nitrobenzene. See under Benzene and Derivatives in Vol **2**, B41-Rff

m-Nitrobenzenediazonium Perchlorate (m-Nitrodiazobenzeneperchlorate). $O_2N.C_6H_4.N(ClO_4):N$, mw 235.57, N 16.89%, OB to CO_2 −54.3%, mp explds at approx 154°, hygr crysts. Prepd by dissolving m-nitroaniline in an excess of dil perchloric acid (d 1.12g/cc), the excess being such that, at the end of the reaction, free acid is present. A sufficient quantity of Na nitrite, in solid form or in a satd soln, is added to effect diazotization. The mixt is cooled during the Na nitrite addition:

$$O_2N.C_6H_4.NH_2+HClO_4+HNO_2 \rightarrow O_2N.C_6H_4.N(ClO_4):N+2H_2O$$

For more details of the prepn, see Davis (Ref 4)

Nitrobenzenediazonium perchlorate is sl sol in w. It is an expl, sensitive to impact and

friction and of not very satisfactory thermal stability. It was patented in 1911 by von Herz (Ref 2), and has been used in Ger in compound detonators, using as a base charge, Nitromannite, or other brisant nitric esters. Other perchlorates of diazocompounds of aromatic hydrocarbons, such as those of toluene, naphthalene, anthracene, etc, were also recommended by von Herz
Refs: 1) Beil – not found 2) E. von Herz, GerP 258679 (1911) & CA **7**, 2687 (1913) 3) Colver (1918), 738 4) Davis (1943), 442

Nitrobenzene Dynamite. A Belg blasting powd, manufd at the turn of the century. It contained NG 86, NC 10 and NB 4%
Ref: Daniel (1902), 493

Nitrobenzoic Acid. See under Benzoic Acid and Derivatives in Vol **2**, B69-Rff

Nitrobenzoic Dynamite (Dynamite Nitrobenzoique). An expl patented in 1882 in Fr contg NG 15 to 45, NC 1 to 3, NB 5 to 10 and AN 50 to 73
Ref: Daniel (1902), 783

Nitrobenzol. Same as Nitrobenzene

Nitrobenzoyl. The monovalent radical, $O_2N.C_6H_4.CO-$, derived from nitrobenzoic acid

o-Nitrobenzoyl Chloride. $O_2N.C_6H_4.COCl$, mw 185.57, N 7.55%, OB to CO_2 –112.1%, colorl crysts, mp 24–25°, bp 148–51° at 12mm. Sol in ether, decompd by w or alc. Explds in the presence of organic impurities

May be prepd by heating 2-nitrobenzoic acid with 5p of thionylchloride, $SOCl_2$, and then distg off the excess $SOCl_2$ by heating under vac on a w bath for 4–5 hours. Several explns (Refs 2 & 3) have been reported during the prepn, although the temp was at 100°. In order to avoid such explns, it has been proposed (Ref 3) to carry out all reactions in soln, using only very pure materials. For example, if pure 2-nitrobenzoic acid is dissolved in benz, treated with one mol of pure SO_2, and refluxed until the evolution of SO_2 and HCl has ceased, the procedure seems to be safe. Another method of prepn consists of heating dry 2-nitrobenzoic acid together with 50g of PCl_5 on a w bath for 1–1½ hours, and then distg off the resulting $POCl_3$ under reduced press. Yields in both methods of prepn are about 85%
Note: o-Nitrophenylacetyl Chloride, $O_2N.C_6H_4.CH_2COCl$, is also likely to expld under similar conditions (Ref 4)
Refs: 1) Beil **9**, 373 & [245–46] 2) N.C. Cook & R.C. Whitmore, C&EN **23**, 2394 (1945) & CA **40**, 1034 (1946) 3) May & Baker Ltd, Chem&Ind **1946**, 89 & CA **40**, 2985 (1946) 4) Anon, "Manual of Hazardous Chemical Reactions", 5th Ed, Natl Fire Protection Assoc, Boston (1973), **491M**, 179

Nitrobenzyl. The monovalent radical, $O_2N.C_6H_4.CH_2-$, derived from nitrotoluene by replacing a hydrogen of the methyl group

Nitro-bis-Benzenediazonium Perchlorate (Nitro-bis-Diazobenzene Perchlorate). $O_2N.C_6H_3.[N(ClO_4).N]_2$, mw 376.04, N 18.63%, OB to CO_2 –14.9%. This compd was prepd and patented by von Herz (Refs 2 & 3) for use in detonators. It has been claimed that this perchlorate is more stable and effective as an initiator than the azides
Refs: 1) Beil – not found 2) E. von Herz, GerP 258679 (1911) 3) Marshall **2** (1917), 512

Nitrobran. See under Bran in Vol **2**, B260-R

Nitrobutane. See under n-Butane and Derivatives in Vol **2**, B366-Rff

Nitrobutanol Nitrate (Nitrobutylic Nitrate, 2-Nitro-butanol-(1)-nitrate). $O_2N.CH(C_2H_5).CH_2(ONO_2)$, mw 164.12, N 17.07%, OB to CO_2 –68.2%, yellowish, somewhat visc liq, d 1.242g/cc at 15.5°. Prepd by Pauwels (Ref 2) by nitrating secondary nitro-normal bu-

tylic acid, $O_2N.CH(C_2H_5).CH_2OH$, with mixed nitric-sulfuric acid. It is a mild expl
Refs: 1) Beil **1**, 370 2) J. Pauwels, Rec **17**, 27–49 (1898) & JCS (Abs) **74** (1), 507

Nitroisobutylglycerin (2-Nitro-2-methylol-1,3-propanediol, 2-Nitro-2-oxymethyl-1,3-propanediol). $O_2N.C(CH_2OH)_3$, mw 151.12, N 9.26%, OB to CO_2 79.4%, mp 144–180°. *Note:* According to Beil **1**, [596] it exists in two modifications, one melting (not sharply) at 144°, and the other at 180°. The second form is obtained by treating the first form with either sulfurylchloride or phosphorous trichloride. After crystn from ethyl acetate & chlf, a substance is obtained which melts sharply at 180°. On standing, the second form slowly reverts to the low melting modification. It is usually found in the form of needles and crysts, and is sol in w, alc and eth

Nitroisobutylglycerin can be prepd by several methods, all of which have been tried at PicArsn (Ref 9). The procedure described by Stettbacher (Ref 7) seems to give the best results, and is based on the reaction, $(O_2N)CH_3+3HCHO \rightarrow (O_2N)(CH_2OH)_3$. Add to a 3-necked 1-liter reaction flask (set in a casserole filled with cold w, and placed on a cold hot plate) 150g of nitromethane and 2g of K carbonate hemihydrate. Gradually add about 200g of 37% formaldehyde, maintaining the temp in the flask below 30°. Add gradually, in about 30 minutes, an addl 475g of 37% formaldehyde, allowing the temp of the mixt to rise to 80°. Maintain the soln at 90° for 2 hours, connect the flask to a 4″ vac and evap to about 1/2 its vol to drive off the bulk of the formaldehyde. Break the vac, dil with w and conc again under reduced press. Repeat dilutions and concns until only a faint odor of formaldehyde remains. After allowing the mixt to cool, separate the red-colored ppt by filtn. Dissolve the crude product in hot alc and cryst by cooling. Recrystallize several times from eth

On nitration it yields an expl trinitrate (see below)
Refs: 1) Beil **1**, 520, (276) & [596]
2) L. Henry, BullSocChim [3], **13**, 1001 (1895)
3) F. Hofwimmer, SS **7**, 43 (1912) & CA **6**, 1228 (1913) 4) E. Schmidt & R. Wilkendorf, Ber **52**, 392 (1919) 5) Naoûm, NG (1928), 239–40 6) I.M. Gorski & S.P. Makarow, Ber **67**, 996–1000 (1934) 7) A. Stettbacher, NC **5**, 159–62, 181–84 & 203–06 (1934)
8) G.A. Hunold, SS **30**, 263 (1935) 9) H. Aaronson, PATR **1125** (1941), 5

Nitroisobutylglycerol Trinitrate (NIBGTN). $O_2N.C(CH_2ONO_2)_3$, mw 286.12, N 19.58% (Nitrate N=14.69%), OB to CO_2 ±0; thick, yellowish, odorless oil which is more viscous than NG; mp, did not freeze at −50°; bp, decomps or deflagrates in 5sec at 180–85° without deton, detonates when heated with flame in a sealed capillary tube; d 1.64g/cc at 20° (1.68g/cc according to Hofwimmer & Naoûm); RI 1.4896 at 25°, 1.4874 at 30°. Insol in w, CS_2 and petr eth; sol in methanol, ethanol, acet, eth, benz & ethylenedichloride
Preparation. Can be prepd by nitration of nitroisobutylglycerol. Following is the method proposed by Stettbacher (Ref 7) and repeated at PicArsn (Ref 10): Add gradually with mechanical stirring, 50g of nitroisobutylglycerol to 304g of mixed acid with compn $HNO_3/H_2SO_4/H_2O$, 38/60/2. The addition should be made in about 1/2 hour while maintaining the temp at below 15°. Stir for an addnl 1/2 hour while cooling the mixt to 5°. Transfer the mass to a separatory funnel, allow to stand for a while, and draw off the bottom layer of acid. Wash the residual oil with w, then with aq Na bicarbonate, and finally with w to neutrality to litmus (2 washes). Collect all the washings, mix them with the spent acid, cool the liq and extract with eth. Wash the eth extract with w, evap the ether, add the oil from the separatory funnel and dry the product in a vac desiccator. The yield was about 95% of theoretical. Nitrate nitrogen content, as determined by nitrometer, gave only 14.12% as against 14.69% theoretical, which indicated that the product was impure
Note: Due to the high viscosity of NIBGTN, its purification by the above described method is usually accompanied by formation of emulsions, which delay the separation of the oil from the aq solns. Much better results are claimed by Crater's method (Ref 9), in which the crude product is washed twice with equal vols of w at 43.5°, and then by concd aq solns of Na sulfite, while agitating the mixt by bubbling compressed

air thru it. After each washing the oil is separated from the aq layers

Heat of Combustion. 1707kcal/mole at C_v and H_2O liq, against 1595kcal/mole for NG detd in the same bomb

Impact Sensitivity. 6cm with 2kg weight against 2cm for NG

Power. When tested as a liq in the Trauzl block test, about 145cc or 55% of TNT. However, when a 75% kieselguhr Dynamite was made with NIBGTN, the Trauzl value was 325cc as compared to the corresponding amount of NG kieselguhr Dynamite (106.5% of NG). On the other hand, its mixt with 7% collodion cotton gave a slightly lower value (580cc) than the corresponding mixt with NG. The latter results are probably due, according to Naoûm (Ref 4) to the fact that the excess oxygen in NG burns the collodion cotton completely, while NIBGTN has no excess oxygen (OB to CO_2 ±0)

Stability. NIBGTN is less stable than NG, as judged by the 82.2° KI test (2 minutes against 10 minutes for NG)

Velocity of Detonation. Like NG or NGk, the vel of deton may be either of high order (7860 m/sec at d 1.64g/cc), or of low order (1000–1500m/sec at d 1.64g/cc), depending on the method of initiation. In both cases, velocities were detd in glass tubes of 10mm diameter and 1mm wall thickness. The reaction at detonation is, according to Hofwimmer (Ref 2),

$(O_2N)C(CH_2ONO_2)_3 \rightarrow 4CO_2 + 3H_2O + 2N_2$

Volatility. At 25°, as determined by loss of weight in grams per cubic cm of surface per 24 hrs, is 0.127×10^{-3}, as against 0.153×10^{-3} for NG

Uses: Has been suggested as a partial substitute for NG in commercial expls, despite its unsatisfactory thermal stability. It is possible that a purer product would be more stable

Refs: 1) Beil **1**, (277) 2) F. Hofwimmer, SS **7**, 43 (1912) & CA **6**, 1228 (1913) 3) Marshall **1** (1917), 240 4) Naoûm, NG (1928), 239–41 5) L. Aubry, MP **25**, 201 (1932–33) 6) I.M. Gorski & S.P. Makarow, Ber **67**, 996–1000 (1934) 7) A. Stettbacher, NC **5**, 159–62, 181–84, 203–06 (1934) 8) G.A. Hunold, SS **30**, 263 (1935) 9) W.deC. Crater, USP 2112749 (1938) & CA **32**, 3964 (1938) 10) H. Aaronson, PATR **1125** (1941), 1–4, 6 & Table I

Nitro-iso-butylglycol (2-Nitro-2-methylpropanediol-1,3, Tertiary Nitrodihydroxybutane, Nitroisobutylenicglycol). $H_3C.C(NO_2)(CH_2OH)_2$, mw 135.12, N 10.37%, monoclinic crysts, mp 139–40°. Sol in w, alc and acet; sl sol in eth. Can be prepd by treating an aq soln of nitroethane and formaldehyde with a little K carbonate or bicarbonate. On nitration it yields an expl, Nitroisobutylglycol dinitrate (see below)

Refs: 1) Beil **1**, 480 & [547] 2) L. Henry, CR **121**, 210 (1895); JCS (Abs) **70** (1), 4 (1896) 3) J. Böeseken, Rec **39**, 181 (1920) & CA **14**, 2472 (1920)

Nitro-iso-butylglycol Dinitrate (NIBGkDN, 2-Nitro-2-methylpropanediol-1,3-Dinitrate). $H_3C.C(NO_2)(CH_2ONO_2)_2$, mw 225.12, N 18.67%, OB to CO_2 –24.9%; yellowish, odorless oil. Insol in w; v sol in eth, alc, benz and chlf

Can be prepd as recommended by Bergeim (Ref 2) by gradually adding nitroisobutylglycol to a stirred mixed acid of approx 40% nitric and 60% sulfuric acid by wt, keeping the temp at 5 to 10°. After allowing the mixt to stand, the oil collects on the surface, from where it is separated and purified by means of w and Na sulfite

NIBGkDN is an expl of great strength, resembling Nitroisobutylglycerol in its properties but being less viscous, and hence more easy to handle during its manuf. It can be used either as a substitute for NG, or in conjunction with it and the other usual ingredients of Dynamite to yield a powder of good strength and sensitiveness. Following is a typical formulation of such a Dynamite: NIBGkDN 15, NG 15, Na nitrate 56, woodmeal 13 and chalk 1% (Ref 2). It can also be used as a substitute for Tetranitrodiglycerin, Nitroglycol (NGk), Glycerinchlorohydrin dinitrate, and Nitrosugars. NIBGkDN can also be used in conjunction with NC to form gelatinized expls, or with various oxidizers such as K nitrate, AP, AN, etc, in the prepn of Dynamites

Refs: 1) Beil – not found 2) F.H. Bergeim, USP 1691955 (1929) & CA **23**, 708 (1929) 3) W.deC. Crater, USP 2112749 (1938) & CA **32**, 3964 (1938)

Nitrocaillebotte. Fr for Nitrocurds. See in Vol **3**, C577-L

Nitrocarbamates. Salts of Nitrocarbamic Acid. See under Carbamic Acid and Derivatives in Vol **2**, C40-Lff

Nitrocarbamic Acid. See under Carbamic Acid and Derivatives in Vol **2**, C40-Lff

Nitrocarbol. Same as Nitromethane. See under Methane and Derivatives in this Vol

Nitro-Carbonitrate (NCN) Blasting Agents. This term has been employed for US federal regulatory purposes to cover and to group a class of competitive (various trade-named) explodable products, less sensitive than Dynamites, employed in blasting operations around quarries and open-pit mines. It covers essentially any materials or mixts consisting of a fuel and oxidizer (substantially inorganic nitrates) combination in which none of the materials are considered to be explosives under the usual definition. This class includes among its products any Amm nitrate preparations sensitized with some form of combustible, usually carbonaceous. These include carbon black, powdered coal, sawdust, sugar, molasses, and more generally, No 2 diesel or home heating fuel oil

All NCN blasting agents and each of their components *must be cap-insensitive,* ie, incapable of being detonated when initiated by a No 8 blasting cap. Both Nitro-Carbonitrates and Amm nitrate are grouped by the ICC as "oxidizing materials" with normal transportation (yellow label) being permitted (Ref 1)

The chief advantages in NCN blasting agent use are related to economy, efficiency and safety. In certain applications, an overall cost saving of up to 75% over conventional NG expls has been reported. Where used under well-controlled conditions, it is reported to perform as well as or better than Dynamites, and, by virtue of its greater gas production, may even give better fragmentation. It is safer to handle and use because its hazard sensitivity is low, and misfires are easily and safely resolved. One of its important virtues is that it is not classified as an explosive; but when mixed in the correct stoichiometric proportions under preferred physical conditions with adequate primage, the mixt becomes a powerful low-cost explosive (Ref 5)

See also under Blasting Explosives in Vol **2**, B202-L to B211-R

Refs: 1) Anon, "The Roseburg, Oregon, Fire, Explosion and Conflagration", Report by the National Board of Fire Underwriters, NY (1959) 2) Anon, C&EN **38** (15), 35–6 (1960) 3) S. Fordham, "High Explosives and Propellants", Pergamon Press (1966), 63 4) Blasters'Hndb (1969), 47–61 5) C.E. Gregory, "Explosives for North American Engineers", Trans Tech Publications, Cleveland (1973), 53–66

Nitrocellulose. See under Cellulose Nitrates in Vol **2**, C100-Lff

Nitrochlorbenzenes. See under Chlorobenzene and Derivatives in Vol **3**, C248-R to C251-R

Nitrochlorin. Low-freezing expl oil used in the manuf of some Dynamites. It consisted of Dinitrochlorohydrin 80 and NG 20%

Refs: 1) Naoûm, Expls (1927), 113 2) PATR **2510** (1958), Ger 119-R

Nitrochloroform. See under Chloroform and Derivatives in Vol **3**, C256-R

Nitrocoal. See under Coal, Nitrated in Vol **3**, C378-L

Nitrocolle. Fr for Nitrated Glue. See in Vol **6**, G85-L

Nitrocolophony. Fr for Nitrorosin

Nitrocopper. Cu_2NO_2. A compd corresponding to this formula was prepd in 1892 by the action of nitrogen peroxide (N_2O_4) on cuprous oxide at room temp. Up to 30% by wt of Cu_2O reacted without change of appearance of the solid compd. When heated in the absence of air, the

nitrogen peroxide was liberated, leaving Cu_2O. This indicated that the peroxide was absorbed and did not react chemically. The N_2O_4 could also be removed by placing Nitrocopper in an inert solvent such as CCl_4 at 65–70°. When placed in w, a violent reaction occurred, with formation of NO, $Cu(NO_3)_2$, and some $Cu(NO_2)_2$
Ref: Thorpe **8** (1947), 527

Nitrocotton. A NC prepd by nitration of cotton. See under Cellulose and Derivatives in Vol **2**, C95-Rff

Nitrocresols. See under Cresol and Derivatives in Vol **3**, C556-R to C558-L

Nitrocresolsulfonic Acid Explosives. See under Cresolsulfonic Acid and Derivatives in Vol **3**, C558-L

Nitrocresylates. Salts of Trinitrocresol. See in Vol **3**, C557-R

Nitrocumenes. See under Nitro Derivatives of Cumene in Vol **3**, C573-R to C574-R

Nitrocurds. See under Curds in Vol **3**, C577-L

Nitrocymenes. See in Vol **3**, C637

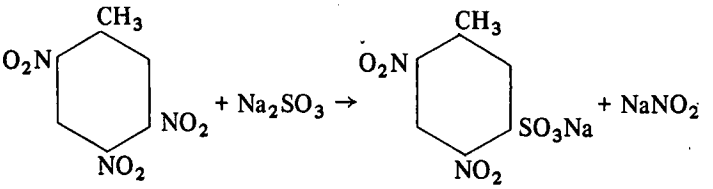
Nitrodextrin. See in Vol **5**, D1115-R

Nitrodiazonaphthol. See under Diazonaphthol and Derivatives in Vol **5**, D1168-R to D1169-R

Nitrodiazophenol. See under Diazophenol and Derivatives in Vol **5**, D1172-L

6-Nitro-4-Diazotoluene-3-Sulfonic Acid (p-Nitrodiazotoluenesulfonic Acid).
$H_3C.C_6H_2(NO_2)(SO_3).N_2$, mw 243.20, N 17.28%, OB to CO_2 −75.7%, brown prisms; mp, explds on heating, as low as 75°, without melting

Can be prepd by diazotization of 6-nitro-4-aminotoluene-3-sulfonic acid with K nitrite and dil sulfuric acid. It has also been isolated by Batik (Ref 2) from the wash w in the sulfite purification of TNT. It was assumed that the following reaction takes place:



On acidification of the waste w, there is formation of sulfurous acid (from excess Na_2SO_3) and nitrous acid (from the $NaNO_2$). The former reduces the NO_2 group in the 4-position to NH_2 and then the latter diazotizes it

P-Nitrodiazotoluenesulfonic acid is insol in w and alc. It is an expl, which may be stored in a dry state. It explds on heating, but not on impact

Note: One reason why TNT waste w should not be acidified is the possible formation of this expl compd

Refs: 1) Beil **16**, 568 2) B. Batik, Chem&Ind Spec No 960-3 (June 1933) & CA **28**, 645 (1934)

1-Nitro-5,5-dimethylhydantoin. See under Dimethylhydantoin and Derivatives in Vol **5**, D1343-R

2-Nitro-2-(3',5'-dinitrophenyl)-propanediol-1,3.
$(O_2N)_2C_6H_3.C(NO_2)(CH_2OH)_2$, mw 287.19, mp 124.6–125.3°, colorl needles

Can be prepd, according to Fieser and Gates (Ref 2, p 2251) by adding 1 ml of triethylamine to a mixt of 10g of 3,5-dinitrophenylnitromethane (prepd by Urbański's method, Ref 1), 10ml of formalin, and 40ml of dioxane. After heating to 60°, the resulting brownish oil was treated with benz (after removing the dioxane) to extract the nitrodinitrophenylpropanediol, which was then crystd twice from benz contg a little acet. The yield was about 69%

On nitration, it gives an expl dinitrate (see below)

2-Nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 Dinitrate. $(O_2N)_2.C_6H_3.C(NO_2)(CH_2ONO_2)_2$, mw 377.19, N 18.57%, OB to CO_2 –40.3%; colorl, flat, rectangular plates from alc contg a little acet, sometimes occurs in the form of prisms; mp 115.2–115.8°. Sol in acet and sl sol in alc

Can be prepd in the following manner: Add 20.0g of 2-nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 in several portions to 130ml of fuming nitric acid (d 1.5g/cc) cooled to 5°. After about 6 minutes all of the material is dissolved and the temp rises to 10°. Drown the mixt in 1.5ℓ of ice w and allow it to stand for 15 minutes. Collect the hardened, gummy material and w wash. Purify by dissolving in acet and crystg by adding alc to the soln. The yield varies between 67 and 86%

Notes: 1) Nitration with mixed nitric-sulfuric acid gives a less satisfactory product and a lower yield (about 52%). 2) Attempts to prepare the product starting with 2-nitro-2-(m-nitrophenyl)-propanediol-1,3 or its dinitrate were unsuccessful

Its expl props were detd by R. McGill et al at the NDRC Res Lab at Bruceton, Pa and were found to be as follows:

Ballistic strength. 126% of TNT, 125.5% of Tetryl, 145.8% of PETN and 150.2% of RDX

Impact sensitivity. slightly less than PETN

Refs: 1) T. Urbański, CR **206**, 1122 (1938) 2) L.F. Fieser & M. Gates, JACS **68**, 2249–52 (1946) & CA **41**, 733 (1947)

Nitrodulcite (Nitrodulcitol). See under Dulcitol and Derivatives in Vol **5**, D1567-R

Nitroerythrite. Same as Erythritol Tetranitrate; see in Vol **5**, E124-L to E125-L

Nitroethanes. See under Ethane, Nitrated and Nitrosated Derivatives in Vol **6**, E143-Rff

Nitroethanols. See in Vol **6**, E177-Rff

Nitroethylenes. See in Vol **6**, E229-Lff

Nitroferrites. Expls patented in 1897 by P.J. Cornil of Belg. *No 1* contained AN 93 to 94, K ferrocyanide 2, sugar 2 to 3, and trinitronaphthalene 2%. *No 2* contained AN 77.0, K nitrate 9.6, K ferrocyanide 4.0, sugar 4.8, flour (toasted) 1.8, and yellow paraffin 2.8%

Refs: 1) Daniel (1902), 522 2) Colver (1918), 277

Nitroform. Same as Trinitromethane; see under Methane and Derivatives in this Vol

Nitrogalactose. See under d-Galactose and Derivatives in Vol **6**, G8-L

Nitrogélatines. Fr term for Blasting Gelatin. Other terms include Gélatine Dynamite, Gélatine Explosible, Gélatine, Dynamite-Gélatine, etc

Ref: Daniel (1902), 325 & 523

Nitrogélatine Picrique. A mixt patented in 1887 by the Deutsche Sprengestoffe Gesellschaft, which consisted of NG plus NC jelly, mixed with about 10% Picric Acid. It proved to be unstable

Refs: 1) Daniel (1902), 523 2) PATR **2510** (1958), Ger 119-R

Nitrogelatinedynamiten. Swiss for gelatine-dynamites containing 20–25% NG (or a low-freezing mixt of 4/1 NG/Nitroglycol) gelatinized with collodion cotton, AN and a liq aromatic nitrocompound (such as drip oil, called **"flussiges Tri"**, which is a mixt of crude DNT and TNT) serving as a phlegmatizer. These expls, among them **Alderfit, Gamsit** and **Telsit**, belong to the class of so-called **"Sicherheitsdynamite"**, which are safe to handle and transport (Handhabungssichere), and safe to use in coal mines

Ref: Stettbacher (1948), 86

Nitrogen Determination in Energetic Materials

The element Nitrogen can exist in the uncombined or free state, as in the atm or in natural gas, or in a combined or bound state,

as in nitric acid, ammonia, amines, nitrates, nitric esters, azides, cyanides, aliphatic and aromatic nitrocompds, etc

The analysis of *free nitrogen* in gas mixts can usually be calcd by difference after detg the concn of the other gaseous ingredients. The presence of free N_2 can be detected by spectrographic (Refs 55 & 60) or colorimetric techniques (See Vol **1**, A114-R & Refs 9 & 17). The element can be quantitatively detd by these means or thru the use of mass spectrometry (See in this Vol & Refs 52, 53, 55 & 61)

The qualitative determination of *combined nitrogen* in energetic materials can be performed using a variety of tests. For salts of ammonia, treatment with Nessler's reagent yields a yellowish-brown coloration or brown ppt (See Vol **3**, C406-Rff & Ref 17). If nitrogen is present as either nitric acid or nitrate (such as KNO_3, $NaNO_3$, NH_4NO_3, NG, NC, etc) a ring test using either diphenylamine (blue ring) or ferrous ammonium sulfate (brown ring) can be used (See Vol **3**, C405-Rff & Ref 17). The presence of azides can be detected using $FeCl_3$ reagent (See Vol **1**, A617-L & R). Several methods for detecting nitrites are available. One procedure, Ilosvay's method, uses sulfanilic acid which yields a red, fuchsia-like coloration (See Vol **3**, C406-4ff & Ref 17). Another procedure, using K permanganate, can also be used quantitatively. If the red color of this reagent disappears there is a possibility of nitrite presence (Ref 17). Detection of a nitrate in the presence of a nitrite can be accomplished using an IrO_2 soln in sulfuric acid. A blue color is developed (Ref 17)

For a complete description of color reactions and reagents used for the detection of over 75 expls and proplnts see Vol **3**, C405-L to C420-L. Additionally, a technique has been developed for the detection of combined nitrogen in microgram samples thru the use of a chelating complex of Zn-8 quinolinol. The complex-nitrogen adduct exhibits intense greenish-yellow fluorescence under ultraviolet light (Ref 25). Also, the use of infrared spectroscopy to identify bound nitrogen groups, and hence their compounds, is another widely used qualitative method (See Vol **7**, I100-R to I101-R & Ref 61)

The quantitative detn of combined nitrogen in energetic materials is of the greatest interest and importance. Of the many procedures to be found in the literature, only the most important and useful will be addressed here (See Vol **1**, A369, A400-R & A474; Vol **6**, E483 to E488

Chromatography in its various forms (thin-layer, column, gas, gas-liq, & electrophoresis) is frequently used to separate and detn NG, NGc, Nitrosamines, Nitramines, etc. In this technique, microgram quantities of a sample are added to a column packed with an absorbing medium or phase. Over this is maintained a flow of mobile phase (gas or liq). The sample components separate because of their relative mobility in the absorbing phase, and thus leave the column at different times (See Vol **1**, A177-R; Vol **2**, C46-L; Vol **3**, C289-L to C298-L [Chromatography]; Vol **5**, D1344-R & D1643-R; Vol **6**, G107-L; Vol **7**, H97 & Refs 45, 48, 49, 50, 55, 56 & 58)

One of the most widely used techniques for the detn of nitrogen content involves the decompn of the sample with subsequent measurement of the evolved nitrogen gas over mercury in a nitrometer, ozometer, eudiometer, Schultze-Tieman app, etc. This method is a standard one employed in many energetic material Specs (See Vol **1**, A373-L to A378-R; Vol **2**, C119-R; Vol **6**, E267 & G105; Vol **7**, L61-R & Refs 4, 16, 17, 21, 38, 43, 54, 56, 57, 61 & 62)

An often used method for the detn of either aminoid or nitrate nitrogen is the decompn-volumetric Kjeldahl (or Chenel) procedure in which the sample is decompd with concd sulfuric acid and suitable catalyzers to yield amm sulfate quant. After release with strong alkali, the ammonia is quant distd into an excess of standard acid and back-titrated with standard alkali (See Vol **1**, A616-R; Vol **2**, C46-L & C50-L; Vol **3**, C276-L & C357-R; & Refs 4, 17, 32, 33, 38, 47 & 63)

Polarography, a well known electroanalytical technique, is currently being used to detn the purity of Tetracene as well as other compds contg nitrate and nitroso groups (Ref 38). This technique involves gradually increasing the potential applied to a micro electrode immersed in a soln of inert electrolyte contg a small quan- of an electroactive species. While the potential is gradually increased, the associated increase in diffusion current is monitored. An X-axis asymp-

totic change in the current curve indicates the end-point of the analysis (See Vol **6**, G161-R & Refs 20, 23, 38, 41 & 61)

A universal procedure for combined nitrogen is the Dumas method. This gasometric procedure is applicable to any organic compd contg nitrogen in any form, such as amino, nitroso, nitro, azo, cyano, nitrate, nitrite, as well as N in heterocyclic compds. The procedure involves combusting the sample in a closed system in a CO_2 atm, with subsequent reduction of the oxides of nitrogen to N_2 which is collected quantitatively in a nitrometer (See Vol **1**, A418-R; Vol **6**, G172-L; & Refs 4, 17, 27, 28, 42, 47, 61 & 63)

Gravimetric methods applicable to energetic materials include the detn of NH_4 in AN using chloroplatinic acid (Ref 17); for nitrates using Nitron (Refs 15 & 17) or the di-cyclohexyl Tl^{+3} ion (Ref 29); for nitrites using Ag bromate (Refs 2 & 17); and for the thiocyanate ion using Ag nitrate (Vol **4**, D1065-L)

There are two important hydrogenation (or reduction) – titration procedures for the detn of N as ammonia. The Devarda method involves the quant reduction of nitrates to ammonia in alkaline soln using an Al-Cu-Zn alloy. The ammonia evolved is distd into standard sulfuric acid & titrated. This procedure is used for K nitrate, nitric acid, nitrites or ammonia (See Vol **6**, G107-L & Refs 3, 4, 14, 17, 19, 31, 34, 43 & 47). Another procedure, the Ter-Meulen hydrogenation method, consists of heating nitrate, nitrite or nitroso contg compds at about 350° in the presence of finely divided Ni, absorbing the ammonia formed in standard acid and titrating with standard alkali soln (Refs 4, 5, 6, 7, 8, 10, 12, 13, 17 & 47)

One of the least expensive and popular techniques for the quant detn of bound N in energetic materials is that of *titrimetry*. There are currently three basic titrimetry systems used: aq acid-base, redox and non-aqueous (involving both acid-base and redox systems in which there is association, not ionization of the reactants). The simple aq acid-base titrimetry system has been shown, earlier in the article, being used in the Kjeldahl, Devarda and Ter-Meulen procedures to detn liberated NH_3. It is also utilized, for example, to detn nitrosylsulfuric acid in mixed acids, total acidity in nitric acid, NG in expl oils, and the N content of ethyldiethanolamine (See Vol **1**, A88-Rff & A304-L; Vol **2**, C138-R; Vol **3**, C276-L; Vol **5**, D1640-Rff; Vol **6**, E226, E266 & G107-L; & Refs 3, 17, 18, 38, 40 & 62).

Redox (reduction-oxidation) titrimetry is used primarily for nitrate detns. Five systems are in current use: ferrous sulfate–dichromate, iodometric, periodic acid oxidation (NaOH titrant), K permanganate, and titanous chloride–ferric ammonium sulfate. The ferrous sulfate–dichromate system is used for MNT & DNT detns (Vol **2**, C162-Lff; Vol **6**, F17-Rff & Ref 17). In the iodometric procedure, the sample (ie, NG) is treated in a CO_2 atm with a satd soln of Mn chloride in concd HCl, the vol reaction products are bubbled thru a K iodide soln, and the liberated iodine is titrated with standard thiosulfate soln (Refs 1 & 17). The periodic acid oxidation procedure is used to detn NG in expl oils (Vol **5**, D1640-R to D1641-R). The NO_2 content of nitric acid is detd with standard K permanganate soln (Vol **1**, A88-R to A89-L & Refs 17, 29 & 54), while the titanous chloride–ferric ammonium sulfate system is primarily employed to detn nitro groups and nitrates in such energetic materials as NG, TNT, RDX, LSt, NGu, nitrobenzenes and nitrated anilines (See Vol **1**, A415-R, A418-L to A419-L & A454-R; Vol **2**, C50-L; Vol **3**, C251-R, C474-R, C476 & C540-L to C541-L; Vol **5**, D1272-R, D1282-L to D1283-R & D1646-L to D1648-R; Vol **6**, E211, F17-R to F19-L, G106-R to G107-L, G160-R to G161-L & G163; & Refs 17, 22, 26, 35, 37, 38, 39 & 54)

Nonaqueous titrimetry has been applied to detn the purity of inorganic stearates, nitrates, RDX, Amm Picrate, Tetryl, Haleite, TNC, K nitrate in M-8 proplnt and NGu (See Vol **1**, A165-R; Vol **3**, D102-L & C625-R to C626-L; Vol **6**, G154-L & G161; & Refs 30, 30a, 30b, 30c, 30d, 30e, 30f, 30g, 36, 59 & 61)

The widely used technique of light spectroscopy has also been applied to the qual and quant detn of bound N in energetic materials. There are five distinct systems used: colorimetry, infrared spectroscopy, polarimetry, Raman spectroscopy and ultraviolet spectroscopy

Colorimetry is employed to detn the purity of such materials as Na Azide and DPA. The method depends on the formation of a colored complex between the bound N group and a me-

tallic ion such as ferric or ferrous (Vol **1**, A303-L & A617; Vol **6**, F18-L; & Refs 9, 11, 17, 38, 39, 54 & 63)

Infrared spectroscopy is used not only to identify functional N contg groups, but to quant measure them. Procedures have been developed for nitrates, aminonitrates, nitrites, the detn of EGDN in the presence of NG, and for Anisole & its derivatives (Vol **1**, A455-L; Vol **6**, E270-L to E278-R, Vol **7**, I100-R to I101; & Refs 36a, 46, 54, 61 & 63)

Polarimetry, in which a beam of polarized light is rotated by passage thru an optically active substance, has been applied to the quant detn of sucrose octanitrate (Vol **5**, D1643-R & Ref 61)

Raman spectroscopy has been utilized in the quant detn of nitramines and nitrosamines (Vol **1**, A177-R & Ref 61), and ultra-violet spectroscopy is employed for the quant measurement of TNT in HBX compn (Refs 39, 61 & 63)

A modern technique for nitrogen detn is known as fast neutron activation analysis. Materials such as RDX are exposed to a high density fast neutron flux which converts the ^{14}N content of the sample into unstable ^{13}N. The N is detd by measuring the ^{13}N produced by the ^{14}N (n, 2n) ^{13}N reaction. This technique is extremely sensitive, but requires specialized instrumentation (Refs 44, 51 & 61)

Written by **H. L. HERMAN**

Refs: 1) F. Gooch & H. Gruener, JSci (3),**44**, 117 (1892) 2) N. Busvold, ChemZtg **38**, 28 (1914) & CA **8**, 1250 (1914) 3) H. Kesseler, R. Röhm & G. Lutz, ZAngChem **35**, 145 (1922) & CA **16**, 2093 (1922) 4) M. Marqueyrel et al, MP **21**, 326–77 (1924) 5) J. Heslinga, Rec **43**, 551 (1924) 6) H. Ter-Meulen, Rec **43**, 463 (1924) 7) Ibid, Rec **44**, 271 (1925) 8) H. Ter-Meulen & J. Heslinger, "Neue Methoden der Organisch-Chemischen Analyse", Leipzig (1927) 9) E. Griffing & C. Alsberg, JACS **53**, 1037 (1931) 10) J. Yoe, "Photometric Chemical Analysis, Colorimetry", Vol I, J. Wiley, NY (1928) 11) H. Ter-Meulen & J. Heslinga, "Nouvelles Methodes d'Analyse Organique", Dunock, Paris (1932) 12) I. Kolthoff & C. Noponeu, JACS **55**, 1448–53 (1933) 13) P. Maes, Bull assoc élèves inst. supér. ferm. Gand **36**, 39–40 (1935) & CA **29**, 2474 (1935) 14) G. Fleury & P. Jourdin, MP **27**, 179–81 (1937) 15) H.A. Fales & F. Kenny, "Inorganic Quantitative Analysis", Appleton Century, NY (1938) 16) A. Bouchonnet et al, MP **28**, 325 (1938/1939) 17) W.W. Scott, "Standard Methods of Chemical Analysis", 5th Ed, Van Nostrand, NY (1939), 629–68 & 1660–1700 18) H. Aaronson, "Development of Assay Method for Ethylenedinitramine", PATR **1200** (1942) 19) R. Carter et al, "Modified Devarda Method for the Determination of Nitrogen in Nitrocellulose", OSRD **3875**, PBL 30764 (1944) 20) I. Kolthoff, W. Harris & G. Matsuyama, "A New Method for the Polarographic Determination of Nitrate", JACS **66**, 1782–6 (1944) & CA **38**, 6235 (1944) 21) C. Dorée, "The Methods of Cellulose Chemistry", London (1947), 245–47 22) B.T. Fedoroff, "Rapid Method for the Determination of Nitrogen Content of Nitrocellulose by the Ferrous Ammonium Sulphate Method", PACLR **122871** (1948) 23) J. Pearson & A. Howard, "Polarographic Estimation of Inorganic Nitrates in Propellants", Anal **74**, 182–5 (1949) & CA **43**, 6417 (1949) 24) A. Potier, MP **32**, 487 (1950) 25) L. Brown & C. Hoffpauir, "Detection of Nitrogen in Organic Compounds", AnalChem **23** (7), 1035–6 (1951) 26) R. Leclercq & J. Mathé, BullBelg **60**, 296–300 (1951) 27) J. Lavitt, B. Banks & I. Kolier, "Determination of Nitrogen, Sulfur, Chlorine & Bromine Content of Organic Compounds", PATR **1894** (1952) 28) J. Noguchi, "Determination of Nitrogen in Organic Compounds", SciPapersOsakiUniv, No **22** (1951) & CA **46**, 3455 (1952) 29) H. Hartman & G. Bäthge, AngChem **65**, 107–109 (1953) 30) S.M. Kaye, "Determination of the Purity of Inorganic Compounds of Ordnance Interest by Titration in Nonaqueous Medium", PATR **1947** (1953) 30a) Ibid, "A Survey of the Application of the Nonaqueous Titration Method to Organic Compounds of Ordnance Interest", PATM **31** (1953) 30b) Ibid, "A Nonaqueous Titration Method for the Determination of the Purity of Ammonium Picrate", PATR **1895** (1953) 30c) Ibid, "A Method for the Determination of the Purity of Barium, Calcium, and Magnesium Stearates and Calcium Resinate by Titration in a Nonaqueous Medium", PATR **1926** (1953) 30d) Ibid, "The De-

velopment of a Nonaqueous Titration Method for the Determination of Purity of RDX and RDX Content of Composition A-3", PATR **1936** (1953) 30e) Ibid, "The Determination of Purity of Tetryl, Haleite and Tetranitrocarbazole by Titration in Nonaqueous Medium", PATR **1947** (1953) 30f) Ibid, "The Development of a Nonaqueous Titration Method for the Determination of RDX Content of Composition C-4", PATR **1958** (1953) 30g) S.M. Kaye, "Nonaqueous Titration Method for Determination of the Purity of Hexahydro-1,3,5-Trinitro-s-Triazine", AnalChem **27**, 292–5 (1955) 31) H. Liogier, MP **36**, 309–13 (1954) & CA **49**, 15621 (1955) 32) D. Louw, "Comparison of Some Catalysts Used in the Kjeldahl Nitrogen Determinations", JSAfricanChemInst **8**, 39–42 (1955) & CA **49**, 15621 (1955) 33) C. Adams & G. Spaulding, "Determination of Organic Nitrogen by Kjeldahl Method Without Distillation", AnalChem **27**, 1003–4 (1955) & CA **49**, 15621 (1955) 34) H. Liogier, R. Dalbert & J. Tranchant, MP **37**, 433 (1955) 35) C. Frejacques & M. Leclerq, MP **38**, 39–44 (1956) 36) H. Herman, "Nonaqueous Titration Method For The Determination of Potassium Nitrate in M-8 Propellant", PATR **2330** (1956) 36a) F. Pristera et al, PATR **2254** (1956) & AnalChem **32**, 498 (1960) 37) L. Marvillet & J. Trauehout, MP **42**, 271–84 (1960) 38) Anon, "Explosives: Sampling, Inspection & Testing", USMilSpec **MIL-STD-650** (1962) 39) Anon, "Explosive Compositions, HBX Type", USMilSpec **MIL-E-22267A** (1963) 40) Anon, "Ammonium Nitrate, Technical", USMilSpec **MIL-A-175A** (1963) 41) A.M. Hartley & D.J. Curran, "Polarographic Determination of Nitrates as 4-Nitro-2,6-Xylenol", AnalChem **35**, 686–691 (1963) 42) H. Wright, "The Rapid Micro Combustion Determination of Carbon, Hydrogen & Nitrogen in High Explosives", Explosivst **14** (12), 274–6 (1966) & CA **66**, 97068 (1967) 43) Anon, "Sodium Nitrate", USMilSpec **MIL-S-322C** (1968) 44) M. Rison, W. Barber & P. Wilkniss, "Fast Neutron Activation Analysis For Nitrogen in Explosives and Propellants", RadiochimActa **7** (4), 196–8 (1967) & CA **68**, 4570 (1968) 45) Anon, "Propellant, Uns-Dimethylhydrazine", USMilSpec **MIL-P-25604D** (1969) 46) H.H. Takimoto & G.C. Denault, "Combustion Residues From N204-MMH Motors", SAMSO **TR-69-373** (1969) 47) H. Wright, "Microcombustion Determination of Carbon, Hydrogen & Nitrogen in High Explosives", Explosivst **16** (8), 176–8 (1968) & CA **70**, 39420 (1969) 48) J.M. Trowell & M.C. Philpot, "Gas Chromatographic Determination of Plasticizers and Stabilizers in Composite Modified Double-Base Propellants", AnalChem **41** (1), 166–8 (1969) & CA **70**, 49143 (1969) 49) J. Trauchant, "Chromatographic Analysis of Stabilizers of Powdered Propellants and Their Nitrated Derivatives", IndChimBelg **32**, 601–5 (1967) & CA **70**, 49146 (1969) 50) F.I.H. Tunstall, "Determination of Gases Evolved From Stored Propellant Compositions by Gas Chromatography", Chromatographia (11–12), 477–80 (1968) & CA **70**, 49147 (1969) 51) R.J. Sparks & G.J. McCallum, "Determination of Trace Elements by Activation Analysis With Charged Particles", JSci **12** (3), 470–5 (1969) & CA **70**, 97975 (1969) 52) Anon, "Analysis of Natural Gases and Related Types of Gaseous Mixtures by Mass Spectrometer", ASTM **D1137-53** (1970) 53) P. Breisacher et al, "Simultaneous Differential Thermal-Mass Spectrometer Analysis of Nitrate Salts of Monomethylhydrazine and Methylamine", SAMSO **TR-70-117** (1970) 54) Anon, "Propellants, Solid: Sampling, Examination and Testing", USMilSpec **MIL-STD-286B** (1971) 55) Anon, "1971 Annual Book of ASTM Standards", Part **30**, E-2 on Emission Spectroscopy (partial), E-14 on Mass Spectrometry & E-19ff, Chromatography, Philadelphia (1971) 56) M. Jurecek, P. Kozak & J. Bartosova, "Analytical Aspects of the Oxidation of Organic Nitrogen Compounds With Chromic Acid. Gas Volume Determination of the Isonitroso Groups", CollectCzechChemCommun **35** (10), 3123-7 (1970) & CA **74**, 71443 (1971) 57) L. Bitterlin, "Apparatus for the Determination of the Nitrogen Content of Diazonium and Diazoamino Compounds", ZAnalChem **253** (2), 120–2, (1971) & CA **74**, 71441 (1971) 58) K. Ono et al, "Microanalysis. IX. Automation of F and M CHN [carbon, hydrogen, and nitrogen] Analyzer", SankoKenkyushoNempo **22**, 34–40 (1970) & CA **74**, 134761 (1971) 59) E.G. Aksenenko & V.M. Aksenenko, "Potentiometric Titration

of Mixtures of β-Nitro Alcohols", ProblAnal-Khim **1**, 112–14 (1970) & CA **74**, 134771 (1971) 60) O.I. Nikitina et al, "Determination of Nitrogen and Oxygen in Metals in a Low-Voltage Spark Discharge at Reduced Air Pressure", ZavodLab **37** (2), 183 (1971) & CA **74**, 106832 (1971) 61) W.F. Pickering, "Modern Chemistry", Marcel Dekker, Inc, NY (1971) 62) Anon, "Potassium Nitrate", USMilSpec **MIL-P-156B** (1974) 63) Anon, "1974 Annual Book of ASTM Standards", Part **47**, Index to ASTM Standards, Philadelphia (1974)

Nitrogen Bromide. See under Nitrogen-Halogen Compounds in this Vol

Nitrogen Chloride. See under Nitrogen-Halogen Compounds in this Vol

Nitrogen Dioxide. See under Nitrogen Oxides in this Vol

Nitrogen Fluoride. See under Nitrogen-Halogen Compounds in this Vol

NITROGEN-HALOGEN COMPOUNDS

Nitrogen Bromides

Bromamide (Bromamine). $BrNH_2$, mw 95.93, N 14.6%; the solid is purple-black when unsolvated, yellow when solvated, and yellow in soln (Refs 4 & 6); mp decomps violently above –80° with evolution of Br (Ref 4). In w there is a UV absorption peak at 277mμ, and in eth at 275mμ, the w peak being more prominent than the peak in eth (Ref 5); CA Registry No 14519-10-9. It was first prepd by the action of Br on liq ammonia which gave a mixt of bromamide and N tribromide solvated with 6 moles of ammonia (see below) (Ref 1). It has also been prepd, along with some bromimide, by the action of Br on ammonia in eth at –80° (Ref 2); in dil aq soln by the action of Br on aq ammonia (Ref 5); and in the vapor phase by the use of an app similar to that used by Sisler to prep chloramine (see above) (Ref 8); yield is low. It can be pptd from eth at –80° by the addn of pentane (Ref 6), and can be identified in aq soln by the adduct it forms with triphenylphosphine, $(H_2NPPh_3{}^+Br^-)$, mp 247–9° (Ref 8). Recent work has shown that bromamide can be stabilized in w by an excess of ammonia (Ref 7)

Bromimide (Dibromamine). Br_2NH, mw 174.82, N 8.01%; in w there is a small UV peak at 235mμ with a broad shoulder at 270–90mμ (Ref 5); CA Registry No 14519-03-0

It is prepd by the action of Br on ammonia in eth soln (Ref 3), or on liq ammonia (Ref 5). It is stabilised in aq soln by an excess of ammonia (Ref 9)

Nitrogen Tribromide, NBr_3, mw 235.72, N 5.5%; its UV spectrum in w has a peak at 227mμ, and in chlf at 267mμ (Ref 5); CA Registry No 15162-90-0

It is prepd by the action of Br on ammonia in w (Ref 5), or on liq ammonia (Ref 1). It is stabilized in aq soln by an excess of Br (Ref 9). The kinetics of the decompn of N tribromide in aq soln were studied. It was found that at a pH of 7 and an ammonia concn of 6.6×10^{-5}M, the 2nd order decompn constant was 4.1ℓ/mole sec (Ref 10)

Refs: 1) G.H. Coleman et al, JACS **56**, 963 (1934) 2) G.H. Coleman & G.E. Goheen, ProcIowaAcadSci **43**, 178 (1936) & CA **32**, 3717 (1938) 3) G.H. Coleman & G.E. Goheen, "Dibromamine" in "Inorganic Syntheses Vol I", McGraw-Hill, NY (1939), 62 4) J. Jander & E. Kurzbach, ZAnorgChem **296**, 117 (1958) & CA **53**, 109 (1959) 5) H. Galal-Gorchev & J.C. Morris, InorgChem **4**, 899 (1965) 6) J. Jander & C. Lafrenz, ZAnorgChem **349**, 57 (1966) & CA **66**, 80038 (1967) 7) J.D. Johnson & R. Overby, ACS, DivWaterAirWasteChem, GenPap **1969**, 108 & CA **73**, 123421 (1970) 8) D.F. Clemens et al, InorgChem **8**, 998 (1969) 9) J.D. Johnson & R. Overby, JSanatEngDiv, ASCE **97** (SA5), 617 (1971) & CA **76**, 37288 (1972) 10) T. Lapointe et al, PreprPapNatl-MeetingDivEnvironChem,ACS **13**, 192 (1973) & CA **82**, 160066 (1975)

NITROGEN CHLORIDES

Chloramine (Chloramide, Monochloramine). $ClNH_2$, mw 51.48, N 27.2%; a colorl liq or crysts, mp −66°, decomps above the mp (Refs 2 & 8). It has an IR absorption peak at 2430Å which can be used for spectrophotometric analysis (Ref 3). It is unstable at room temp except in aq soln, so it is stored and handled in this form (Ref 4); CA Registry No 10599-90-3

It has been prepd by various procs using chlorinating agents, ie, Cl gas or hypochlorites in aq or anhyd ammonia. For example, the interaction of Cl:ammonia:N 1:2.04:12.73 at 300° in a flow reactor gives chloramine which is absorbed in a suitable solv at 75° (Ref 9). An app is described in Ref 10 for the improved prepn of chloramine using a Cl:ammonia:N ratio of 1:8.6:3.2, max yield 95%. It has also been prepd by the hydrolysis of N,N′-dichlorourea (Ref 1)

Uses: It is one active ingredient present in water which has been purified by chlorination (Ref 6). It is used as an intermediate for the prepn of hydrazine and substituted hydrazines. Recently there has been a renewed interest in chloramine as a possible intermediate for the prepn of UDMH (see Vol **7**, H203-R) which avoids handling the highly carcinogenic dimethylnitrosamine (Refs 5 & 7)

Refs: 1) R.L. Datta, JCS **101**, 166 (1912) 2) W. Marckwald & M. Wille, Ber **56**, 1319 (1923) 3) J. Kleinberg et al, AnalChem **26**, 1388 (1954) 4) E. Colton & M.M. Jones, JChemEduc **32**, 485 (1955) 5) G.M. Omietanski et al, JACS **78**, 3874 (1956) 6) Y. Isomura, BullChemSocJapan **40**, 835 (1967) (Eng) & CA **67**, 57181 (1967) 7) R.G. Laughlin, ChemZtg,ChemApp **92**, 383 (1968) & CA **69**, 51465 (1968) 8) Gmelin, Syst Nr 6, Erg [B] (1969), 490 9) W.R. Grace & Co, BritP 1149836 (1969) & CA **71**, 23368 (1969) 10) H. Prakash & H.H. Sisler, AllgPraktChem **21**, 123 (1970) & CA **73**, 20977 (1970)

Dichloramine (Dichloramide, Chlorimide). Cl_2NH, mw 85.92, N 16.3%; CA Registry No 3400-09-7

Chlorimide is an unstable gas which can be stored in aq soln; the pure gas decomps within 7 min (Ref 2). It is the least stable of the chloramines (Refs 3 & 5). It is best prepd by the interaction of Cl and Amm salts in w at a pH betw 4.4 and 8.5 (Ref 1). The IR spectrum of mixts of chloramines is given in Ref 2. It is one of the active species present when w contg Amm salts or amines is purified with Cl (Ref 4)

Refs: 1) R.M. Chapin, JACS **51**, 2112 (1929) 2) G.E. Moore & R.M. Badger, JACS **74**, 6076 (1952) 3) R.E. Corbett et al, JCS **1953**, 1927 4) Y. Isomura, BullChemSocJapan **40**, 835 (1967) (Eng) & CA **67**, 57181 (1967) 5) Gmelin, Syst Nr 6, Erg [B] (1969), 489

Nitrogen Trichloride. NCl_3, mw 120.38, N 11.63%; a dense yel liq, mp −27°, bp (extrapolated) 71° (Ref 8); Q_f in C tetrachloride −55.0kcal/mole (Ref 5); CA Registry No 10025-85-1

The expl nature of N trichloride has been known since the end of the 18th century when Sir H. Davy reported, "The fulminating oil which you mentioned roused my curiosity and nearly deprived me of an eye. After some months confinement I am again well." (Ref 12). The early history of this compd is reviewed in this Ref. It is readily prepd by the action of Cl on ammonia or Amm salts (Refs 2, 6 & 13); or by the electrolysis of an unstirred concd soln of Amm chloride at 35–40° (Ref 4). A procedure for the prepn of a soln of N trichloride in chlf is described in Ref 1, and prepn on an industrial scale in Ref 7

Explosive Properties. It is a sensitive and powerful expl (Ref 9). Mixts of N trichloride, H, & Cl expld with a bright flash (Ref 10). It also explds violently on heating, exposure to light, or on contact with org compds (Ref 8); Q_e ca −55 kcal/mole (Ref 11)

Uses. It is one active species present when w contg Amm salts or amines is purified by chlorination (Ref 11)

Refs: 1) W.A. Noyes, JACS **50**, 2904 (1928) 2) J.G.A. Griffiths & R.G.W. Norrish, TrFaradSoc **27**, 451 (1931) 3) L. Pauling, JACS **54**, 3570 (1932) 4) F. Jirsa, ZElektrochem **41**, 321 (1935) & CA **29**, 7818 (1935) 5) Bichowski & Rossini (1936), 218 6) W.A. Noyes, "Nitrogen Trichloride" in "Inorganic Syntheses Vol I", McGraw-Hill (1939), 65 7) Korenschoof N.V., BritP631327 (1949) & CA **44**, 3820 (1950) 8) Sidgwick, ChemElems

1 (1950), 705 9) G.E. Moore & R.M. Badger, JACS **74**, 6076 (1952) 10) P.G. Ashmore, Nature **172**, 449 (1953) 11) Y. Isomura, BullChemSocJapan **40**, 835 (1967) (Eng) & CA **67**, 57181 (1967) 12) H.A.M. Snelders, ChemTechRev **22**, 457 (1967) & CA **68**, 9212 (1968) 13) Gmelin, Syst Nr 6, Erg [B] (1969), 483

Chlorine Azide (Trinitrogen Chloride). ClN_3, mw 77.47, N 54.2%; an orange-yel liq or orange solid, mp ca −100°, bp ca −15° (Refs 2 & 5). It is extremely sens and can expld without provocation at any time, but can be stored indefinitely at low temp in sealed ampules when shielded from light (Ref 2). Its UV and visible spectra are in Ref 6

It has been prepd by the action of Cl on Ag azide in eth (Ref 1), or better by the addn of acet ac to a mixt of Na azide and Na hypochlorite (Ref 2)

The expln limits of mixts of gaseous Cl azide with Ar, N, and C dioxide are in Ref 3. The shock wave formed by the expansion of the gas into a vacuum is sufficient to cause decompn (Ref 5); Q_e −93.2 ± 1.5kcal/mole, flame temp at 20mm 3380°K (Ref 6). Mixts of Cl azide:N trifluoride:H 1:1:2 at 12–24 torr are initiated with a Xe flash lamp to produce explns which excite a H fluoride laser. Cl azide, S hexafluoride, H mixts were similarly used (Ref 7)

Refs: 1) F. Rashig, Ber **41**, 4194 (1908) 2) W.J. Frierson et al, JACS **65**, 1696 (1943) 3) C. Paillard et al, CR **264**(C), 832 (1967) & CA **67**, 13444 (1967) 4) C. Paillard, CR **264**(C), 1721 (1967) & CA **68**, 6980 (1968) 5) Gmelin, Syst Nr 6, Erg [B] (1969), 488 6) T.C. Clark & M.A.A. Clyne, TrFaradSoc **65**, 2994 (1969) 7) R.J. Jensen et al, USP 3662280 (1972) & CA **77**, 41277 (1972)

CHLOROFLUORAMINES

Chlorodifluoramine, $ClNF_2$, mw 86.47, N 16.0%; a colorl gas, bp −67° (Ref 7); $Q_f$gas 3.2 ± 2.9 kcal/mole; Q_f liq at −67°, −2.2kcal/mole; energy of NCl bond 35.5kcal/mole (Ref 5); CA Registry No 13637-87-1

It has been prepd by the action of phosgene or H chloride on fluorimide (Ref 3); by the action of F diluted with N on a mixt of Na azide and Na chloride (Ref 1); by the action of Cl on fluorimide in the presence of Na fluoride (Ref 4); in 68% yield by the action of Cl on the adduct of trifluoroformamide (F_2NCOF) with K fluoride in perfluoracetone (Ref 6); or by the photolysis of a mixt of tetrafluorohydrazine and thionyl chloride (Ref 8)

It decomps slowly when stored in metal cylinders (Ref 5). Its expl props have not been examined

Dichlorofluoramine, $FNCl_2$, mw 103.91, N 13.5%; a gas, bp −3 to −2° (Refs 2 & 7); CA Registry No 17417-38-8

It is prepd by the action of Cl monofluoride on Na azide, yield 20% (Ref 2)

Refs: 1) T.A. Austin & R.W. Mason, InorgChem **2**, 646 (1963) 2) B. Sukornik et al, InorgChem **2**, 875 (1963) 3) E.A. Lawton & J.Q. Weber, JACS **85**, 3595 (1963) 4) W.C. Firth, InorgChem **4**, 254 (1965) 5) A.N. Zercheninov et al, ZhFizKhim **40**, 2101 (1966) & CA **66**, 14587 (1967) 6) G.W. Frazer & J.M. Shreeve, InorgChem **6**, 1714 (1967) 7) Gmelin, Syst Nr 6, Erg [B] (1969), 588 8) L.M. Zamborski et al, InorgChem **8**, 2005 (1969)

NITROGEN FLUORIDES

Inorganic Compounds, compounds derived from ammonia

Fluoramine (Nitrogen Dihydrogen Fluoride, Amine Fluoride). FNH_2, mw 35.62, N 39.32%; a colorl gas, subl −77° and 760mm (Refs 3 & 4); CA Registry No 15861-05-9. The isolation of fluoramine was first claimed by Ruff & Staub who isolated it in low yield by the electrolysis of molten Amm fluoride (Ref 1). They reported it to be an expl gas which has a distinctive odor and is very toxic (Refs 1 & 2). More recently it was found that fluoramine could be conveniently prepd by the acid hydrolysis of N-fluorourethanes, and that the mat isolated by Ruff & Staub was probably impure (Ref 5)

Salts, **Methanesulfonate,** $FNH_3^+MeSO_3^-$, mp 103–05° with decompn; CA Registry No 20175-02-4. It is prepd by the reaction of N-fluorourethane (FNHCOOEt) with methanesulfonic acid in chlf (Ref 5)
Perchlorate, $FNH_3^+ClO_4^-$, mp 104–05° with decompn; prepd by addn of N-iso-Pr-N-fluorourethane to a soln of perchloric acid in chlf (work must be done behind a good safety shield as compds are expl) (Ref 5)

Trifluoromethanesulfonate, $FNH_3^+F_3CSO_3^-$, mp subl; CA Registry No 42138-65-5. It is prepd by the reaction of N-fluorourethane with trifluoromethanesulfonic acid in methyl chloride (Ref 6). It is more stable than the salts listed above (Ref 6), and upon subln at low press, it dissociates into fluoramine and trifluoromethanesulfonic acid without further decompn (Ref 7)
Refs: 1) O. Ruff & L. Staub, ZAnorgChem **198**, 32 (1931) & CA **25**, 5105 (1931) 2) O. Ruff & L. Staub, ZAnorgChem **212**, 399 (1933) & CA **27**, 4471 (1933) 3) F.C. Rossini et al, "Selected Values of Chemical Thermodynamic Properties", NBS Circular 500 (Feb 1952), 566 4) Gmelin, Syst Nr 5, Erg (1959), 249 5) V. Grakauskas et al, JACS **90** 3480 (1968) 6) V. Grakauskas, JInorgNuclChem **35**, 3034 (1973) & CA **79**, 125749 (1973) 7) S. Highsmith & E. Grunwald, JPhChem **78**, 1431 (1974)

Difluoramine (Fluorimide, Fluorimine). HNF_2, mw 63.02, N 22.23%; a colorl gas, mp $-116 \pm 3°$, bp –23.6° (Refs 4 & 6), crit temp 130° (Ref 5), vapor d 1.424 –0.00202t (Ref 6), an odor resembling H cyanide, and is extremely toxic (Ref 1); CA Registry No 10405-27-3. The first prepn of difluoramine was claimed by Ruff & Staub who claimed to have obtained it in low yield by the electrolysis of molten Amm bifluoride (Ref 1), although more recent work indicates their prod was impure (see below). More recent prepns are by the reaction of tetrafluorohydrazine (F_2NNF_2) with thiophenol, yield up to 74% (Ref 7); by treatment of triphenylmethyldifluoramine with sulfuric acid, yield almost quant, purity by mass spec 99% (Ref 10); and by fluorination of: 1) cyanuric acid (Ref 5); 2) sulfamide, yield 45% (Ref 14) [Kelly and Sukornick found that sulfamic acid, w, and F will react continuously in a flow reactor to generate difluoramine in 77% yield based on F consumed (Ref 15)] ; or 3) urea, yield 15% (Ref 6). Exptl details of the prepn from urea are given in Ref 9, and further exptl details including necessary precautions are given in Ref 20. Its purification is difficult (Ref 2) and is best done in a high vacuum system by trap-to-trap distn (Ref 7)
Hazards. Solid difluoramine, upon warming from liq N temp to its mp, can detonate without warning (Ref 13); the pure compd in the solid or liq state can detonate at any time without warning (Ref 5); and it can expl on contact with air (Ref 7). Above 100° it decomps explosively (Ref 3). It can be stored indefinitely in glass (Ref 5), and is best handled and stored as an aq soln (Ref 5)
Thermochemical Data. In the ideal gas state at 1 atm and from 200 to 2000°K the following values were obtained: entropy 51.731–84.336, heat capacity 8.937–18.717, heat content 8.182–15.238, and free energy 43.549–69.098kcal/deg/mole (Ref 8); Q_f^{gas} –15.6, Q_f^{liq} -22 ± 1.5kcal/mole (Ref 19); Q_v 5940 cal/g (Ref 16)
Spectra. IR spectrum is in Ref 11 and the mass spectrum cracking pattern is in Ref 5
Thermal Decomposition. It decomps in the gas phase at 275° in Teflon or Monel to give N, H fluoride, and tetrafluorohydrazine (Ref 21)
Reactions. It reacts with an aq soln of low pH to form difluorodiazine (FN:NF) and nitrous oxide, and with Fe^{+++} to form tetrafluorohydrazine in good yield (Ref 13). It reacts with carbonyl compds under mild conditions to give alpha-difluoroamino alcohols (Ref 18); and under vigorous conds, ie in presence of concd sulfuric acid, to give gem(bisdifluoroamino) compds; and with 2,3-unsaturated carbonyl compds to give $(F_2N)_2CCH_2CHNF$ (Ref 17)
Uses. Its primary use is in the prepn of organic difluoroamino compounds. A 1:1 adduct of difluoramine with methyl ether can be used as a rocket proplnt, Isp 229sec at 1000psia. In the range difluoramine:methyl ether 4–8:1 the Isp is 282–93sec; and in the range difluoramine: ether 5–8:1 the Isp is 283–92sec; other ethers can be used (Ref 12)
Refs: 1) O. Ruff & L. Staub, ZAnorgChem **198**, 32 (1931) & CA **25**, 5105 (1931) 2) O. Ruff,

Ber **69A**, 181 (1933) 3) O. Ruff & L. Staub, ZAnorgChem **212**, 399 (1933) & CA **27**, 4471 (1933) 4) Gmelin, Syst Nr 5, Erg (1959), 249 5) A. Kennedy & C.B. Colburn, JACS **81**, 2906 (1959) 6) E.A. Lawton & J.Q. Weber, JACS **81**, 4755 (1959) 7) J.P. Freeman et al, JACS **82**, 5304 (1960) 8) G. Nagarajan, IndJPureApplPhys **1**, 403 (1963) & CA **60**, 4878 (1964) 9) E.A. Lawton & J.Q. Weber, JACS **85**, 3595 (1963) 10) W.H. Graham & C.O. Parker, JOC **28**, 850 (1963) 11) C.B. Colburn, "Nitrogen Fluorides and their Inorganic Derivatives" in M. Stacey et al, eds "Advances in Fluorine Chemistry" **3**, Butterworths, London (1963), 92 12) E.A. Lawton & J.Q. Weber, USP 3101446 (1963) & CA **59**, 13764 (1963) 13) K.J. Martin, JACS **87**, 394 (1965) 14) Allied Chem Corp, BelgP 658521 (1965) & CA **64**, 7729 (1966) 15) D.H. Kelly & B. Sukornick, BritP 1029707 (1966) & CA **65**, 3400 (1966) 16) B.H. Justice & I.H. Carr, "The Heat of Formation of Propellant Ingredients", **DCC AR-T0009-1S-67** (Dec 1967), **AD-387455**, 8 17) K. Baum, JACS **90**, 7083 (1968) 18) J. Grior & J. Peters, BritP 1119602 (1968) & CA **69**, 96058 (1968) 19) A.V. Pankratov et al, ZhFizKhim **43**, 394 (1969) & CA **70**, 118752 (1969) 20) C.O. Parker & J.P. Freeman, InorgSyn **12**, 307 (1970) 21) J.B. Levy & V.R. Desai, "The Pyrolysis of Difluoramine", George Washington Univ Rept **SL-100** (1970), **AD-707428**

Difluorodiazine (Dinitrogen Difluoride). N_2F_2, mw 66.02, N 42.4%; a colorl gas, freezes to lustrous transparent cubic crysts, odor similar to N dioxide (Ref 1); bp $-110°$ (Ref 1); CA Registry No 10578-16-2

It is prepd by the thermal decompn of F azide (Ref 1); as a by-prod from the fluorination of Amm bifluoride (Ref 2); by the photolysis of tetrafluorohydrazine at room temp (Ref 4); or by the fluorination of Na azide (probably thru F azide followed by decompn)(Ref 6)

The crude compd can be fractionated into two isomers:

cis-Difluorodiazine (Z-Difluorodiazine). FN‖FN, mp below $-195°$, bp $-105.7°$ (Ref 2); Q_v 3670cal/mole, crit temp $-1°$ (Ref 2), Q_f at bp 20.5±2.0kcal/mole (Ref 5); CA Registry No 13812-43-6

trans-Difluorodiazine (E-Difluorodiazine). NF‖FN, mp $-172°$, bp $-111.4°$ (Ref 2); Q_v 3400cal/ mole, crit temp $-13°$ (Ref 2); CA Registry No 13776-62-0

It has been proposed that the higher boiling, more reactive isomer is $F_2N{:}N$ (Ref 3), but more recently, electron diffraction studies have confirmed that the two isomers are **cis** and **trans** forms (Ref 7). Both isomers react with Hg and can expld on contact with org mat. Stopcocks and valves of vac app should be lubricated with silicone grease (Ref 2)

Refs: 1) Gmelin Syst Nr 5, Erg (1959), 246 2) C.B. Colburn et al, JACS **81**, 6397 (1959) 3) R.H. Sanborn, JChemPhys **33**, 1855 (1960) 4) C.L. Bumgardner & L. Lustig, InorgChem **2**, 662 (1963) 5) A.V. Pankratov et al, ZhFizKhim **37**, 1399 (1963) & CA **59**, 8191 (1963) 6) A.V. Pankratov & O.M. Sokolov, ZhNeorgKhim **11**, 1497 (1966) & CA **65**, 11744 (1966) 7) R.K. Bohn & S.H. Bauer, InorgChem **6**, 309 (1967)

Nitrogen Trifluoride. NF_3, mw 71.01, N 18.67%; a colorless gas, mp $-206.71°$ (Refs 4 & 7), bp $-129.01°$, triple point 66.361±.373°K (Ref 3); CA Registry No 7783-54-2

It was first prepd by the electrolysis of fused Amm bifluoride (Ref 1) and later by sparking a mixt of F and N at liq N temp, yield 30% (Ref 11). It is now being prepd commercially by the former proc (Ref 12)

Explosive Properties. N trifluoride is the most stable of the N halides, but it can detonate in the presence of hydrazoic acid (Ref 13) or org compds (Ref 10). Ozone, which is one by-prod of the electrolysis of Amm bifluoride, was found by Ruff and coworkers to cause violent explns in the reaction vessels and gas lines. They found that the ozone could be removed by passing the off-gas thru pyrolusite, thus reducing considerably the expln hazard (Ref 1). It also decomps explosively above 100° (Ref 2)

Flammability. The flammability limits of mixts ofN trifluoride with gaseous fuels and the effect of N as a diluent are given in graphic form in Ref 18. Fuels examined are H, butane, and hexafluoroethane. The authors also report that

the flame vel of N trifluoride/hydrocarbon mixts is 3 times that of O/hydrocarbon mixts, hence the danger of fire and expln with N trifluoride is much greater than with O mixts. They also concluded that the fire hazard of N trifluoride is much greater at elevated temps and that it will ignite most materials if the temp is high enough (Ref 18). By diluting the gas or liq to below 9.4 mole % with an inert mat such as N, the expln hazard can be almost eliminated (Ref 12)

Spectrum. The IR spectrum is in Ref 17

Thermodynamic Properties. Energy of N–F bond 61.1kcal/mole (Ref 15); Q_f^{gas} –31.440 kcal/mole (Ref 17)

Toxicity. A 1% concn of the gas in air is lethal to rats in 1 hour, its effect being similar to C monoxide; the LD50 in rats when injected intraperitoneally is 8.2ml/kg (Ref 16). Earlier workers assumed that the toxicity of N trifluoride would be similar to H fluoride and that the latter would be formed by hydrolysis in body tissues (Ref 1). This has recently been shown to be erroneous, and that it is stable under physiological conds. The toxic effect is due to its ability to complex with the hemoglobin of the blood causing anoxia. This effect is reversible, and animals receiving a sublethal dose recover rapidly upon removal from contact with N trifluoride (Ref 14)

Uses. A review of its use as an oxidizer in rocket proplnts is given in Ref 6. A 50:50 mixt of N trifluoride:F, with ammonia as fuel, yields a specific impulse of 295sec and a d impulse (specific impulse X d) of 340 (Ref 6). Mixts with methyl fluoride, 1,1-difluoropropane, and 1,3-difluoropropane have been patented as monoproplnts (Ref 9). A N trifluoride/H flame has been proposed as a cutting and welding torch (Ref 8)

Refs: 1) O. Ruff, AnorgAllgemChem **172**, 417 (1928) & CA **22**, 4398 (1928) 2) O. Ruff & L. Staub, ZAnorgChem **198**, 32 (1931) & CA **25**, 5105 (1931) 3) L. Pierce & E.L. Pace, JChemPhys **22**, 1271 (1954) 4) L. Pierce & E.L. Pace, JChemPhys **23**, 551 (1955) 5) L. Pierce & E.L. Pace, JChemPhys **23**, 1248 (1955) 6) J.F. Gall, IEC **49**, 1331 (1957) 7) Gmelin Syst Nr 5 Erg (1959), 238 8) H.H. Rogers, IEC **51**, 309 (1959) 9) I.A. Kanareck, USP 2968145 (1961) & CA **55**, 13582 (1961) 10) C.C. Colburn, "Nitrogen Fluorides and their Inorganic Derivatives" in M. Stacey et al, eds, "Advances in Fluorine Chemistry" **3**, Butterworths, London (1963), 94 11) W. Maya, InorgChem **3**, 1063 (1964) 12) J.F. Tompkins & E.S.J. Wang, USP 3235474 (1966) & CA **64**, 12248 (1966) 13) V.G. Voronov & A.S. Rozenberg, DoklAkadN **177**, 835 (1967) & CA **68**, 61112 (1968) 14) F.N. Dost et al, "Metabolism and Pharmacology of Inorganic and Fluorine Containing Compounds", Aerospace Medical Research Laboratories **AMRL-TR-67-224** (Aug 1968), **AD-681161**, p 8 15) A.N. Zercheninov et al, ZhFizKhim **43**, 390 (1969) & CA **70**, 100370 (1969) 16) F.N. Dost et al, Toxicol-ApplPharmacol **17**, 585 (1970) & CA **74**, 30505 (1971) 17) H. Prophet & A.N. Syverud, "Investigation and Compilation of the Thermodynamic Properties of High Temperature Chemical Species", **DCC T0009-4-69** (Jan 1970), **AD-867952**, p 50 & CA **77**, 169574 (1972) 18) F.J. Pisacane et al, "Reactions of NF_3 with Gases and Condensed Matter" in 12th JANNAF Combustion Meeting, Vol I, **CPIA Pub 273** (Dec 1975), 585

Tetrafluoroammonium Salts

Tetrafluoroammonium Hexafluoroarsenate, $NF_4^+AsF_6^-$, mw 278.95, a white solid, decomps ca 175° (rapid heating) into N trifluoride, As pentafluoride, and F (Ref 8); CA Registry No 16871-75-3

It is prepd by heating a mixt of N trifluoride, As pentafluoride, and F in a Monel tube reactor at 200° for 2–5 days (Ref 1); or by passage of the same reagents thru a glow discharge (Ref 4). Differential thermal analysis indicates that on slow heating the decompn starts ca 270° (Ref 2). Its IR and NMR spectra are given in Ref 3. It is a useful fluorinating agent and oxidizer for solid rocket proplnts (Ref 6)

Tetrafluoroammonium Tetrafluoroborate, $NF_4^+BF_4^-$, mw 176.81, a white solid, decomps betw 240 and 350° into N trifluoride, B trifluoride, and F (Ref 5), Q_f –380kcal/mole (Ref 5); CA Registry No 15640-93-4

It has been prepd by irradiation of a mixt of B trifluoride, N trifluoride, and F with 3 mev radiation from a Van der Graff generator (O

must be rigorously excluded to avoid explns) (Ref 7); or by irradiation of the same reagents in a sapphire reactor with unfiltered UV radiation (Ref 10). The IR spectrum is given in Refs 5 & 10, and the X-ray diffraction pattern indicates the crystal to be cubic with a 7.35Å (Ref 5). It has been proposed as an oxidizer in solid rocket proplnts and as a source of active F radicals for a H fluoride/D fluoride laser (Ref 10)

Tetrafluoroammonium Hexafluoroantimonate, $NF_4^+SbF_6^-$, mw 325.76, a white solid, decomps ca 350° (Ref 1); CA Registry No 16871-76-4

It is prepd by heating a mixt of N trifluoride, Sb pentafluoride, and F in a Monel tube reactor at 200° for 2.5 days (Ref 1); or by irradiating the same reagents with UV radiation in a quartz bulb (Ref 9)

Other tetrafluoroammonium salts which have been prepd are **Tetrafluoroammonium Pentafluorogermanate,** $NF_4^+GeF_5^-$, decomps 249°; **Tetrafluoroammonium Hexafluorophosphate,** $NF_4^+PF_6^-$, decomps 245°; and **Bis(tetrafluoroammonium) Hexafluorogermanate,** $(NF_4^+)_2GeF_6^{--}$, decomps 238° (Ref 9)

Refs: 1) W.E. Tolberg et al, InorgNuclChemLetters **2**, 79 (1966) & CA **65**, 6709 (1966) 2) K.O. Christe et al, InorgNuclChemLetters **2**, 83 (1966) & CA **65**, 8320 (1966) 3) K.O. Christe, InorgChem **6**, 533 (1967) 4) I.J. Solomon, "Kinetics of Synthesis and Decomposition Reactions of Ionic Compounds Containing N–F Cations", Illinois Institute of Technology Research Institute, **IITRI C-6140** (Jan 1969), **AD-682497**, p 5 & CA **77**, 131206 (1972) 5) S.M. Sinel'nikov et al, DoklAkadN **194**, 1341 (1970) & CA **74**, 37927 (1971) 6) K.O. Christe et al, USP 3503719 (1970) & CA **72**, 123534 (1970) 7) C.T. Goetschel et al, InorgChem **11**, 1696 (1972) 8) I.J. Solomon et al, JFluorineChem **2**, 129 (1972–73) & CA **77**, 131206 (1972) 9) K.O. Christe et al, InorgChem **12**, 2478 (1973) 10) K.O. Christe et al, "Annual Report, Inorganic Halogen Oxidizer Research", Rocketdyne Division, Rockwell International **R-9881** (Jan 1976), **AD-A020482**

Tetrafluorohydrazine (Dinitrogen Tetrafluoride). N_2F_4, mw 104.01, N 26.9%; a colorl gas at room temp, in the condensed phase it varies from white to blue-black depending on the % N difluoride free radical present (see below). This, in turn, depends on how quickly and from what temp the tetrafluorohydrazine is condensed (Ref 4). The odor is described as musty (Ref 7); CA Registry No 12357-40-3

Physical Properties. mp −163° (Ref 7), bp −73°, crit temp 36°, crit pres 77 atm (Ref 1); Q_v 3170cal/mole, Q_f gas at 25° −2.0±2.5kcal/mole (Ref 2)

Preparation. Its prepn was first carried out by the action of metals as F acceptors on N trifluoride in a flow reactor at 375°, conversion 42–62%, yield 62–71% (Ref 1). It has also been prepd by the passage of N trifluoride thru a fluidized bed of powd C at 400–500°, conversion 38%, yield 77% (Refs 3 & 3a); or by the oxidn of difluoramine (Ref 6)

Explosive Properties. It undergoes an expl reaction with H_2, but concn and temp limits of the expln were not reproducible in Pyrex or stainless steel reactors, probably due to the presence or absence of initiating radicals on the walls. The results became more reproducible after the walls were coated with silicone oil. Addn of tetrafluorohydrazine to H_2/difluoramine or H_2/N trifluoride mixts caused immediate explns (Ref 9). It also can expld on contact with reducing agents or from high press produced by shock wave or blast (Ref 11)

Its toxicity is high and similar to H fluoride (Ref 11)

Reactions. It exists in equil with the N difluoride free radical $N_2F_4 \rightleftharpoons 2.NF_2$ which is shifted to the right as the temp is raised (Ref 4); $Q_{dissociation}$ 20 ± 1.0kcal/mole (Ref 5). It decomps at 350–480° and 150–1200mm into N_2 and N trifluoride (Ref 8). It undergoes a large number of thermal and photochem reactions with org compds (for individual reactions see in the Encycl under the parent org compd)

Uses. Its principal use is for the prepn of difluoramine-contg org compds. Mixts with H_2 have been proposed as rocket proplnts, but all attempts to use these mixts as such have been plagued by erratic, unsteady reactions, accompanied by low order explns. The addn of O_2 seems to reduce this problem somewhat (Ref 10)

Refs: 1) C.B. Colburn & A. Kennedy, JACS **80**, 5004 (1958) 2) G.T. Armstrong et al,

"Heat of Formation of Tetrafluorohydrazine", NBS Rept **6584** (Oct 1959), AD-232598 3) J.R. Gould & R.A. Smith, GerP 1138382 (1960) & CA **58**, 3130 (1963) 3a) C.B. Colburn et al, "Quarterly Progress Report on Physical Chemistry", RHC(H) Rept **P-59-9** (July 1959), AD-309143 4) F.A. Johnson & C.B. Colburn, JACS **83**, 3043 (1961) 5) C.B. Colburn, ChemBrit **2**, 336 (1966) & CA **65**, 11744 (1966) 6) E.A. Lawton & J.Q. Weber, USP 3294495 (1966) & CA **66**, 67504 (1967) 7) Kirk & Othmer **9** (1966), 629 8) V.N. Cherednikov et al, ZhNeorg-Khim **14**, 873 (1969) & CA **71**, 25068 (1969) 9) L.P. Kuhn & C. Wellman, InorgChem **9**, 602 (1970) 10) T. Houser, "Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants", Western Mich U Chem Dept **AFOSR-TR-71-2993** (Nov 1971), AD-734796, p 34 11) Sax (1975), 1150

Fluorine Azide (Trinitrogen Fluoride). FN_3, mw 61.02, N 73.2%; a greenish yellow gas at room temp, a greenish yellow oily liq (Ref 1); odor similar to Cl dioxide (Ref 1); mp -143° (Ref 3), bp -82° (Ref 1); UV and visible absorption maxima are in Ref 3. It is prepd by fluorination of H azide with F:Ar mixts 1:200 (Ref 2). Best yields are obtained when the ratio of H azide to F is 2:1 (Ref 2). As the danger of explns is great, the reaction must be well shielded (Ref 1). Explns of liq or solid F azide are described as unusually violent and brisant (Ref 1). Evapn of solid or liq F azide frequently results in explns (Ref 2)

Refs: 1) Gmelin Syst Nr 5, Erg (1959), 247 2) D.E. Milligan & M.E. Jaycox, JChemPhys **40**, 2461 (1964) 3) E. Gipstein & J.F. Haller, ApplSpectros **20**, 417 (1966)

Nitrogen Iodides

Iodamide (Iodamine). INH_2, mw 142.93, N 9.8%, a black solid; prepd by the action of I on liq ammonia at -90° followed by evapn of the excess ammonia; further removal of ammonia under high vacuum converts it to N triiodide (Ref 11). Under apparently similar conditions the same workers later isolated a red complex contg 1 mole of ammonia which loses the mole of ammonia under high vacuum, regenerating the black iodamide (Ref 12)

Nitrogen Triiodide, NI_3, mw 394.77, N 3.5%; a black powd, detons when dry, exposed to light, or an elec spark (Refs 8 & 10); Q_f 35kcal/mole (Ref 7). It is formed by the interaction of free I or I_3^- on liq, gaseous, or aq ammonia (Refs 1, 8 & 10). N triiodide forms a series of solvates with excess ammonia: $NI_3.NH_3$, bright red needles, explds when dry (Ref 2). The damp solid was pumped dry under vacuum at 0°, and it detond when the last trace of w was removed; below -11° it decomps slowly (Ref 6); Q_e -42 ± 2.0kcal/mole, N–I bond strength 48 ± 4kcal/mole (Ref 14); CA Registry No 14014-86-9

$NI_3.2NH_3$, yellow crysts (Ref 5). It was shown later by X-ray diffraction that this is a mixt of a red and a green solvate (Ref 11)

$NI_3.3NH_3$, oliv-green needles (Refs 5 & 11); CA Registry No 15823-38-8

$NI_3.12NH_3$, a brown-black powd (Ref 4). This was also shown by X-ray diffraction to be a mixt (Ref 11)

Iodine Azide. IN_3, mw 168.92, N 24.9%; a black solid, decomps on standing or in the presence of S compds (Refs 9 & 13); CA Registry No 14696-82-3

It is prepd by the action of I on Ag azide (Ref 3); or more easily in soln by the interaction of I chloride and Na azide (Ref 13). Solns of I azide react readily with olefins to give 2-iodoalkyl azides which lose H iodide to form unsaturated azides (Ref 13)

Refs: 1) B. Courtois, AnnChim **88**, 309 (1813) 2) F.D. Chatterjay & K.J.P. Orton, AmChemJ **24**, 345 (1900) 3) A. Hantzsch, Ber **33**, 522 (1900) 4) O. Ruff, Ber **33**, 3027 (1900) 5) C. Hugot, CR **130**, 507 (1900) 6) F.R. Meldrum, PrRoySoc **A174**, 410 (1940) 7) F.R. Meldrum, PrRoySoc **A174**, 425 (1940) 8) Gmelin, Syst Nr 8 (1955), 593 9) Gmelin, Syst Nr 8 (1955), 600 10) J. Eggert, PrRoySoc **A246**, 242 (1958) 11) J. Jander & U. Engelhardt, "Coordination Problems of Nitrogen-Iodide Compounds in Liquid Ammonia" in Proc8thIntConfCoordChem, Springer, Vienna

(1964), 330 & CA **66**, 119430 (1967) 12) J. Jander & U. Engelhardt, ZAnorgChem **341**, 146 (1965) & CA **64**, 10592 (1966) 13) A. Hassner & F.W. Fowler, JOC **33**, 2686 (1968) 14) M.V. Andrews et al, JInorgNuclChem **33**, 3945 (1971) & CA **76**, 77390 (1972)

Written by: **C. H. McDONNELL**

NITROGEN OXIDES

Nitrogen Monoxide (Nitrous oxide, Hyponitrous Oxide, Laughing gas). N_2O, mw 44.02, N 63.65%, colorl gas with sweetish odor and taste, mp −90.86°, bp −88.48°, d 1.9777g/ℓ. It is appreciably sol in w and more sol in alc. Commercial prepn is by the decompn of AN thru gentle heating; $NH_4NO_3 = N_2O + 2H_2O$. Heating above 200° should be avoided because the salt will start to decomp with formation of NO, N_2 and NH_3. If the salt is heated to slightly above 250°, an expln occurs. Nitrogen monoxide supports combustion more vigorously than air, since, on decompn, it yields a gas contg 1/3 its vol of O_2 as compared with 1/5 with air

Although it forms expl mixts with CO, NH_3, CS_2, and phosphine, it is not used in the expls industry. It also forms combustible mixts with NO and fuels such as butane, benz, cyclohexane and p-xylene (Ref 8)

Nitrogen monoxide is used as an oxidizer in biproplnt systems with carbon monoxide or methanol-w as fuels, and it is added to N_2O_4 to advantageously modify the frp and bp of this oxidizer. It is also employed as a high enthalpy flow medium in hypersonic wind tunnels (Ref 10), and as an oxidizing gas in atomic absorption spectroscopy (Ref 12). Q_f −19.7 kcal/mole (Ref 3)

Refs: 1) Gmelin, Syst **4** (1955), 509–99 2) Scott & Furman (1939), 2400 3) W. Latimer & J. Hildebrand, "Reference Book of Inorganic Chemistry", MacMillan, NY (1940), 195–6 4) Mellor **8** (1947), 385–404 5) Thorpe **8** (1947), 514 6) L.G. Cole, "The Nitrogen Oxides as Rocket Fuel Oxidants Including The Theoretical Performances of Propellant Systems Employing Nitrogen Tetroxide", JPL PR **No 9-23**, CalInstTech, Proj No TU2-1, Contract No W-04-200-ORD-1482 (1948) 7) Partington (1950), 573–76 8) B.B. Brandt et al, KhimProm (1961), 204–10 & CA **55**, 21589–90 (1961) 9) W.L. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, NY (1964), 69–71 10) J.R. Nicholson et al, "An Experimental Investigation of the Use of Nitrous Oxide in Hypersonic Windtunnel Testing Facilities", ARL **66-0011**, OARUSAF (1966) 11) Sax (1968), 977 12) W.F. Pickering, "Modern Analytical Chemistry", Marcel Dekker, Inc, NY (1971), 136 13) M. Harmatz, "Spectral Identification of Compounds formed by Nuclear Radiation in Air for Remote Fallout Survey", RDTR ECOM-**4053** (1972) 14) C.R. Mastromonico & F.S. Forbes, "Blast Hazards of CO/N_2O Mixtures", AF RPL-**TR-73-89** (Sept 1973) 15) Anon, "Fire Protection Guide On Hazardous Materials, 5th Edition", NFPA, Boston, Mass (1973) 16) C. Wilton and A.B. Willoughby, "Blast Hazards of the Liquid Propellants LCO and LN_2O", **URS-7309-12**, Contract No F04611-73-C-0053, AFRPL (1974) 17) ChemRubHdbk (1975), B-115

Nitrogen Oxide (Nitric oxide). NO, mw 30.01, N 46.68%; colorl gas, blue in liq or solid form; mp −163.6°, bp −151.8°, d 1.3402g/ℓ, 1.269 g/ℓ at −150.2° (liq), RI 1.330 at −90°. Sol in w, 7.34ml at 0°; alc, 26.6ml; sulfuric acid, 3.5ml, aq Fe sulfate and conc nitric acid

Nearly pure NO can be prepd by heating a mixt of K nitrate, Fe sulfate and dil sulfuric acid; $6FeSO_4+2HNO_3+3H_2SO_4 = 3Fe_2(SO_4)_3+2NO+4H_2O$. It is also produced by the action of UV light or lightning on the atm, and as a by-product of nuclear and chemical explns (Ref 1)

Nitric oxide is the most stable oxide of nitrogen. It decomps above 1000° and will not support combustion below this temp. When mixed with hydrogen, it can be expld by a long duration, intense electric spark (Ref 8). It is very endothermic, its Q_f being −21,575cal/g at RT (Ref 5)

The gas has no practical application as an expl. It is of importance, however, as an additive to N_2O_4 to depress the fr p of this biproplnt hypergolic oxidizer (Ref 7). It is also

one of the principal compds dealt with in the manuf of nitric acid by the ammonia oxidn process, as well as in the manuf of expls by various nitration procedures (Refs 9 & 10)

The inhalation of concns of 200 to 700ppm may be fatal after even very short exposure (Ref 11). Also see under Nitrous Fumes in this Vol

Refs: 1) Gmelin, Syst **4** (1955), 600–736 2) Scott & Furman (1939), 2346 & 2400 3) W. Latimer & J. Hildebrand, "Reference Book of Inorganic Chemistry", MacMillan, NY (1940), 197–200 4) W.L. Badger & E.M. Baker, "Inorganic Chemical Technology", McGraw-Hill, NY (1941), 98 5) Thorpe **8** (1947), 517–22 6) Mellor **8** (1947), 417–49 7) L.G. Cole, "The Nitrogen Oxides as Rocket Fuel Oxidants Including The Theoretical Performances of Propellant Systems Employing Nitrogen Tetroxide", JPL PR No **9-23**, CalInstTech, Proj No TU2-1, Contract No W-04-200-ORD-1482 (1948) 8) Partington (1950), 570–73 & 575 9) Urbański **1** (1964), 77 10) R. Powell, "Nitric Acid Technology Recent Developments 1969", Noyes Development Corp, Park Ridge, NJ (1969), 4–92 11) Sax (1975), 961-R 12) ChemRubHdbk (1975), B-115

Nitrogen Pentoxide (Dinitrogen pentoxide, Nitric anhydride), N_2O_5, mw 108.02, N 25.94%; white crysts, very hygr; mp 29.5°; pure N_2O_5 sublimes at 32.4°; bp, starts to boil at about 45° having previously darkened in color due to partial decompn; d 2.05g/cc at 15/4°, 1.642 g/cc at 18°. Sol in w and nitric acid to about 30 wt-% at 25°. See Ref 9 for properties of N_2O_5 solns in nitric acid

Prepd by dehydrating concd nitric acid with phosphorus pentoxide (Refs 3 & 4). Explds if heated suddenly (Ref 4). Can also be prepd by the flash photolysis of O_2–N_2O–He mixts (Ref 11), and by the radiolysis of N_2O_4–HNO_3 with γ rays (Ref 12)

Its principal military use is as a nitrating agent, either in the vapor phase or when dissolved in an inert solvent such as CCl_4, for such substances as alkyl nitrites, cellulose and Nitrobenzene (Refs 2a, 8 & 13)

Refs: 1) Gmelin, Syst **4** (1955), 818–37 2) Scott & Furman (1939), 2400 2a) H. Aaronson, "Evaluate Method of Nitrating Cellulose Developed by the Stein Hall Co", PATR **1331** (1943) 3) W. Latimer & J. Hildebrand, "Reference Book of Inorganic Chemistry", MacMillan, NY (1947), 195 & 202 4) Partington (1950), 569 5) F. Miles, "Nitric Acid Manufacture and Uses", Oxford Univ Press, London (1961), 20 6) W. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, Inc, NY (1964), 70 & 83 7) Hackh's (1972), 457 8) Urbański **1** (1964), 10, 11, 19, 61, 105, 106 & 107 9) J. Lagowski, "The Chemistry of Non-Aqueous Solvents", Vol **2**, AcademicPress, NY (1967), 175 10) A. Julg & Y. Ozias, RevChimMiner **6** (1), 201–14 (1969) & CA **71**, 116696 (1969) 11) W. DeMore, JChemPhys **52** (8), 4309–10 (1970) & CA **72**, 138077 (1970) 12) L. Dmitriev et al, KhimVysEnerg(USSR) **4** (1), 68–73 (1970) & CA **72**, 105843 (1970) 13) G.B. Gustave & N.W. Cannon, USP 3549686 & CA **74**, 99452 (1971)

Nitrogen Tetroxide (Nitrogen Peroxide, Nitrogen Dioxide, Dinitrogen Tetroxide). NO_2 or N_2O_4, mw 46.01 or 92.02, N 30.45%, mp –9.30°, bp 21.20°, d 1.4494 g/cc at 20/20°; RI 1.40 at 20°. Reddish-brn gas at RT with a pungent smell, having the formula N_2O_4. When heated it becomes paler, because of dissociation; $N_2O_4 = 2NO_2$; and finally colorl, because of decompn to NO and O. When cooled it becomes a dark orange-red liq which becomes paler on further cooling, and finally becomes a nearly colorl solid, N_2O_4. Sol in w, alk, carbon disulfide, chlf, nitric and sulfuric acids

Prepd industrially from nitric acid and air. A convenient lab prepn is by decompn of Pb nitrate by heat; $2Pb(NO_3)_2 = 2PbO+4NO_2+O_2$ (Refs 2, 3, 4, 10 & 11)

Nitrogen tetroxide is formed as an undesirable product in several instances, eg, during the storage of some energetic materials, particularly NC, NG and mixts contg them, such as proplnts and Dynamite. In these the nitric esters decomp at elevated temps. In some cases, even such stable nitrocompds as TNT can begin to evolve NO_2 when stored at higher than ambient temps.

This usually occurs when all the acid was not neutralized in the washing process, and remains in the finished product to react with the nitrocompd in storage

Nitrogen tetroxide is also formed during the manuf of nitric acid and in the nitration of org substances

Perhaps its most undesirable reaction is that with ozone; $N_2O_4+O_3 = N_2O_5+O_2$. Under closed vessel conditions, using an electric spark, this reaction is explosive (Ref 33). However, when the reaction occurs in the atm, it proceeds at a slower rate, and effectively works to strip the UV shield of ozone surrounding the earth greatly increasing the possibility of skin cancer (Ref 40)

When liq ammonia is mixed with solid N_2O_4 at about $-80°$, an expln occurs. The action of gaseous ammonia at $-20°$ is less vigorous (Ref 11). Spontaneous explns occur on contact between liq N_2O_4 and hydrazine-type fuels (Ref 18). Contact-type explns also occur with such materials as acetic anhydride, liq ammonia, methyl and ethyl nitrate, and propylene (Ref 33). N_2O_4 also forms expl mixts with incompletely halogenated hydrocarbons, NGu, carbon disulfide, etc (Ref 33). The effect of spontaneous decompn by oxidation-reduction reactions when N_2O_4 is mixed with a number of fuels (hydrazine, gasoline, liq paraffin, etc) has resulted in its extensive use in liq proplnt rocket engines (Refs 12, 22, 27 & 35)

Nitrogen tetroxide is a powerful oxidizing agent, as well as a good nitrating agent (Refs 18 & 24). Hence, extreme care must be taken in handling and storage (Refs 25, 28 & 33). A recommended USAF guide in this connection is Ref 20. Compatibility studies with spacecraft materials are reported in Refs 23, 29 & 32

Pure N_2O_4 forms nitrocompds readily at elevated temps with either aliphatic or aromatic hydrocarbons in the gaseous or vapor state. It therefore finds extensive use in the commercial prepn of nitrocompds in both the expls and dye industries (Ref 24). Nitrations can be conducted in either the liq or vapor phase (Ref 8), and the N_2O_4 can be used as such or dissolved in an inert solvent such as CCl_4. Recently, Castorina et al (Refs 19 & 36) have shown that gamma irradiated liq N_2O_4 can be ionized to the extent of being able to directly nitrate benz to NB and DNB at RT

Because of its powerful oxidizing properties, nitrogen tetroxide has also been used in mixts with combustible materials in the so-called *Sprengel* type expls. The first expls of this type were *Pantclastites*, proposed by Turpin in 1881. In them liq N_2O_4 was mixed just before use with a combustible substance such as CS_2, NB or light petroleum. These mixts were extremely sensitive to shock, and had to be handled with the greatest of care. Another expl mixt contg N_2O_4 was *Anilite* (see Vol **1**, A443-R), used by the French during WWI as a bomb filler. PicArsn evaluated *Myrite* (see in this Vol), a mixt of NO_2 and CS_2, and concluded that it was not suitable for military use

Nitrogen tetroxide expls were thoroughly investigated by Kast and Günther (Ref 4), who tested mixts of liq N_2O_4 with the following substances: C_6H_6, TNT, C_7H_8, NB, CCl_4 and CS_2. They found that only mixts with NB and CS_2 were strongly expl, and that both were fairly stable on storage at RT, although NB is slowly attacked by N_2O_4. Both mixts were easily absorbed by kieselguhr, resulting in soft, non-plastic masses which exhibited fp's too high for military use. In order to counteract this, Kast and Günther proposed using 35 parts of a 65/35 mixt of NB and CS_2, to which was added 65 parts of N_2O_4. The expl properties of this mixt were:

Brisance. By Kast app ("Stauchprobe") using a 10.5mm high Cu cylinder; 4.5mm compression vs 5.1mm for NG and 4.0mm for PA

Impact Sensitivity. As detd in a special app designed for liq expls; less sensitive than NG and more sensitive than PA

Trauzl Pb Block Expansion. 435cc with 10g sample vs 493cc for NG and 305cc for PA

More recent work in liq expls using N_2O_4 is that of Herickes and Ribovich (Ref 14) who made a two year study for the purpose of providing a material which could be used for mine field clearance. It resulted in two stoichiometric mixts, one of N_2O_4–benz (18.5 wt % benz), and the other of N_2O_4–nitromethane (64 wt % NM). These mixts exhibited the fol-

lowing properties:
Detonation Rate. For both mixts at 0°, 6900m/sec
BurMines Card Gap Test. For both mixts, over 2000 mils
Power by Plate Dent Test. For both mixts, using a 4″ thick steel plate, 0.133″ indentation
Rifle Bullet Impact. Detonation in 5/5 trials with either mixt
The conclusion drawn from these and other tests was that since these liq N_2O_4 expls were relatively short lived when exposed to air, reacted with w, were toxic, and propagated unsatisfactorily on the ground, that they were not practical for mine clearing use

Nitrogen tetroxide is one of the most insidious gases in terms of human toxicity. Inflammation of the lungs may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. 100ppm is dangerous for even a short exposure, and 200 ppm may be fatal (Ref 25). Also see under Nitrous Fumes in this Vol

There is no US military specification for Nitrogen tetroxide

For additional information on Nitrogen tetroxide, see under **Liquid Propellants** in Vol **7**, L34-R to L44-R; **Hypergolic Propellants** in Vol **7**, H254-L to H259-R; **Nitrogen Determination in Energetic Materials**, and **Mass Spectrometry** in this Vol

Refs: 1) Gmelin, Syst **4** (1955), 748–818 2) H. Kast & P. Günther, SS **14**, 81–4 & 103–5 (1919); Ibid JSCI **38**, 603A (1919) & CA **13**, 3319 (1919) 3) P. Pascal, "Explosifs, Poudres, Gas de Combat", Hermann, Paris, Russ Ed (1932), 139–40; Ibid, BullFr 4, **25**, 309 (1919) 4) H. Kast & P. Günther, SS **14**, 81–84 & 103–04 (1919); Ibid, JSCI **38**, 603A (1919) & CA **13**, 3319 (1919) 5) A. Klemenc & K. Muha, ZAnorgChem **134**, 208–20 (1924) 6) F. Raschig & W. Prahl, ZAngChem **42**, 253–7 (1929) & CA **23**, 2787 (1929) 7) Scott & Furman (1939), 2400 8) H.B. Hass & E. Riley, ChemRevs **32**, 381 (1943) 9) Davis (1943), 355 10) Mellor **8**, 529–50 (1947) 11) Thorpe **8**, 524–28 & 572–81 (1947) 12) L.G. Cole, "The Nitrogen Oxides As Rocket Fuel Oxidants Including The Theoretical Performances of Propellant Systems Employing Nitrogen Tetroxide", **JPL PR No 9-23**, Cal Tech, Proj No TU2-1, Contract No W-04-200-ORD-1482 (1948) 13) Partington (1950), 581–84 14) J.A. Herickes & J. Ribovich, "Study of Military Applications of Nitrogen Tetroxide Explosives", Summary Report No **3746**, BurMines, NSDI (1956) 15) P. Gray, "The Chemistry of Dinitrogen Tetroxide", The Royal Inst Chem; Lectures, Monographs & Reports No **4** (1958) 16) E.L. Harris et al, "Method For The Analysis of Nitrogen Tetroxide (N_2O_4)", **AFFTC-TR-60-25**, ARDC USAF (1960) 17) F.D. Miles, "Nitric Acid Manufacture and Uses", Oxford Univ Press, London (1961) 18) R. Friedman et al, "A Study of Explosions Induced By Contact of Hydrazine-Type Fuels With Nitrogen Tetroxide", **ASD-TDR-62-685**, AD 289035 (1962) 19) T.C. Castorina, "Cobalt-60 Gamma Radiolysis of Liquid Dinitrogen Tetroxide", PATR **3072** (1963) 20) Anon, "Handling And Storage of Nitrogen Tetroxide", **RTD-TDR-63-1033** (May, 1963) 21) W.L. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, NY (1964) 22) R.L. Chuan et al, "Propellant Reaction Characteristics in Space Environment Test Facilities", **AFRPL-TR-65-19** (1965) 23) R.F. Muraca et al, "The Results of Long-Term Storage Tests For Compatability of Nitrogen Tetroxide With Various Spacecraft Materials", SR No **2**, JPL Contract No 951581 (NAS7-100) (1967) 24) Urbański **1** (1964), 92–105 & **2** (1965), 289, 291 25) Merck (1968), 739-L 26) R. Powell, "Nitric Acid Technology – Recent Developments 1969", Noyes Dev Co, Park Ridge, NJ (1969) 27) J. Kiselyk, "MMH/N_2H_4 Combustion Stability Comparison", **AFRPL-TR-69-45** (1969) 28) A. Jensen, "Chemical Rocket Propellant Hazards. Volume III. Liquid Propellant Handling, Storage and Transportation", **CPIA-Pub-194**, Contract No NOW-62-0604 (1970) 29) J.A. Letos, "Materials Compatibility With Liquid Rocket Propellants", Rept No **D2-113073-1**, Boeing Co, Seattle, Wash, ASD (1970) 30) N.C. Paul, "Mass Spectrophotometric Analysis of Complex Gas Mixtures", **ERDE-TN-28** (Engl), TRC, BR-25066 (1971) 31) W.F. Pickering, "Modern Analytical Chemistry", Marcel Dekker Inc, NY (1971) 32) C.C. Addison, "Flow Decay", **TR-71-104**, AnnSciRept, Nottingham

Univ (Engl), AF Proj 3148, Contract F 61052-70-C-0035, AFRPL (1971) 33) Anon, "Fire Protection Guide on Hazardous Materials", 5th Edn, NFPA, Boston (1973) 34) P.V. Marrone, "Plume Interference Assessment And Mitigation", Calspan-**KC-5134-A-6**, Contract No DAHC 60-69-C-0035 (1973) 35) R.A. Jamieson, "Altitude Testing of the Aerojet AJ-10-179 Liquid Rocket Engine", **AFRPL-TR-72-128** (1973) 36) A.F. Smetna & T.C. Castorina, "Radiation-Induced Nitration of Benzene With Dinitrogen Tetroxide", Explosivst No **4** (1973) 37) D.T. Williams et al, "Evaluation of Second Derivative Spectroscopy For Monitoring Toxic Air Pollutants", SAM **TR-74-19**, Proj AF-7164, Contract F 41609-73-C-0011 (1974) 38) N.S. Garman et al, "Evaluation of Propellant Quick Test to Ascertain Serviceability of Artillery Propellant Stock", PATR **4647** (1974) 39) ChemRubHdbk (1975), B-115 40) L. Timnick, "Chemical Fertilizers, Cars, Power Plants–Scientist Labels New Ozone Threats", Newark Star Ledger, Newark, NY, 17 (Nov 15, 1975)

Nitrogen Peroxide. Same as Nitrogen Dioxide; see under Nitrogen Oxides in this Vol

Nitrogen Selenide. (Selenium Nitride). See under List of Nitride Compounds in this Vol

Nitrogen Sulfide. (Sulfur Nitride, Nitrogen Tetrasulfide). See under List of Nitride Compounds in this Vol

Nitrogen Trioxyfluoride (Fluorine Nitrate, Pernitryl Fluoride). NO_3F, mw 81.01, N 17.29%, F 23.45%; colorl, irritating gas; bp about –42°. Sl sol in w, from which it liberates oxygen

First prepd and described in 1934 by Cady (Ref 4) by passing fluorine, dild with N, O or air, thru a specially constructed app made of Ni, Pt and Monel metal contg approx 3N nitric acid cooled to 0° or below. The resulting gaseous product was collected and analyzed. Later, Ruff et al (Ref 5) showed that the use of 100% nitric acid in a quartz app at room temp was more advantageous. Prior to the above work, Moissan in 1891 (Ref 3) observed that explns occurred when fluorine was passed thru concd nitric acid. Yost et al (Ref 6) obtained NO_3F from a fluorine reaction with solid K nitrate, and its prepn and general props were confirmed by Hill et al (Ref 8)

NO_3F is a powerful oxidizing agent, liberating iodine from iodides; $NO_3F+2KI = KNO_3+I_2+KF$. The gas is stable at room temp, but *explds violently* on heating

Refs: 1) Mellor, not listed in Vol **2** under F, or in Vol **8**, under N 2) Gmelin, Syst Nr 5, not listed 3) H. Moissan, AnnChimPhys (6), **24**, 224 (1891) 4) G.H. Cady, JACS **56**, 2635 (1934) 5) O. Ruff & W. Kivasnik, AngChem **48**, 238 (1935) 6) D.M. Yost & A. Beerbower, JACS **57**, 782 (1935) 7) G.H. Cady, USP 2076364 (1937) & CA **31**, 3647 (1937) 8) D.G. Hill & L.A. Bigelow, JACS **59**, 2127 (1937) 9) Thorpe **8** (1947), 540 10) Sidgwick, ChemElems **1** (1950), 703–4

Nitro-α-Glucoheptose. See d-α-Glucoheptose Hexanitrate in Vol **6**, G82-L

Nitroglucosan. See β-Glucosan-2,3,4-trinitrate in Vol **6**, G83-R

Nitroglucose. See d-Glucose Pentanitrate in Vol **6**, G83-R

Nitroglucosides. Wrightsman patented the prepn of expls by the nitration of a methanol soln of glucosides, or a polyhydric alc soln of polysaccharides

Ref: A. Wrightsman, USP 1836568 (1931) & CA **26**, 1125 (1932)

Nitroglycerin (Nitroglycerol). See Glycerol Trinitrate or Nitroglycerin (NG) in Vol **6**, G98-Rff, and in Vol **5**, D1593-L to D1594-L

Nitroglycerin-Nitrocellulose Dynamites (Ger). Several Dynamites suitable for rock blasting or for use in potash mines were prepd by processing surplus WWI double-base proplnts and mixing the pulverized products with other ingredients such as organic nitrocompds, inorganic nitrates, etc. Among these were *Energit or Mining List No 33 Nitroglycerin Powder:* According to Naoûm (Ref 1, p 449), the Nobel Co ground different types of double-base proplnt in Excelsior Mills between steel discs, with an abundant flow of w, to a particle size of 0.5 to 2mm, dried the material, incorporated a variety of ingredients, and packed it in cartridges 25 to 30mm in diameter. The compn formulation was NG 30 to 40 and NC 70 to 60%, with added nitroderivatives of toluene and/or naphthalene 0 to 5, and paraffin and/or urethane and/or carbamide and/or dicyandiamide 0 to 10%. Its expl properties were: strength by Trauzl Test, 330 to 350cc, and detonation velocity 3000 to 5000m/sec. The mining authorities prescribed the use of the strongest blasting cap to ensure detonation, but when well confined, a fuse alone caused expln (See also Ref 3, E1; Ref 4, Ger 42-L & Ger 121-L)

Lehalleur (Ref 2) states that Energit can be prepd by wetting small grains of double-base proplnt in a kneader with equal quantities of such volatile solvents as acet and furfurol, adding liq aromatic nitrocompds and other ingredients, and then kneading the mixt until it is thoroughly blended. Finally, the solvents were removed by evapn (See also Ref 4, Ger 42-L)

Triwestfalit SN had the same compn as Energit but was prepd by WASAG (Westfälisch-anhaltische Sprengstoff Aktienggesellschaft) by crushing the proplnt in rollers or edge runners to thin plates and then reducing it to small grains (Refs 1 & 4)

Other expls prepd from surplus proplnts included *Mining List No 35 Explosive:* NG with NC jelly 94 to 96, and 6 to 4 parts of a 50% aq soln of Ca nitrate (Refs 1 & 4); *Mining List No 36 Explosive:* NG with NC jelly 97 to 99, and 3 to 1 parts of substituted urethanes (Refs 1 & 4)

Refs: 1) Naoûm, NG (1928), 449–50 2) Pepin Lehalleur (1935), 457 3) Clift & Fedoroff **2** (1943), E1 (Energit) 4) PATR **2510** (1958), Ger 42 (Energit), Ger 121 (NG-NC expls), and Ger 209 (Triwestfalit SN)

Nitroglycerin Powder. Same as Energit (see above)

Nitroglycerin Shells. See Vol **6**, G108-L

Nitroglycols or Glycol Nitrates. See Vol **5**, D1594-L & Vol **6**, G114-R to G115-L

Nitroglyoxime. See Vol **6**, G119-L

Nitroguanidine. See Vol **6**, G154-Rff

Nitroheptanes. See under Heptane and Derivatives in Vol **7**, H61-Rff

Nitrohydantoin. See Vol **7**, H188-L

Nitrohydrene. Nitrated mixt of glycerol and sugar introduced by DuPont in 1911 as a component of low-freezing Dynamites. Such expls found extensive use in the USA until nitrated glycol was introduced in 1926

Ref: Anon, IEC **50**, 41A (1958)

Nitroindene Polymer (N.I.P.). Evaluated at PicArsn as a substitute for charcoal in fuze powders. The N.I.P. fuze powders gave longer burning times and lower dispersions in M54 Time Fuzes under rotation and reduced pressure than the corresponding charcoal powders. They were also more sensitive to impact

Ref: D. Hart, "Investigation of the Use of Nitroindene Polymer in Powder for M54 Time Fuze", PATR **1296** (1943) & PATR **1525** (1945)

Nitro-iso-butanetriol (Trimethylolnitromethane). See Vol **2**, B371-R

Nitrokrakites. Expls invented by Alvisi in 1899 which contained AN as the principle ingredient, together with NG and NC
Ref: Daniel (1902), 396–7 & 558

Nitrol. Early Brit plastic safety expl, patented by O. Silberrad in 1912 (Ref 2). A typical formulation is Nitrol 10, highly nitrated benzene hydrocarbons 20, collodion cotton 0.5, and AN 69.5%. Under the same name, O. Silberrad took Brit and US patents on expl mixts contg Nitromethylnaphthalene 20–25, oxidizer (nitrates, chlorates, perchlorates, etc) 50–60, collodion cotton 0–5 and woodmeal 0–5% (Ref 1)
Refs: 1) O. Silberrad, BritP 19381 (1912) & USP 1092758 (1914) 2) Colver (1938), 261

Nitrolactose. See Vol **7**, L1-R to L2-R

Nitrolic Acids. Acids of the general formula $R.C(:NOH).NO_2$ or $R.C(:NO.OH).NO$ where R stands for CH_3, C_2H_5, etc. Nitrolic acids can be prepd by mixing, in the absence of O_2, a primary nitroparaffin with aq alkali (about 1:1), an inorganic nitrite such as $NaNO_2$, and then gradually adding the mixt to a mineral acid at below 15°. The following reaction takes place: $RCH_2.NO_2+HO.NO \rightarrow R.C(:NOH).NO_2+H_2O$. The resulting compds are yellowish oils, which turn red in the presence of alkalies. These red salts are usually very powerful expls. Some Nitrolic acids, on being added to Diesel oils, make the ignition more effective
Refs: 1) Sidgwick (1937), 241–2 & 340 2) Houben **4** (1941) 3) E.M. Nygaard et al, USP 2370185 (1945) & CA **39**, 3551 (1945) 4) E.M. Nygaard, USP 2401267 & 2401268 (1946) & CA **40**, 6092 (1946) 5) Hickinbottom (1948), 354–5

Ethylnitrolic Acid (Nitroacetoxime, Acetnitrolsäure in Ger). $H_3C.C(:NOH).NO_2$, mw 104.07, N 26.92%, OB to CO_2 –46.1%, colorl to yel rhombic crysts, mp 84–85° (decompn), bp decomps with expl violence. Sol in w, alc, eth and in most common org solvents. Can be prepd by one of the following methods: 1) by dissolving nitroethane in aq KOH, adding Na nitrite, and acidifying with dil sulfuric acid; 2) by treating isonitrosopropionic acid with N_2O_4; and 3) by acidifying a soln of Na 2-nitropropanate and Na nitrite in dil KOH with 5N sulfuric acid at –10°

Ethylnitrolic acid is an expl compd and forms numerous metallic salts, some of which are expls:
Potassium Salt. $KC_2H_3O_3N_2$, colorl amorph powder, sl sol in methanol; a weak expl
Silver Salt. $AgC_2H_3O_3N_2$, white amorph powder, insol in w and dil alc. Sensitive to light, explds on heating
Refs: 1) Beil **2**, 189–90, (86) & [185] 2) J.C. Earl et al, JCS **1928**, 2702–3 3) Hickinbottom (1948), 355

Methylnitrolic Acid (Nitroformoxime, Nitromethanoxim in Ger). $HC(:NOH).NO_2$, mw 90.04, N 31.11%, OB to CO_2 0.0%, colorl needles, mp 64–68° (decompn), bp explds below 100°, v sol in w, alc and eth. Can be prepd by the action of a mixt of K nitrite and sulfuric acid on nitromethane
Refs: 1) Beil **2**, 92–3 2) V. Meyer & E.J. Constan, Ann **214**, 334 (1882)

Propylnitrolic Acid. $H_3C.CH_2.C(:NOH).NO_2$, mw 118.09, N 23.72%, OB to CO_2 –81.3%, prisms from alc, mp 66°, bp deflagrates on rapid heating, sol in w, alc and eth. Can be prepd by treating potassium 1-nitropropanate with K nitrite and dil sulfuric acid. Nygaard prepd it (Refs 2 & 3) by dissolving 0.2 mol (105p by wt) of 1-nitropropane in 0.22 mol Na hydroxide (10% soln), and adding 16.8p of Na nitrate with stirring. After adding 100p of ice and cooling the mixt in an ice-salt bath, a soln of 50.6p of concd HCl and 110p of w were added, while the temp was maintained between –12° and +2°. It was then allowed to stand for 16 hours. Extrn with eth produced propylnitrolic acid. It is a weak expl
Refs: 1) Beil **2**, 247 2) E.M. Nygaard, USP 2370185 (1945) & CA **39**, 3551 (1945) 3) E.M. Nygaard, USP 2401268 (1946) & CA **40**, 6093 (1946)

Nitrolin. Fr name for nitrated flax

Nitroline. An expl prepd by the nitration of stearin (12p) and sugar syrup (15p) with nitric (80p) and sulfuric (170p) acids. It was used in compound expls called *Vigorine* or *Vigorite,* patented in Engl in 1875:
No 1: Nitroline 40, Cellulosa 22, K nitrate 22 and K chlorate 16%
No 2: Nitroline 30, Cellulosa 10, K nitrate 20, K chlorate 20, sawdust 10 and peaflour 10%. Cellulosa is prepd by nitrating 3p of peaflour with a mixed acid contg nitric (5p) and sulfuric (10p) acids. These expls were sometimes called *American Vigorines*
Ref: Daniel (1902), 72–3 & 785

Nitrolit. See 2,4,6-Trinitroanisole in Vol **1**, A450-L to A452-R

Nitrolite. An expl patented by Carl Lamm contg NG 94–99p; K, Na or Amm nitrate 50–150p; NC, nitrostarch or nitrostraw 1–6p; with or without NB
Ref: Daniel (1902), 560

Nitrolkrut. An expl patented in 1876 by Berg of Sweden contg NG 5–40, K & Na nitrates 25–75, and K chlorate 5–50%
Ref: Daniel (1902), 560

Nitromagnite (Dynamagnite). Dynamite invented in 1878 by E. Jones consisting of 20% NG absorbed in *magnesium alba,* which is a mixt of Mg hydrocarbonates. It is similar in compn to the *Fulgurites* (see Vol **6**, F215-L), manufd in Hungary and by the Hercules Powder Co at one time in the USA
Ref: Daniel (1902), 560

Nitromaltose. See in this Vol under Maltose Octanitrate, M10-R

Nitromannitane. See in this Vol under Mannitane Tetranitrate, M13-L

Nitromannite (Nitromannitol). See in this Vol under Mannitol and Derivatives, M13-Lff

Nitromannose. See under D-Mannose Pentanitrate in this Vol, M17-L

Nitrometer. An app used for the estimation of nitrogen in inorganic and organic nitrates by their reaction with Hg and sulfuric acid. For details of construction and operation see Vol **1**, A373-L to A377-L

It was invented by Lunge in 1890 under the name "gasvolumeter" (Ref 1). Ten years later, in the USA, it was modified and improved by F.I. duPont and described by Pitman as the "duPont Nitrometer" (Ref 2). At present, both macro and semi-micro nitrometers are in use, the latter being designed by Elving and McElroy (Ref 7)
Refs: 1) G. Lunge, ZAngChem **3**, 139–44 (1890); Ibid, JSCI **9**, 547–9 (1890); Ibid, JSCI **20**, 100–2 (1901) 2) J.R. Pitman, JSCI **19**, 982–86 (1900) 3) W.C. Cope & J. Barab, JACS **38**, 2552–8 (1916) 4) M. Marqueyrol & D. Florentin, BullFr **9**, 231–40 (1911); Ibid, MP **21**, 326 (1924) 5) J. Witt, SS **15**, 145 (1920) 6) H.W. Webb & M. Taylor, JSCI **41**, 362T (1922) 7) P.J. Elving & W.R. McElroy, IEC (AnalEd) **14**, 84 (1942) 8) M. Roth et al, "Nitrometer Reaction Bulb" PATR **2579** (1958)

Nitromethane (Nitrocarbol). See under Methane in this Vol, M69-L ff

Nitromethoxymethoxymethyl Nitrate (Nitronitroxymethylol). $O_2N.CH_2.O.CH_2.O.CH_2.O.NO_2$, mw 182.1, N 15.38%, OB to CO_2 −17.6%, oily liq, bp 88–89° at 9mm. Usually present in the products of nitration of symm-dichloromethyl ether in the prepn of nitromethoxymethyl nitrate (see below), from which it can be sepd by fractional distn in vac at about 90°. It is a powerful expl. Houben and Pfankuch (Ref 2) reported that when they attempted the vac distn at 110°, violent expln occurred
Refs: 1) Beil **1**, [649] 2) J. Houben & E. Pfankuch, Ber **59**, 87 & 89 (1926)

Nitromethoxymethyl Nitrate. $O_2N.CH_2.O.CH_2.ONO_2$, mw 152.07, N 18.42%, OB to CO_2 ±0%; colorl, volatile oil; d 1.52206 g/cc at 4°, 1.5005g/cc at 12°; RI 1.4328 at 12°

Can be prepd by treating symm-dichloromethyl ether with mixed nitric-sulfuric acids; $ClCH_2OCH_2Cl+O_2NONO_2$ (nitrogen pentoxide) = $O_2NCH_2OCH_2ONO_2+Cl_2$. It is a very powerful expl, extremely shock sensitive. It is an excellent solvent for NC, even at temps as low as 0°. It has been claimed that a gel contg 7% NC (12.11% N) with this compd developed a greater gas volume on expln than a corresponding mixt with NC

Refs: 1) Beil **1**, (318) & [649] 2) A. Moreschi, AttiRAcadLincei(5), **28**, I, 277 (1919) & JCS **116**, 385 (1919) 3) J. Houben & E. Pfankuch, Ber **59**, 86–88 (1926)

Nitromethyl-iso-nitramine. $CH(N_2O_2H)(NO_2H)$, mw 121.06, N 34.71%, OB to CO_2 +6.61%. It forms expl heavy metal salts, which according to Urbański, are weaker initiators than the corresponding metal salts of methylenedi-isonitramine. The decreasing order of brisance of these salts, when primed with MF, in the Pb plate test were Na, Ca, Ba, Tl and Pb

Refs: 1) T. Urbański & T. Wesolowski, WiadTechnUzbr **18**, 28 (1932) 2) T. Urbański, IX CongrInternQuimPuraAplicada **4**, 438–46 (1934) & CA **30**, 3649 (1936) 3) Urbański **3** (1967), 223

N′-Nitro-N-methyleneaminoguanidine. $(O_2N).NH.C(:NH).NH.N:CH_2$, mw 131.10, N 53.42%, OB to CO_2 −54.9%, needles, sl sol in w. Can be prepd from N′-nitro-N-aminoguanidine and formaldehyde in w. Explds on heating

Ref: Beil **3**, [101]

Nitro-α-methyl-d-mannosite. See α-Methylmannite Tetranitrate in this Vol

Nitron (4,5-Dihydro-1,4-diphenyl-3,5-phenylimine-1,2,4-triazole, or 1,4-Diphenyl-3,5-endoanilino-4,5-dihydro-1,2,4-triazole). $N:C(NPh)_2.CH.N.Ph$, $C_{20}H_{16}N_4$, mw 312.36; intensely yel leaflets from alc, solvated needles from chlf; mp 189–90° decompn. Practically insol in w; sol in alc, benz, acet, chlf, et acet and dil acids; sl sol in eth

Nitron was prepd in 1905 by M. Busch by heating N″-anilino-N,N′-diphenylguanidine with 90% formic acid in a press tube at 175° (Ref 2). Other methods are given in Ref 1

Nitron forms v sl sol compds with metallic nitrates, perchlorates, picrates, trinitrocresylates, as well as with organic nitrates such as NG, NC, Nitromannitol, etc, and can serve as a gravimetric reagent. The Nitron method for the detn of N is based on the fact that it ppts inorganic nitrates from w soln, and forms an insol addition product, $C_{20}H_{16}N_4.HNO_3$, mw 375.3

Refs: 1) Beil **26**, 349 2) M. Busch, Ber **38**, 858 & 4054 (1905) & JCS (Abs) **88**, I, 307 (1905) 3) Ibid, Ber **38**, 861–66 (1905) [Quant detn of nitric acid by the Nitron method] 4) M. Busch & S. Schneider, SS **1**, 232–33 (1906) [Detn of N in NC by the Nitron method and comparison of results with those obtained by nitrometer] 5) W.C. Cope & G.B. Taylor, "The Determination of Nitrogen in Substances Used in Explosives", USBurMines, **Tech Paper 160**, Washington, DC (1917), 18–20 6) N.H. Furman, Ed, "Standard Methods of Chemical Analysis", 5th Ed, Van Nostrand Co, NY (1939), 635 & 639–40 7) Merck (1968), 740-L 8) CondChemDict (1971), 624-L 9) Hackh's (1972), 460-L

Nitronaphthalenes. See under Naphthalene and Derivatives in this Vol

Nitronaphthols. See under Naphthol and Derivatives in this Vol

2-Nitro-2-(m-nitrophenyl)-propanediol-1,3 Dinitrate (2-Nitro-2-(3′-nitrophenyl)-propane-1,3-diol Dinitrate). $(O_2N).C_6H_4.C(NO_2)(CH_2.O.NO_2)_2$, mw 332.19, N 16.86%, OB to CO_2 −57.8%, colorl crysts from alc, mp 72.6–73.6°, bp ignites at 270° but does not expld even when heated at 360°. Insol in w and moderately sol in alc

Was prepd by Fieser and Gates (Ref) by adding 200mgs of 2-nitro-2-(m-nitrophenyl)-propanediol-1,3 to a well-cooled mixt of 0.4ml of concd sulfuric and 0.15ml of nitric (d 1.41 g/cc) acids, previously freed from nitrous acid by the addition of urea. After soln was complete, the liq was left standing for 10 minutes and was then drowned in ice w. The heavy oil which separated was treated with alc and left standing until crystn took place (after two weeks). A second recrystn from alc gave a fairly pure product

It is an expl which is slightly more powerful than TNT (114% as detd by ballistic mortar at the Res Lab of NDRC at Bruceton, Pa), and slightly less sensitive to impact. Its thermal stability is satisfactory and it is nonhygroscopic

Ref: L.F. Fieser & M. Gates, JACS **68**, 2249 (1946) & CA **41**, 733 (1947)

Nitropenterythrite. Fr for Pentaerythritol Tetranitrate

1-(o-Nitrophenyl)-2-nitroethyl Nitrate (α-(2-Nitrophenyl)-β-nitroethyl Nitrate). $O_2N.C_6H_4.CH(O.NO_2).CH_2.NO_2$,, mw 257.16, N 16.34%, OB to CO_2 −77.8%; colorl, diamond shaped crysts; mp 132.2–132.7°; bp, does not decomp when heated to 360°. Sol in acet, v sol in alc

Can be prepd by condensing o-nitrobenzaldehyde and nitromethane, with triethylamine as solvent, and then adding concd nitric acid with cooling; $O_2NC_6H_4CHO+CH_3NO_2+HNO_3 \rightarrow O_2NC_6H_4CH(ONO_2)CH_2NO_2+H_2O$. It is decompd by hot w with the formation of nitrous acid

It is an expl which is as powerful as TNT (99% by ballistic mortar), but more sensitive to impact, being comparable to Tetryl. Its 120° Vacuum Stability Test yields 8cc for a 5g sample in 8 hours, as compared with 6.5cc/5g sample in 15 hours for PETN and 3.8cc/5g sample in 48 hours for Tetryl

Refs: 1) Beil, not listed in General Index
2) L.F. Fieser & W.H. Daudt, JACS **68**, 2248–9 (1946)

Nitrophycite. An older name for Erythritol Tetranitrate

Ref: Daniel (1902), 480

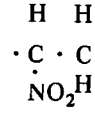
Nitropolene (Nitropoline). A mining expl invented by Volkmann contg K nitrate, K ferrocyanide and sawdust

Ref: Daniel (1902), 568 & 788

Nitropolyglycerin. Same as Tetranitroglycerin; see in Vol **5**, D1261-L

NITROPOLYMERS

The term "nitropolymer" refers to nitrated polymeric compds, usually thermoplastic, having nitro–carbon bonding, viz;



There are quite a few expl compds in this category, including polymerized nitro olefins. Since nitro olefins are of especial interest they are presented in a separate article in this Vol

The nitro ion adds to a double bond in a manner similar to the action of halogens. It can be generated by either nitric acid, N_2O_5 or N_2O_4. In some instances the polymer is nitrated *after* polymerization as with many of the polyurethanes; usually, however, a nitrated monomer is reacted with itself (called *homopolymerization*) or with a different monomer species (called *heteropolymerization*). Some monomers are self polymerizing when exposed to air, forming viscous, gummy polymers. Some require catalysts and form crystalline (cross-linked) polymers. However, postpolymerization nitration usually eliminates cross-linking and results in an amorphous polymer with no well defined mp

The selected nitropolymers in this article are presented alphabetically with respect to their polymeric designation, viz, (poly) acrylate, (poly) amide, (poly) ester, etc. Each of these polymeric types is defined in each entry by graphic formula. The sole amide and polyester discussed

as well as the ureas and urethanes were developed by the Aerojet General Corp of Azusa, Calif, under ONR contracts during the 1940's and 1950's. These compds were referred to in Vol **1**, A108-L under "Aerojet Propellants". They were not listed at the time of publication of Vol **1** because of their confidential classification. However, they are now unclassified and, therefore, can be treated

Refs: 1) H.F. Mark, Ed, "Encyclopedia of Polymer Science And Technology", J Wiley & Sons, Inc, NY, Vols **1** & **13** (1964) 2) K.H. Sweeney & K.W. Bills, "Application of Nitropolymers to Smokeless Propellants", Report **No 1104**, Aerojet-General Corp, Azusa, Calif; ONR Contract NOrd 16584 (25 April 1956), 33 3) Urbański **1** (1964), 80–100

Nitroallyl Acetate Polymer.

Monomer

Nitroallyl Acetate. $H_2C{:}C(NO_2).CH_2.(O_2)C.CH_3$,

mw 145.13, N 9.66%, OB to CO_2 −104.73%, lt green mobile liq, mp 17.5°, 68° at 2mm, d 1.217g/cc, RI 1.4528 at 25°. V sol in acet, toluene and alc; sol in w. Prepn of the compd is in three steps: 1) gas phase reaction of methyl nitrate with formaldehyde to yield dimethylol nitromethane;

$CH_3NO_3(g)+2CH_2O(g) \rightarrow (CH_2OH)_2CHNO_2(g)$,

2) esterification using acetic acid in the liq phase;

$(CH_2OH)_2CHNO_2(liq)+CH_3COOH(liq) \rightarrow (CH_2OOCCH_3)_2CHNO_2(liq)$, 3) selective oxidation to a mono ester olefin using mild conditions such as dil aq $KMnO_4$;

$$\begin{array}{lcl} CH_2OOCCH_3 & & CH_2 \\ | & \xrightarrow[\text{OXID}]{\text{MILD}} & \| \\ CH.NO_2 & & C.NO_2 \\ | & & | \\ CH_2OOCCH_3 & & CH_2OOCCH_3 \end{array}$$

Polymer

Nitroallyl Acetate Polymer.

$$\left[\begin{array}{l} -CH_2- \\ | \\ -C(NO_2)- \\ | \\ -CH_2OOCCH_3 \end{array}\right]_n$$

mw $(145.13)_n$. Prepn of polymer by exposure of the monomer to air at RT The polymer is compatible with both NC and rubber at all ratios of from 20–80% (compd/material). Impact sensitivity using BM machine with a 2kg weight is no functioning at 100cm (RDX is 30cm). Q_c 4240cal/g at 25°(Ref liq H_2O). Q_f^p −94kcal at 25°. Thermal stability at 65.5° using a 1–3g sample and KI-starch paper showed color in 19min, no appearance change in 5hrs (Ref NC, no color in 10min); during the 134.5° thermal stability test in which methyl violet paper is used, expl decompn occurred in 10min (Ref NC, 30min, no color)

Considered an irritant, fumes dangerous to inhale; an expl hazard especially with heat or oxidant exposure

Refs: 1) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", Report No **345**, Aerojet Engrg Corp, Azusa, Calif, ONR contract N7 onr-462, Task Order 1; (4 Jan 1949), 7–13 2) P.J. Blatz et al, "Research in Nitro Polymers and Their Application to Solid Smokeless Propellants", Report No **622**, Aerojet Engrg Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I (26 June 1952), Appendix 29–32 3) Sax (1968), 383–4, 960–1

Nitro Ethyl Acrylate Polymers. See Vol **6**, E201-R to E202-R

2,2-Dinitropropylacrylate (DNPA).

Monomer

$$\begin{array}{l} H \quad O \quad\quad H\ NO_2\ H \\ C{:}C.\dot{C}.O.C.\dot{C}—CH \\ H\ H \quad\quad H\ NO_2\ H \end{array}$$

mw 204.10, N 13.73%, OB to CO_2 −109.75%, off-wh cryst, mp 175° (decompn), bp 96° at 0.2mm, d 1.302g/cc at 60/25°, RI 1.4596. Sol in acet and dimethylthionate. DNPA is prepd by dissolving 2,2-dinitro propanol and acrylic chloride in CCl_4 and heating for 12 hrs at 55°. The dried product of the reaction is then mixed with powd Ag and vac distd. A 55% yield is obtd. Q_e^v 1.06kcal/g; Q_f −539cal/g; heat test at 120° on a 0.25g sample exposed for 22 hrs yielded 0.04–0.06cc of gas. Impact sensitivity on sandpaper using a 5kg wt is over 177cm for 50% all-fire probability

Rapid absorption of DNPA causes marked irritation of respiratory tract, skin and eyes

DNPA is used as a binder in artillery propInts and in concns of 10–15% has a burning

rate of 0.19–0.62inch/sec at 1000psi (Ref 3). DNPA monomer has also been copolymerized with methyl acrylate and hydroxy alkyl acrylates to form a *terpolymer* useful as an expl binder (Ref 8)

polymer (p-DNPA).

$[-CH_2.CH.COO.CH_2.C(NO_2)_2.CH_3]_n$, mw $(204.10)_n$, mp 248° (decompn), d 1.379g/cc. Sol in dimethyl thionate. The polymer is prepd by reacting a mixt of DNPA, toluene and azobisisobutyronitrile under dry N_2 at 80° for 45 mins. A 25% conversion is obtd

Poly-DNPA has an expln temp at const vol of 250°, deton vel at RT is 6100m/sec

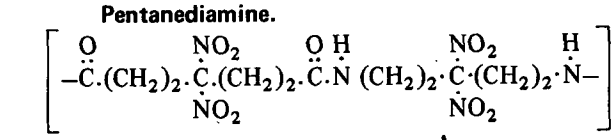
Tests. P-DNPA can be detd spectrophotometrically using a calib curve from the absorption of the carbonyl group near 1750cm^{-1} while dissolved in dimethyl thionate

As an ingredient of expl compns such as **LX-09-0** (HMX 93, p-DNPA 4.6, Bis(2,2-dinitro-2-fluoro ethyl) formal 2.4%)

Refs: 1) B.A. Stott, "Castable Explosive Compositions based on Dinitropropylacrylate and HMX", **NOTS TP 4387** (1967) 2) W. Selig, US Atomic Energy Comm No **UCRL-7873**, pt II, 11–16 (1965) & CA **67**, 118712 (1967) 3) Ibid, **UCID-15202** (1967) & CA **69**, 37577 (1968) 4) M.G. Baldwin, "Acrylic Prepolymer Binders Containing Nitro Groups", Rohm & Hass Co, **TR5-161**, USAMC DAAH01-67-C-0632 & 0655 (1968) 5) D.E. Dodds et al, "Crosslinking poly (2,2-dinitropropyl acrylate) in plastic-bonded explosives", USAtEnergyComm, **UCRL-50434** (1968) &CA **70**, 39419 (1969) 6) K. Takahashi et al, "The Polymerization and Copolymerization of Nitro Alkyl Acrylates and Nitroalkyl Methacrylates", JApplPolymerSci **12** (7) 1683–95 (1968) & CA **69**, 44469 (1968) 7) H.F. Mark ed, "Encyclopedia of Polymer Science and Technology", Vol **9**, Interscience Pub, NY (1968), 320 8) S. Goldhagen & J. Rothenstein, "Development of New High Energy Explosive Compositions (u)", Aerojet General Corp, Azusa, Calif, Report **No 1174-81-Y1** (Conf), NOL Contract No N609210670C-0365 (17 July 1967 to 17 July 1968) 9) W. Selig, USAtEnergyComm, **UCRL-7873** (pt 3), 29–32 (1969) & CA **74**, 23999 (1971) 10) Nitrochemie G.m.b.H., FrP 2024616 (1970) & CA **75**, 8099 (1971) 11) M. Dobratz ed, "Properties of Chemical Explosives and Explosive Simulants", **UCRL 51319**, Rev 1, Lawrence Livermore Laboratory, Calif (1974), 3-1, 4-4, 9-1, 18-17, 18-49

Of the many nitro polymers developed as proplnts by Aerojet General Corp, one polyamide polymer resulted which can be considered an expl and is presented below:

The Polyamide Polymer of 4,4-Dinitro-1,7-Heptanedioyl Chloride and 3,3-Dinitro-1,5-Pentanediamine.



mw 2600, N 20.69%, OB to CO_2 –90.56%, yellow powder or mahogany-colored solid, mp 80–85°. Sol in acet, dioxane, tetrahydrofuran and dimethylformamide, sl sol in chlf. The polymer is prepd using anhydr Na succinimide as one of the monomers; liberating the pentadiamine in reaction. Using the succinimide, equivalent amounts of the monomers (56g total wt) are added to 250ml dioxane with stirring. The temp is kept at 30° for 3 days. The soln is filtered and then poured into ice w. The product is vacuum steam distd from the ice w-dioxane soln

The polyamide has a Q_c of 3880cal/g (Ref liq H_2O at 25°). The impact sensy at the 50% point is 55–60cm using a BM machine with a 2kg wt (RDX, 28cm). The polyamide polymer is stable in storage at RT. Thermal stability at 65.5° shows no failure in 5 hrs using a 1.3g sample and KI-Starch indicator paper (Ref NC, 10 min, no color); at 134.5° using a 2.5g sample with Methyl violet indicator paper, no failure is shown after 80 min (Ref NC, 30 min, no color)

Ref: M.H. Gold et al, "Research in Nitro Polymers and Their Application To Solid Smokeless Propellants", Report **No 482**, Aerojet Engineering Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 45, 48, 52; appendix, 9 to 12

Glycidyl 4,4,4-Trinitrobutyrate Polymer.

Monomer.

Glycidyl 4,4,4-Trinitrobutyrate.

$(O_2N)_3.C.(CH_2)_2.C(O)_2.CH_2.\underset{\diagdown O \diagup}{\overset{H\ H}{C-CH}}$,

mw 279.19, N 15.04%, OB to CO_2 −54.44%, light yellow, clear, viscous liq, mp −12° to −14°, d 1.464g/cc, RI 1.4750 at 25°. Miscible with acet and toluene. The prepn of the monomer requires three steps, viz; 1) esterification of propenoic acid with allyl alcohol yielding allylpropenate, 2) formation of 3,3,3-trinitropropylpropenate by double bond addition using K trinitromethyl in sulfuric acid medium, and 3) formation of the monomer from the trinitro product of step 2 using perbenzoic acid

The monomer can be readily decompd by concns as low as 1% NaOH. Compatible with NC from 20–80% compd/80–20% NC and with rubber from 50–80% compd/50–20% rubber

The monomer has a Q_c of 2999cal/g at 25° (Ref liq H_2O); Q_f^p −128kg cal at 25°. Impact sensy using a BM machine and a 2kg wt is 100cm at the 50% all-fire point (RDX, 34cm). Thermal stability at 65.5° using a 1.3g sample and KI-Starch paper showed no color in 5 hrs (Ref NC, 10 min, no color); at 134.5° methyl violet paper colored in 34 min and the sample expld in 64 min (Ref NC, 30 min, no color)

Polymer

$[(NO_2)_3C.(CH_2)_2.CO_2.CH_2.\underset{|}{CH}.CH_2.O-]_5$(approx), mw about 1500, brittle solid, mp 40–45°. Sol in ethylene dichloride. Prepn of the polymer requires that $SnCl_4$ (0.5 mole %) dissolved in anhydrous ethylene chloride be added dropwise with stirring to a −2° soln of the monomer (25 mole %) in ethylene dichloride. After 5 days the solvent is evaporated off at 60° and 2 microns press. The product is then treated with activated alumina, the $SnCl_4$ neutralized with Na bicarbonate and the product filtered off

The polymer has an impact sensy using a BM machine and a 2kg wt of 40cm at the 50% point (RDX, 34cm). Thermal stability at 65.5° (KI-starch paper) was unchanged after 2 hrs (Ref NC, 10 min, no change); at 134.5° the sample ignited after 15 min (Ref NC, 30 min, no color with methyl violet paper)

Toxicity. Unknown, but should be hazardous considering other glycidyl compds

Refs: 1) P.J. Blatz et al, "Research in Nitro Polymers and Their Application to Solid Smokeless Propellants", Report No **622**, Aerojet Energy Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, (26 June 1952), 41, 42, appendix 1-4 2) Sax (1968), 797

1-Nitro-Butyne Polymer.

Monomer

1-Nitro-Butyne -(1).

$CH_3.CH_2.C{:}C.NO_2$, mw 99.10, N 14.14%, OB to CO_2 −137.24%, red, sticky, odiferous oil. Prepn from 1-bromo-1-nitro-butene-(1) by reacting with methylamine in ethanol

The monomer explds when heated

Polymer

1-Nitro-Butyne-(1) Polymer.

$[CH_3.CH_2.\underset{|}{\overset{|}{C}}.\underset{|}{\overset{|}{C}}.NO_2]_n$; mw $(99.10)_n$. Prepn by allowing the monomer to react with air at RT for a short time

Emits dangerous fumes on decompn

Refs: 1) Beil **1**, {925} 2) J. Loevenich et al, Ber **63** (1930), 642 & CA **24**, 3211 (1930)

Of the many nitro polymers developed as propInts by the Aerojet General Corp, one polyester polymer resulted which can be considered an expl and is presented below:

The Polyester Polymer of 4,4-Dinitro-1,7-Heptanedioyl Chloride and 2,2-Dinitro-1,3-Propanediol.

$$\left[-\ddot{C}.(CH_2)_2.\dot{\underset{NO_2}{C}}.(CH_2)_2.\ddot{C}.O.CH_2.\dot{\underset{NO_2}{C}}.CH_2.O-\right]_{11\text{-}24}\text{(approx)}$$

mw 4000–9000, N 14.74%, OB to CO_2 −58.91%, yellow powder, mp 180–185°. Sol in dimethyl formamide; sl sol in acet, dioxane and tetrahydrofuran; v sl sol in chlf. The polyester is prepd by dissolving equivalent amounts of the monomers in dioxane followed by maintaining the temp at 30° for 3 days. The soln is then filtered, poured into ice w and vacuum steam distd to obtain the product

The polyester has a Q_c of 2970cal/g (Ref liq H_2O at 25°); a Q_f^p of −222kg cal at 25°. The impact sensy at the 50% point is 85–95cm using a BM machine with a 2kg wt (RDX, 28cm).

The polyester is stable in storage at RT. The thermal stability at 65.5° using a 1.3g sample and KI-Starch indicator paper is failure after 100 mins (Ref NC, 10 min, no color); at 134.5° using a 2.5g sample and Methyl violet paper, failure is shown after 80 mins (Ref NC, 30 mins, no color)

Ref: M.H. Gold et al, "Research in Nitro Polymers and Their Application to Solid Smokeless Propellants", Report No **482**, Aerojet Engrg Corp, Azusa, Calif, ONR contract N7 onr-462, Task Order I (15 Dec 1950), 45, appendix 5 to 8

Nitro Ethylene Polymer. See Vol **6**, E229-R to E230-L

α-Chloro-α-Nitro-Ethylene Polymer

Monomer

1-Chlor-1-Nitro-Ethane (α-Chloro-α-Nitro-Ethylene). CH_2:C.Cl.NO_2, mw 109.50, N 12.79%, OB to CO_2 −43.84%, blk oil, bp 149–151°. Prepn from β-chloro-β-nitro ethyl-alcohol and P_2O_5 by gently heating the reactants to 170°

Polymer

α-Chloro-α-nitro-Ethylene Polymer.

$[CH_2.\underset{|}{C}.Cl.NO_2]_n$, mw $(109.50)_n$, yel amorph flakes, mp 126–130° (decompn). V sol in alc, ether, chlf and ligr; sol in dil acetic acid; insol in w. Prepn by reacting with N carbonate soln at RT

The chloro-nitro-ethylene polymer explds when heated over an open flame

Emits dangerous fumes on decompn

Refs: 1) Beil **1**, [166] 2) Sax (1968), 961

Ethylene Glycol Dinitrate Polymers. See Vol **6**, E278-R to E279-L

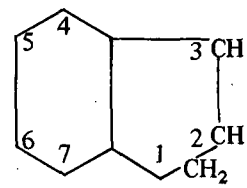
Ethylene Glycol Polymers Nitrated. See Vol **6**, E279-R to E280-L

Nitroindene Polymer

The polymer is made from indene and then nitrated

Monomer

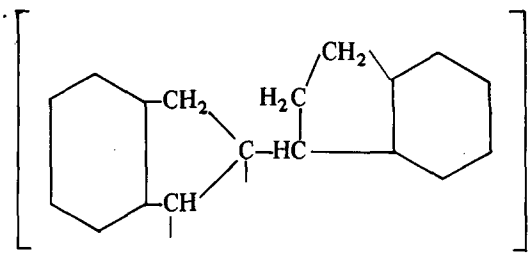
Indene (Indonaphthene). C_9H_8, mw 116.16, OB to CO_2 −303.03%, light yel, cryst, mp −1.8 to −1.5°, bp 182.6°, d 0.996g/cc at 20/4°, RI 1.5768 at 20°. V sol in alc and eth, sol in acet, benz, py & CS_2. Prepn by fractional distn of coal tar fractions at 20mm with further purification by cooling and crystg out the indene



Indene can be detd by elution chromatography, gas chromatography, and polarographic techniques (Ref 6)

Uses. Indene monomer is used as a food additive and to form the Polymer

Polymer

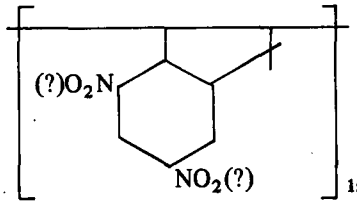


$_{13}$(approx) mw > 3000, pale yel resin, mp 250°, d 1.10–1.15g/cc, RI 1.63–1.64 at 25°. Sol in acet, hot CCl_4 and benz. Prepn is accomplished by reacting pure indene dissolved in boiling CCl_4 (61°) with $SnCl_4$ as the catalyst. The polymer is pptd with alc. On being heated under pressure indene polymerizes slowly up to 175°, then the reaction becomes expl (Ref 6). Q_{poly} 15000 cal/mole

Indene polymer can be identified from IR spectra and the indene picrate which melts at 98°; a pink color is imparted to a CCl_4 soln of the indene polymer by $SbCl_5$ (Ref 6)

Besides its usage in foods, indene polymer is used in the coatings industry, inks, floorings and in rubber applications. Some use has been made of the nitrated polymer as an ingredient in fuze powder (substituting for charcoal), but because of the sensy to impact this use is discontinued (Ref 3)

Nitro indene polymer.



mw > 3000, N 8.69 or 13.53%, OB to CO_2 –188.63% or –332.35% (depending on the number of NO_2 groups per polymer unit), brn amorph solid, mp 230°. Insol in ordinary solvents. Prepn of nitroindene is presented in Classified Brit Ordn Board Proceedings such as Ref 2

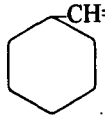
Expln temp is above 360°. Impact sensy is 50cm using a BM machine. Hygry test at 90% RH showed gain of 0.88%, and at 100% RH a gain of 1.61% was demonstrated. The International Heat Test at 75° showed a 1.1% loss of wt. Stability testing at 135° for 300 mins showed no acidity or expln. Vacuum stability; a 5g sample yielded 12cc of gas in 48 hrs (Ref 3)

Nitroindene was considered for use in the USA M54 Time Fuze but was found to be too sensitive to impact (Ref 3)

Refs: 1) Beil **5**, (248) & [410] 2) Anon, Brit R&D Board Proc, **RD4410/42**, WA-3454a, to NDRC (Feb 6, 1943) 3) D. Hart et al, "Investigation of Use of Nitroindene Polymer in Powder for M54 Time Fuze", PATR **1296** (1943) 4) Kirk & Othmer **11** (1956), 242–260 5) Sax (1968), 591-L 6) H. Mark, Ed, "Encyclopedia of Polymer Science and Technology", **4**, John Wiley & Sons, NY (1970), 242 to 292 7) ChemRubHdb (1975), C-342

Dinitropolystyrene. An expl weaker than DNT (Ref 2). Prepd from the *polystyrene polymer* by nitration. It is not possible to prepare the expl by nitration of styrene followed by polymerization (Ref 4)

Monomer.

Styrene (Phenyl Ethylene, Ethenylbenzene or Vinylbenzene).  –CH=CH_2, mw 104.16,

OB to CO_2 307.22%, colorl oil, mp –30.63°, bp 145.2°, d 0.9060g/cc at 20/4°; RI 1.5468. V sol in benz and petr eth; sol in alc, eth, acet, methanol and CS_2. Styrene occurs naturally in Styrax resin or as a by-product from water-gas pyrolysis. It can also be prepd by the reaction of benz and acetylene in the presence of Al chloride or by the dehydrogenation of ethylbenzene, which is the principal method currently used (Ref 8)

Expl limits of styrene in air are 1.1 to 6.1% at 30°; Fire point (Tag open cup) is 94°F. Styrene polymerizes exothermally at above RT conditions. A run-away polymerization can be expl

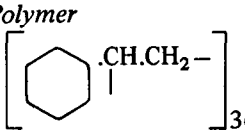
Gas chromatography and fp measurements are the currently used procedures for styrene detn which are accurate within 0.05% (Ref 9)

Exposure to over 2000ppm of styrene can cause anesthesia; 10000ppm for 30–60 mins is dangerous. (Ref 9)

Styrene is used primarily to provide the polymer resin, polystyrene

A Mil Spec, MIL-S-14195A (Ref 6a), covers the USA military requirement for styrene

Polymer



361 to over 5700, mw ≥ 38000–600000, colorl, amorph or cryst, mp 240–250°, d (amorph) 1.04–1.065g/cc; RI 1.59–1.60. Sol in CCl_4, et benz, tol, et acet, benz, methyl et ketone, chlf, tetrahydrofuran, methyl isobutyl ketone, methylene chloride, o-dichlorobenz, py and cyclohexane. Styrene polymer can be prepd in many ways. The simplest procedure is that of heating the pure monomer. The general reaction can be represented as:

$$n\ \underset{C_6H_5}{CH_2{:}CH_2} \rightarrow (-\underset{C_6H_5}{CH.CH_2}-)_n$$

At 140°, over 90% conversion can be obtained in a few mins; at 80°, 30% conversion requires over 90 hrs. *Commercially*, styrene is polymerized by either suspending it in w as a carrier with stabilizing agents plus catalysts to enhance the reaction rate, or by using w with emulsifiying agents to give extremely small particles. In both processes a combination of two or more initiators such as benzoyl peroxide and tert-butyl hydroperoxide are used with a programmed reaction temp

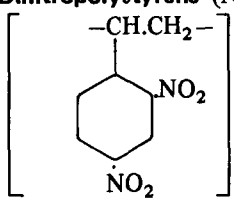
The *Laboratory* prepn for amorph styrene involves thermal conditions or the use of butyllithium at 50°. *Crystalline* polystyrene can be

prepd by using butyllithium at 0°

Dynamic differential thermal analysis is used to measure the phase transitions of the polymer. IR is used to determine the degree of unsaturation in the polymer. Monitoring of the purity and mw is done commercially using gas phase chromatography for fractionization and RI with UV absorption at 260 nanometers for polystyrene identification and measurement

Polystyrene is one of the most widely used plastics because of fabrication ease and the wide spectrum of properties possible. Industries using styrene-based plastics are: packaging, appliance, construction, automotive, radio and television, furniture, toy, houseware and baggage. Styrene is also used by the military as a binder in expls and rocket proplnts

Dinitropolystyrene (Nitropolystyrene).



$_{200}$(approx), mw ≥ 38000, N 14.81%, OB to CO_2 −126.88%, mp > 260°, d 0.25g/cc. Sol in 90% nitric ac, DNT, NG, nitrobenz and cyclohexanone. Prepn is by nitration of isotactic polystyrene with an anhydr mixt of $HNO_3/H_2SO_4/SO_3$ in the ratio of 4.51/2/1 at 15–20° for a few mins, heating to 50–55° for 2 hrs, followed by cooling to 25°. A yield of 33% of the w washed and dried nitropolystyrene is obtd

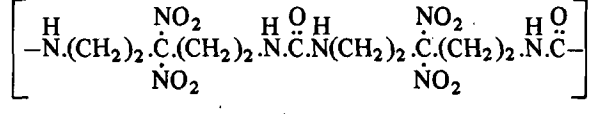
Nitropolystyrene burns without melting. When confined in steel tubing of 36–42mm diam, at a d of 0.25g/cc, and driven by PA, a deton vel of 1510m/sec is obtd. No explns are obtd using a 10kg wt at 300cm on nitropolystyrene of 0.162g/cc d. Lead block expansion for a mixt of 5g of nitropolystyrene and 5g Hexogen (RDX) is 293cc (PA=295cc)

Nitropolystyrene has been suggested for use in mining. Of the more than several expl formulations developed for such a purpose one is presented here as an example: Nitropolystyrene 7.2, DNT 10.8 and Penthrite 82.0%. With a d of 1.58g/cc the deton vel of this expl compn is 7520m/sec

Refs: 1) Beil **5**, 474, (228) & ⟨362⟩ 2) L. Médard, MP **34**, 99–105 (1952) & CA **48**, 4837–8 (1954) 3) K.C. Tsou et al, USP 3154448 (1964) & CA **62**, 1507–8 (1965) 4) Urbański **1** (1964), 418–20 5) A. Simko et al, PracovniLekar **18** (8)(Czech), 348–52 (1966) & CA **66**, 21934 (1967) 6) F. Huzl et al, PracovniLekar **19** (3)(Czech), 121–5 (1967) & CA **66**, 118580 (1967) 7) Anon, "Styrene Monomer", US Military Specification, **MIL-S-14195A** (17 Feb 1970) 8) Sax (1968), 1012–13 9) H.F. Mark, ed, "Encyclopedia of Polymer Science and Technology", Vol **13**, J Wiley & Sons, NY (1970), 128–449 10) ChemRub-Hdb (1975), C-494

Of the many nitropolymers devised as proplnts by Aerojet General Corp, one regular and one post nitrated polyurea polymer resulted which can be considered expls and are presented below:

The Polyurea Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 3,3-Dinitro-1,5-Pentanediamine.



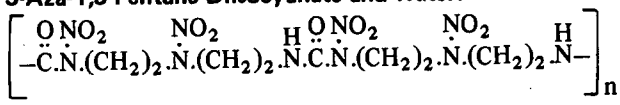
(approx)

mw 7000, N 25.68%, OB to CO_2 −87.99%, white powd or translucent grn solid, mp 110–115°. Sol in acet, tetrahydrofuran and dimethylformamide; sl sol in dioxane; v sl sol in chlf. The polyurea is prepd by dissolving equivalent amounts of the monomers (80g total wt) in dimethylformamide. Using separate solns, 125ml of the diisocyanate is slowly added to 120ml of the amine soln while keeping the temp below 20°. After standing 18 days at RT, most of the dimethylformamide is vacuum evapd at 50° and the syrupy residue is kept at 50° for 48 hrs. Acet diln is followed by filtration, then pptn in ice w. The product is vacuum steam distd at 30°; then dried over P_2O_5

The nitro polyurea has a Q_c of 3740cal/g (Ref liq H_2O at 25°), a Q_f^p of −181kg cal at 25°; an impact sensy at the 50% point of 80–85cm using a BM machine with a 2kg wt (RDX, 28cm). The thermal stability at 64.5° showed no failure in 5 hrs (Ref NC, 10 mins, no color) using a 1.3g sample with KI-Starch indicator paper; at 134.5° a failure after 75 mins is shown

using a 2.5g sample and Methyl violet paper (Ref NC, 30 mins, no color)
Ref: M.H. Gold et al, "Research in Nitro Polymers and Their Application To Solid Smokeless Propellants", Report **No 482**, Aerojet Engrg Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 47, 48; Appendix 13 to 16

The Post Nitrated Polyurea Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and Water.

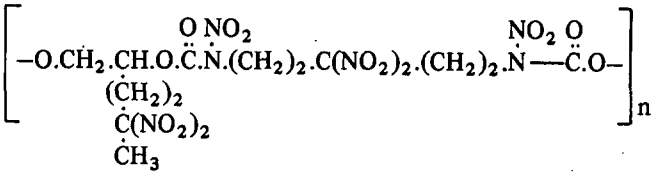


mw $(438.38)_n$, N 31.96%, OB to CO_2 −69.35%, amorph solid, mp 80–90°. Sol in acet and dimethylformamide. The initial polymer is prepd by dropwise addn over a 30 min period of a soln of 1.0 equiv wt of the diisocyanate in absol dimethylformamide to 0.50 equiv wt of w in abs dimethylformamide while maintaining a temp of 60–70°. The reaction mixt is heated to 80–90° for 1 hr and then kept at 50° for 24 hrs. The crystalline polymer (98% yield) is ground with acet, acet washed, and vacuum dried. Post nitration is performed by soln in 100% nitric acid at RT using a ratio of 1.0g polyurea to 20ml acid. Pptn in ice w followed by vacuum drying produces a 90% yield

The post nitrated polyurea has a Q_c of 3245 cal/g (Ref liq H_2O at 25°), an impact sensy of 60cm (at the 50% point) using a BM machine with 2kg wt (RDX, 28cm), a storage stability of no apparent decompn within 4 weeks at RT and a rel visc using a 1% soln in dimethylformamide of 1.11 centipoises at 25°
Refs: 1) P.J. Blatz et al, "Research on Nitropolymers and Their Application To Solid Smokeless Propellants", Report **No 740**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I; Contract NO as 53-618-C (15 Sept 1953), 31, 32 2) Ibid, Report **No 772** (30 Dec 1953)

Presented next below are the polyurethanes, which were originally designed by Aerojet-General Corp as proplnts but may be considered expls. These entries are subdivided into polymerized compds and post polymerization nitrated compds

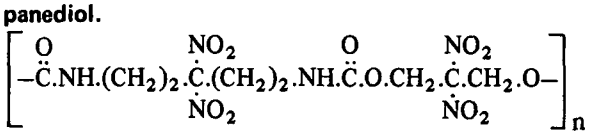
The Polymethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,5-Dinitro-1,2-Hexanediol.



mw $(542.39)_n$, N 20.66%, OB to CO_2 −56.05%, amorph powder, mp 55–65°. Sol in acet. The polymer is prepd in two steps: 1) the monomers are dissolved together using 80% equiv wts as reactants in anhyd dioxane, and then maintained at 50° for 569 hrs. The polymer was pptd in w, w washed, and vacuum dried over P_2O_5; 2) nitration of the polymer is accomplished using 100% nitric acid at 0°. The washed and dried yield is 97%

The polymer's Q_c is 2996cal/g at 25° (Ref liq H_2O at 25°). Impact sensy using the BM machine with a 2kg wt is 100cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using KI-Starch paper is 23 min (Ref NC, 10 mins, no color); thermal stability at 134.5° using Methyl violet paper shows no failure in 5 hrs (Ref NC, 30 mins, no color)
Ref: P.J. Blatz et al, "Research in Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **638**, Aerojet Engrg Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, (7 Oct 1952), 35–37

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.



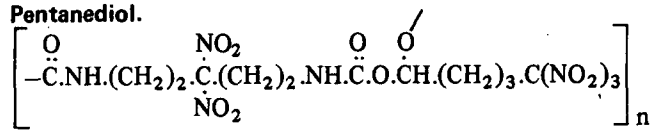
mw $(410.30)_n$, N 20.49%, OB to CO_2 −58.49%, amorph solid, mp 75–78°, d 1.57g/cc. Sol in acet and dioxane. The polymer is prepd by adding a soln of the diol and 0.05% of ferric acetylacetonate catalyst dropwise to a dioxane soln of an equiv amt of the diisocyanate over a period of 1 hr. Polymerization requires 408 hrs to complete at 50°. The yield is then dild with dioxane, pptd in w and vacuum dried

The nitro polymer has a deton rate of 6200 m/sec, a Q_c of 2880cal/g (Ref liq H_2O at 25°),

an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a power by Bal Mortar of 90 (TNT=100), a thermal stability at 65.5° of over 300 mins using a 1.3g sample with KI-Starch paper as indicator (Ref NC, 10 mins, no color), a thermal stability at 134.5° of 195 mins using Methyl violet paper (Ref NC, 30 mins, no color), and a rel visc of 1.8 centipoises using a 1% soln in acet

Refs: 1) W. Brooks et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **686**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (3 April 1953), 19–25 2) Ibid, Report **No 1162** (28 Sept 1956), 152 3) J.R. Fischer et al, "Explosives Research", Report **No 1166**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-46208 (24 Sept 1956), 28

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

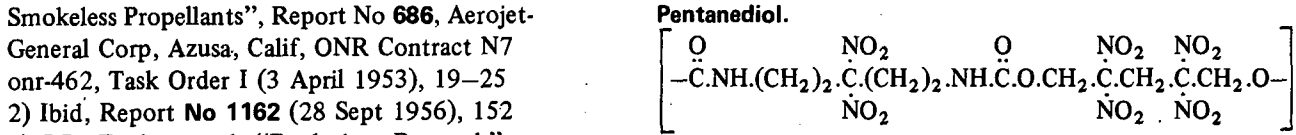


mw $(483.36)_n$, N 20.29%, OB to CO_2 –61.24%, fibrous, tan-colored solid, mp 85–95°. Sol in acet and dioxane. The polymer is prepd by cautious admixture of the monomers plus ferric acetylacetonate catalyst by soln in absol dioxane so as to maintain the temp at 45–55°. The approx ratio used is diol, 1g/diisocyanate, 1g/catalyst, 0.0004g/dioxane, 1ml. Completion of the polymerization requires 258 hrs at 50°. The polymer is then dild with dioxane, filtered, pptd in w, and vacuum dried. The yield is 99%

The polymer has a Q_c of 3096cal/g (Ref liq H_2O at 25°), an impact sensy of 85cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), power by Bal Mortar of 96 (TNT=100), a thermal stability at 65.5° of 10 mins using a 1.3g sample with KI-Starch paper as the indicator (Ref NC, 10 mins, no color), a thermal stability at 134.5° of 78 mins using Methyl violet indicator paper (Ref NC, 30 mins, no color), and a rel visc of 1.7 centipoises using a 1% acet soln at 25°

Refs: 1) W. Brooks et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **686**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (3 April 1953), 25–26 2) Ibid, Report No. **1162** (28 Sept 1956), 152 3) J.R. Fischer et al, "Explosives Research", Report No. **1166**, Aerojet-General Corp, Azusa, Calif, ONR N7 onr-46208 (24 Sept 1956), 28

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 2,2,4,4-Tetranitro-1,5-Pentanediol.

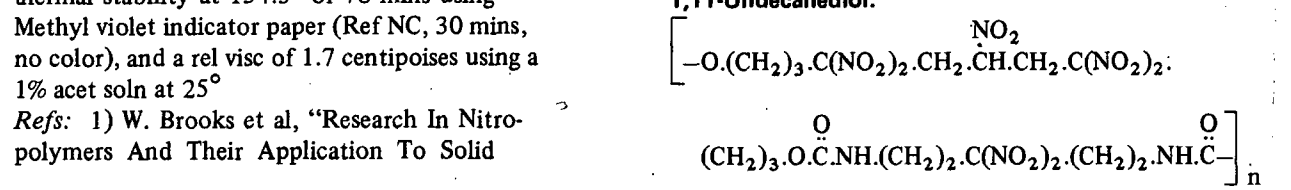


mw $(528.36)_n$, N 21.21%, OB to CO_2 –48.45%, amorph solid, mp 70–80°, d 1.64g/cc. Sol in acet. The polymer is prepd by adding dropwise to an equiv amount of the diol dissolved in anhyd dioxane, the diisocyanate plus $5x10^{-4}$ mole of ferric acetylacetonate catalyst. The polymerization requires 360 hrs to complete while keeping the mixt at 20–25°. After pptn in w the polymer is vacuum dried

The polymer has a Q_c of 2756cal/g (Ref liq H_2O at 25°), an impact sensy of 80–85cm at the 50% point using a 2kg wt with a BM machine (RDX, 28cm), a thermal stability at 65.5° of 12 mins using a 1.3g sample and KI-Starch indicating paper (Ref NC, 10 mins, no color), a thermal stability at 134.5° of 13 mins using Methyl violet indicating paper (Ref NC, 30 mins, no color), and a rel visc of 1.64 centipoises using a 1% acet soln

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **712**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7, onr-462, Task Order I and Contract NO as 53-618-C (10 July 1953), 17 2) Ibid, Report No **1162** (28 Sept 1956), 152

The Polymethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 4,4,6,8,8-Pentanitro-1,11-Undecanediol.

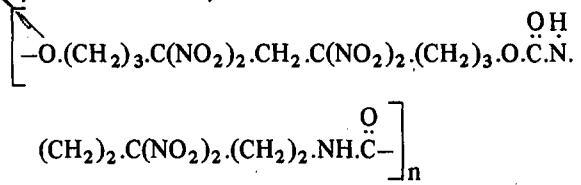


mw $(657.54)_n$, N 19.18%, OB to CO_2 −76.65%, white amorph powder, mp (approx) 40°, d 1.50 g/cc. V sl sol in w and toluene; approaches miscibility with acet. The polymer is prepd by dissolving mol equiv wts of the monomers in anhydr dioxane together with 1.5 the mol equiv wt % of BF_3 etherate as a catalyst. The soln is maintained at 40–50° for several weeks. The product is then pptd in w and steam distilled to remove solvent

The nitro polymer is compatible with both NC and rubber in wt % ratios of from 20–80%. The Q_c is 3556cal/g at 25° (Ref liq H_2O). The Q_f^p is −278kg cal at 25°. Impact sensy using a BM machine with a 2kg wt is over 100cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° for a 1.3g sample using KI-Starch paper colored the paper in 11 mins (Ref NC, 10 mins, no color), at 134.5° the Methyl violet paper colored in 10 mins and then the sample expld in 22 mins (Ref NC, 30 mins, no color)

Ref: P.J. Blatz et al, "Research in Nitro Polymers and Their Application to Solid Smokeless Propellants", Report No **622**, Aerojet Engrg Corp, Azusa, Calif, ONR Contract onr-462, Task Order I, (26 June 1952), appendix 37–40

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 4,4,6,6,8,8-Hexanitro-1,11-Undecanediol,

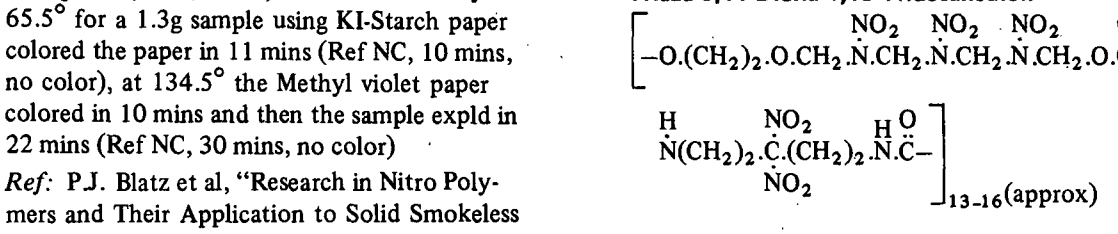


mw $(702.54)_n$, N 19.94%, OB to CO_2 −66.05%, light yel amorph powder, mp 40°, d 1.551g/cc. V sl sol in w and toluene; approaches miscibility with acet. The polymer is prepd by dissolving mol equiv wts of the monomers in anhyd dioxane together with 1.5 mol equiv wt % of BF_3 etherate as the catalyst. The mixt is then maintained at 40–50° for several weeks. The product is pptd in w and the solvent removed by steam distn

The nitro polymer is compatible with both NC and rubber in wt % ratios of 20–80%. The Q_c is 3329cal/g at 25° (Ref liq H_2O). The Q_f^p is −277kg cal at 25°. Impact sensy using a BM machine with a 2kg wt is over 100cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using a 1.3g sample colored KI-Starch paper in 8 mins (Ref NC, 10 mins, no color); at 134.5° the sample colored Methyl violet paper and expld in 8 mins (Ref NC, 30 mins, no color)

Ref: P.J. Blatz et al, "Research In Nitro Polymers and Their Application To Solid Smokeless Propellants", Report No **622**, Aerojet Engrg Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, (26 June 1952), appendix 41–44

The Polymethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,7,9-Trinitro-5,7,9-Triaza-3,11-Dioxa-1,13-Tridecanediol.

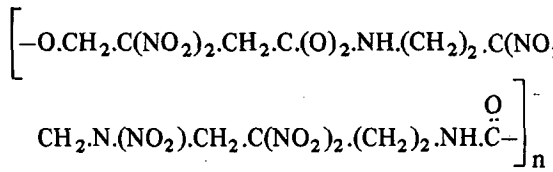


mw 7000–9000, N 23.25%, OB to CO_2 −71.70%, white transparent solid, mp 55–60°. Sol in acet, dioxane, tetrahydrofuran and dimethylformamide. The nitropolymer is prepd by placing equiv amts of the monomers in dimethylformamide soln and maintaining the temp for 28 hrs at 30°. The white granular polymer is pptd in ice w, steam distd, filtered and vacuum dried. The yield is 43.92%

The nitropolymer has a Q_c of 3350cal/g (Ref liq H_2O at 25°), a Q_f^p of −281 kg cal, an impact sensy of 80–85cm at the 50% point (RDX, 28cm). The thermal stability at 65.5° is no failure in 5 hrs using a 1.3g sample and KI-Starch indicator paper (Ref NC, 10 mins, no color); at 134.5° there is no failure in 5 hrs using a 2.5g sample and Methyl violet indicator paper (Ref NC, 30 min, no color)

Ref: M.H. Gold et al, "Research In Nitro Polymers and Their Application To Solid Smokeless Propellants", Report No **482**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 38, 49, 50; appendix 17–20

The Polyurethane Polymer of 3,3,5,7,7-Pentanitro-1,9-Nonane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

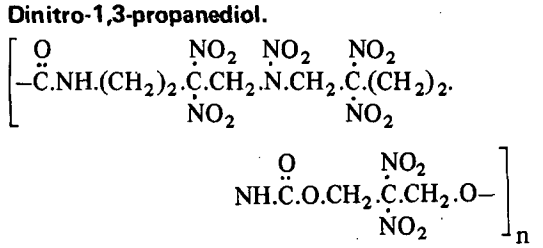


mw $(601.42)_n$, N 20.97%, OB to CO_2 −51.88%, yel amorph powder, mp 85–90°, d 1.560g/cc. V sl sol in toluene; almost miscible with acet. The polymer is prepd by dissolving mol equiv amts of the monomers in anhydr dioxane and adding 1.5 mol equiv % of BF_3 etherate, and keeping the mixt at 50° for several weeks. Water pptn and steam distn produces the polymer

The nitro polymer is compatible with NC and rubber from 20 to 80 wt %. The Q_c is 2887cal/g at 25° (liq H_2O ref). The Q^p_f is −253 kg cal at 25°. Impact sensy using a BM machine with a 2kg wt is 78cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using a 1.3g sample with KI-Starch paper showed color in 10 mins (Ref NC, 10 mins, no color) and at 134.5° the Methyl violet paper showed color in 7 mins; however, the sample expld in 29 mins

Ref: P.J. Blatz et al, "Research in Nitro Polymers and Their Application to Smokeless Propellants", Report No **622**, Aerojet Engrg Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, (26 June 1952), appendix 5–8

The Polyurethane Polymer of 3,3,5,7,7-Pentanitro-5-Aza-1,9-Nonane Diisocyanate and 2,2-Dinitro-1,3-propanediol.

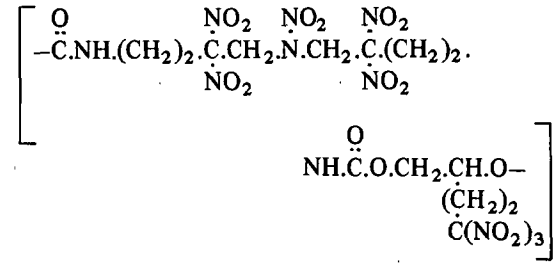


mw $(602.41)_n$, N 23.26%, OB to CO_2 −45.15%, amorph solid, mp 75–85°. Sol in acet and dimethylformamide. The polymer is prepd by dissolving equiv amts of the monomers in abs dioxane in a ratio of 1g/ml plus 0.04% of ferric acetylacetonate catalyst, and maintaining the mixt at 20–30° for 24 days. After dilution with acet the polymer is then pptd in rapidly stirred ice w and dried

The polymer has an impact sensy of 40cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability of 13 mins using a 1.3g sample with KI-Starch indicator paper (Ref NC, 10 mins, no color), also, a rel visc of 1.50 centipoises at 25° using a 1% acet soln

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **907**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I and Contract NO as 54-399-C (15 Dec 1954), 16 & 17

The Polyurethane Polymer of 3,3,5,7,7-Pentanitro-5-Aza-1,9-Nonane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

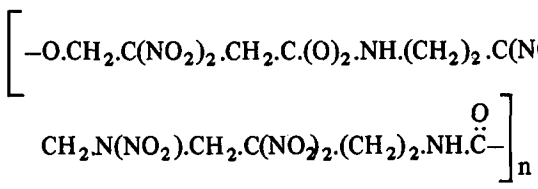


mw $(696.68)_n$, N 22.81%, OB to CO_2 −47.08%, amorph solid, mp 65–75°. Sol in acet. The polymer is prepd by dissolving equiv amts of the monomers in abs dioxane in the ratio of 1g/ml plus 0.03% of ferric acetylacetonate catalyst, and maintaining the temp of the mixt at 30° for 50 hrs

The polymer has a Q_c of 2954cal/g avg (Ref liq H_2O at 25°) an impact sensy of 65cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 20 mins using a 1.3g sample and KI-Starch paper as the indicator (Ref NC, 10 mins, no color); and a rel visc of 1.18 centipoises at 25° using a 1% acet soln

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **907**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I and Contract NO as 54-399-C (15 Dec 1954), 11

The Polyurethane Polymer of 3,3,5,7,7-Pentanitro-5-Aza-1,9-Nonane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

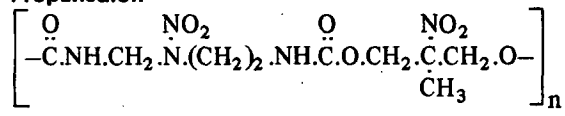


mw $(602.45)_n$, N 23.26%, OB to CO_2 −45.15%, amorph solid, mp 75–85°. Sol in acet, dimethylformamide and dioxane. Prepn by dropwise addition of a hot, anhyd dioxane soln of the diisocyanate monomer to a dioxane soln of the propanediol monomer with ferric acetylacetonate catalyst, and maintaining a 50° temp for one week. During this time a 2.8% excess of the diisocyanate monomer is added in small increments. After acet dilution the polymer is pptd in w. A 95% yield is obtd

Polymer impact sensy is 40cm using a 2kg wt at the 50% point (RDX, 28cm)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, Contract NOas 53-618-C (Dec 1953), 14

The Polyurethane Polymer of 2-Nitraza-1,4-Butane Diisocyanate and 2-Nitro-2-Methyl-1,3-Propanediol.

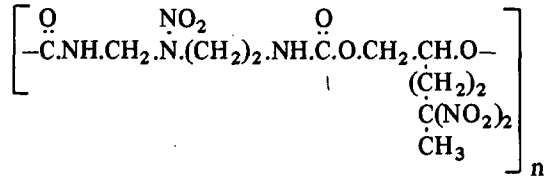


mw $(329.29)_n$, N 21.80%, OB to CO_2 −85.03%, amorph solid, mp 90–100°. Sol in acet, dimethylformamide and butyrolactone. The polymer is prepd by the dropwise addition of a soln of 36.98g of the diisocyanate in abs dioxane to a soln of 26.19g of the diol plus 0.013g of ferric acetylacetone catalyst in abs dioxane while the temp is at 30–40°. Polymerization requires 100 hrs at 50° for completion. After acet dilution the polymer is pptd by drowning in rapidly stirred ice w. The w washed and dried yield is 95%

The polymer has a Q_c of 3512cal/g (liq H_2O 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of over 5 hours using KI-Starch paper with a 1.3g sample (Ref NC, 10 mins, no color change), and a rel visc of 1.21 centipoises (1% soln in acet)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **807**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, Contract NOas 53-618-C (13 April 1954), 15

The Polyurethane Polymer of 2-Nitro-2-Aza-1,4-Butane Diisocyanate and 5,5-Dinitro-1,2-Hexanediol.

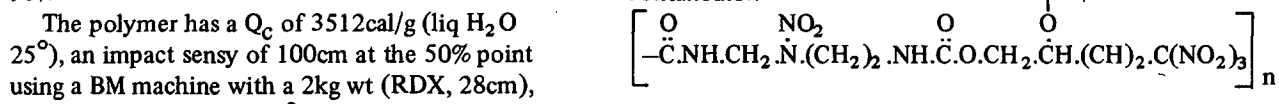


mw $(394.35)_n$, N 21.32%, OB to CO_2 −85.20%, amorph solid, mp 70–80°. Sol in acet, butyrolactone and dimethylformamide. The polymer is prepd by dissolving equal quantities of the monomers in abs dioxane in a 1g/1ml ratio plus 0.13% of ferric acetylacetonate catalyst and maintaining a temp of 50° for 117 hrs. The product is then dissolved in dimethylformamide and pptd in stirred ice w. The yield is 96.3%

The polymer has a Q_c of 3571cal/g (Ref liq H_2O at 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of greater than 6.5 hrs using a 1.3g sample and KI-Starch paper as an indicator (Ref NC, 10 mins, no color), and a rel visc in acet (1% soln) of 1.10 centipoises at 25°

Ref: L.T. Carleton et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **833**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 June 1954), 20

The Polyurethane Polymer of 2-Nitraza-1,4-Butane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.



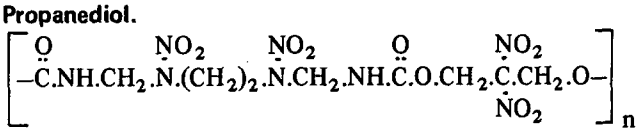
mw $(425.32)_n$, N 23.06%, OB to CO_2 −58.31%, amorph solid, mp 80–90°. Sol in acet, butyro-

lactone and dimethylformamide. The polymer is prepd by adding a dioxane soln of 28.14g diisocyanate dropwise to a soln of 35.16g of diol and 0.052g ferric acetylacetonate in dioxane, while the temp is maintained at 30–40°. The polymerization requires 51 hrs to complete at 50°. The yield is 95%

The polymer has a Q_c of 2931cal/g (Ref liq H_2O at 25°), an impact sensy of 55cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5°, using a 1.3g sample with KI-Starch paper, of a color change at 38 mins and a failure at 2 hrs (Ref NC, 10 mins, no color), and a rel visc of 1.22 centipoises using a 1% acet soln at 25°

Ref: P.J. Blatz et al, "Research in Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **807**, Aerojet-General, Azusa, Calif, ONR Contract N7 onr-462, Task Order I, Contract NOas 53-618-C (13 April 1954), 17

The Polymethane Polymer of 2,5-Dinitraza-1,6-Hexane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

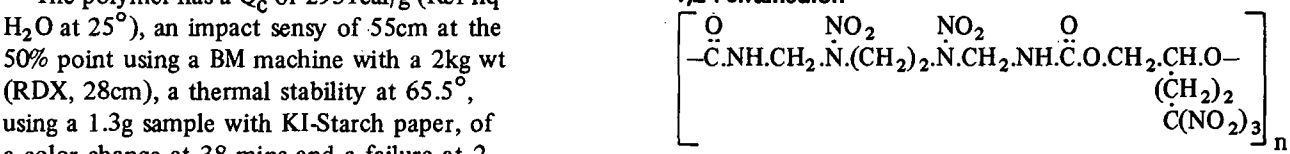


mw $(426.31)_n$, N 26.29%, OB to CO_2 –48.79%, amorph solid, mp 85–95°. Sol in acet and dimethylformamide. The polymer is prepd by dissolving equal quantities of the monomers in acet in a ratio of 1g/ml plus 0.03% of ferric acetylacetonate catalyst, and maintaining a temp of 30–40° for 30 mins. The soln temp is then kept at 50° for 66 hrs to complete the polymerization. The polymer is then pptd from soln by pouring it into rapidly stirred ice w

The polymer has a Q_c of 2767 and 2827cal/g (separate values)(Ref liq H_2O at 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 1.5 hrs using 1.3g sample and KI-Starch paper as indicator (Ref NC, 10 mins, no color), and a rel visc of 1.34 centipoises at 25° using a 1% soln in dimethylformamide

Ref: K.W. Bills et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **868**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (17 Sept 1954), 29

The Polyurethane Polymer of 2,5-Dinitraza-1,6-Hexane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

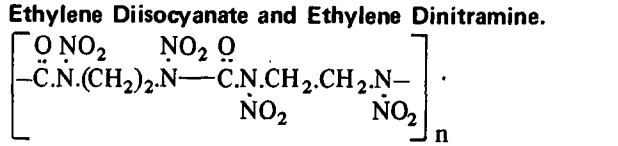


mw $(538.96)_n$, N 25.25%, OB to CO_2 –48.98%, amorph solid, mp 90–100°. Sol in acet and dimethylformamide. The polymer is prepd by dissolving equiv quantities of the monomers in abs dioxane in the ratio of 1g/ml plus $1x10^{-4}$ moles of ferric acetylacetonate catalyst, and maintaining the mixt at 50° for 164 hrs. After completion of the polymerization the product is pptd in ice w and dried.

The polymer has a Q_c of 2942cal/g (avg) (Ref liq H_2O at 25°), an impact sensy of 60cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 1 hr using a 1.3g sample with KI-Starch indicator paper (Ref NC, 10 mins, no color), and a rel visc of 1.13 centipoises at 25° using a 1% acet soln

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **907**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I and Contract NOas 54-399-C (15 Dec 1954), 12

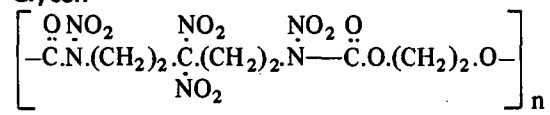
The Postnitrated Polyurethane Polymer of Ethylene Diisocyanate and Ethylene Dinitramine.



mw $(348.18)_n$, N 32.19%, OB to CO_2 –18.38%, white powder, mp 173° (decompn). The initial polymer is prepd by dissolving 0.01 mole of each of the monomers in abs dioxane and heating the mixt at 80° for 24 hrs. The product of this step is then dissolved in 100% nitric acid, the soln heated at 70° for twenty

mins, and the nitrated product pptd with ice w, acet-eth washed, and dried
Ref: L.H. Brown & R.D. Geckler, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", Report No **345**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (4 Jan 1949), 46–7

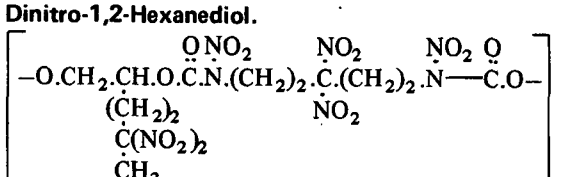
The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and Ethylene Glycol.



mw $(348.39)_n$, N 21.21%, OB to CO_2 −55.11%, amorph solid, mp 40–45°. Sol in acet. The initial polymer is prepd by combining the monomers in equivalence plus 0.02% HCl in abs dioxane to give 80 wt % of the monomers in soln. Polymerization requires 746 hrs at 50° for completion. The product is obtd by acet dilution of the reaction mixt with subsequent pptn in w and vacuum drying. Post polymerization nitration is accomplished by treating 5.16g of the polymer with 50ml of 100% nitric acid at 0° for 30 mins. The 98% yield is pptd in ice w and dried

The postnitrated polymer has a Q_c of 2716 cal/g (Ref liq H_2O at 25°), an impact sensy at the 50% point of 85cm using a BM machine with 2kg wt (RDX, 28cm), and a rel visc of 1.5 centipoises at 25° using a 2% acet soln
Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **638**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462. Task Order I (7 Oct 1952), 33 & 39
2) Ibid, Report No **1162** (28 Sept 1956), 184

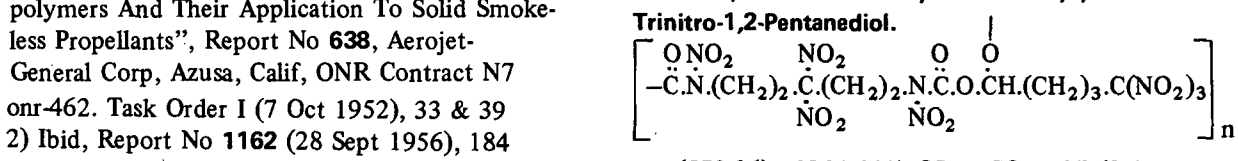
The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,5-Dinitro-1,2-Hexanediol.



mw $(542.39)_n$, N 20.66%, OB to CO_2 −56.05%, amorph solid, mp 55–65°. Sol in acet. The initial polymer is prepd by combining the monomers in equivalence plus 0.02% HCl in abs dioxane to give 80 wt % of the monomers in soln. Polymerization requires 746 hrs at 50° for completion. The product is obtd by acet dilution of the reaction mixt with subsequent pptn in w and vacuum drying. Post polymerization nitration is accomplished by adding 5.269g of the polymer to 50ml of 100% nitric acid at 0° and stirring for 30 mins. The 97% yield is obtd by pptn in ice w and vacuum drying

The postnitrated polymer has a Q_c of 2996 cal/g (Ref liq H_2O at 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 23 mins using a 1.3g sample with KI-Starch indicator paper (Ref NC, 10 mins, no color), a thermal stability at 134.5° using Methyl violet paper as the indicator of over 5 hrs exposure with no failure (Ref NC, 30 mins, no color), and a rel visc of 1.38 centipoises using a 2% soln in acet at 25°
Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **638**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (7 Oct 1952), 33 & 39
2) Ibid, Report No **1162** (28 Sept 1956), 184

The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.



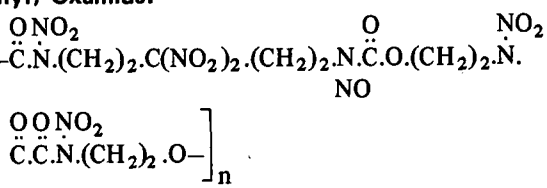
mw $(573.36)_n$, N 21.99%, OB to CO_2 −37.67%, amorph solid, mp 50–70°. Sol in dioxane. The initial polymer is already described earlier in this article. The post polymerization nitration is accomplished by adding 250ml of cold 100% nitric acid to 30.7g of the initial polymer and then bringing the temp to 50° for 20 mins. Pptn in ice w and vacuum drying produces the desired product

The postnitrated polymer has a Q_c of 2491 cal/g (Ref liq H_2O at 25°), an impact sensy of

30cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 5 mins using a 1.3g sample and KI-Starch indicator paper (Ref NC, 10 mins, no color), and a rel visc of 1.6 centipoises using a 2% dioxane soln at 25°

Refs: 1) P.J. Blatz et al, "Research In Nitro Polymers And Their Application To Solid Smokeless Propellants", Report No **622**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (26 June 1952), 32 2) Ibid, Report No **663** (23 Dec 1952), 27 &28 3) Ibid, Report No **1162**, (28 Sept 1956), 184

The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane with N,N'-Bis(2-Hydroxyethyl) Oxamide.

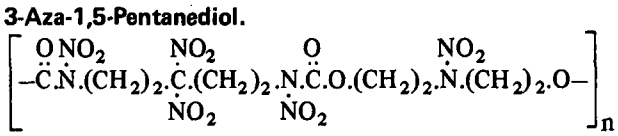


mw $(600.39)_n$, N 23.33%, OB to CO_2 −42.64%, white, amorph powder, mp 85–90°, d 1.66g/cc. Sol in acet, tetrahydrofuran and eth acetate, sl sol in n-heptane and methanol; v sl sol in toluene and w. Prepn of the initial polymer is from a dioxane soln at 50° of 2.0 equiv mol wts each of the monomers using either 1.5 equiv wt % of boron trifluoride etherate or 2.0 equiv wt % of vanadyl acetylacetonate as a catalyst to enhance the polymerization rate. Complete polymerization or gel is accomplished in about 70 hrs at 50°. The reaction rate is further enhanced by the addition of 0.072 equiv wt % of the isocyanate monomer after the initial reaction, resulting in gelation after 40 hrs at 50°. The hot dioxane soluble product is w pptd, vacuum steam-distd and dried. Post polymerization nitration of the polymer is accomplished with 100% nitric acid at 65°

The postnitrated polyurethane polymer has a Q_c of 2531cal/g (Ref liq H_2O at 25°) a Q_f^p of −234kg cal; an impact sensy of 93cm at the 50% point (RDX, 35cm; 2kg wt on a BM machine); a 65.5° thermal stability of 19 mins using a 1.3g sample with KI-Starch paper (Ref NC, 10 mins, no color). The 134.5° thermal stability sample ballooned up in 11 mins but did not color the Methyl violet test paper. The IR spectrum shows peaks at 6.1, 8.0, 7.2 & 8.4 microns. The polymer has a rel visc of 1.16 centipoises at 25° using a 2% acet soln

Refs: 1) P.J. Blatz et al, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", Report No **622**, Aerojet Engrg Corp, Calif, ONR Contract No N7 onr-462 (25 June 1952), 24 & 25 2) Ibid, Report No **633** (15 Nov 1952) 3) Ibid, Report No **638** (7 Oct 1952), 40 & 41

The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 3-Nitro-3-Aza-1,5-Pentanediol.

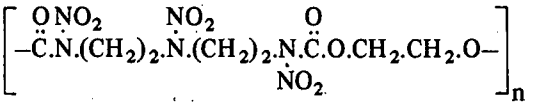


mw $(484.35)_n$, N 23.14%, OB to CO_2 −52.85%, amorph solid, mp 40–50°. Sol in acet. The initial polymer is prepd by dissolving equal amts of the monomers in abs dioxane in a ratio of 1g/ml plus 0.018% of ferric acetylacetonate catalyst and maintaining a temp of 50° for 100 hrs. The product is then dissolved in acet and pptd in rapidly stirred ice w. The yield from this step is 96.9%. Post polymerization nitration is accomplished by dissolving the polymer in 100% nitric acid at 0° in a ratio of 1g/20ml. After acid soln the excess acid is vacuum distd at RT. The yield is then dissolved in acet and pptd in methylene chloride

The postnitrated polymer has a Q_c of 2844 cal/g (Ref liq H_2O at 25°), an impact sensy of 75cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 5 mins using a 1.3g sample and KI-Starch paper as the indicator (Ref NC, 10 mins, no color), and a rel visc of 1.19 centipoises using a 1% acet soln at 25°

Ref: L.T. Carleton et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **833**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 June 1954), 21

The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and Ethylene Glycol.

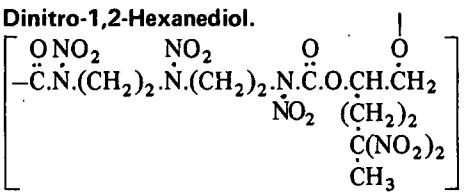


mw $(352.26)_n$, N 23.86%, OB to CO_2 –54.51%, amorph solid, mp 50–60°. Sol in dimethylformamide. The initial polymer is prepd by cautious admixt of the monomers in equiv amts together with $5x10^{-4}$ moles of ferric acetylacetonate catalyst in abs dimethylformamide in the ratio of 1g/ml. Polymerization at 50° is complete in 24 hrs. The 98% high density (1.576g/cc) crystalline yield is acet washed and vacuum dried. Post polymerization nitration is accomplished by addition of 100ml of 100% nitric acid to 10g of the polymer. After soln, the acid excess is distd off at RT under vacuum. The 97% yield is dissolved in abs dimethylformamide and pptd in chlf

The post nitrated polymer has a Q_c of 2832 cal/g (liq H_2O at 25°), an impact sensy of 90cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 10 mins using a 1.3g sample with KI-Starch indicator paper (Ref NC, 10 mins, no color), and a rel visc of 1.13 centipoises at 25° using a 1% dimethylformamide soln

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers and Their Application To Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Sept 1953), 26 2) Ibid, Report No **1162** (28 Sept 1956), 184

The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and 5,5-Dinitro-1,2-Hexanediol.

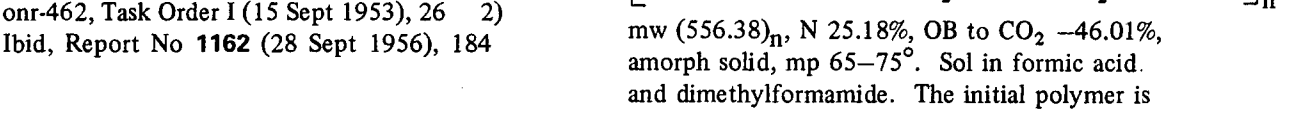


mw $(498.38)_n$, N 22.49%, OB to CO_2 –61.00%, amorph solid, mp 50–60°. Sol in acet and dimethylformamide. The initial polymer is prepd by cautious admixt of the monomers individually dissolved in abs dioxane in equiv proportions plus 5×10^{-4} mole of ferric acetylacetonate catalyst (the total is represented by the ratio of 1 g monomers /0.65ml dioxane). The polymerization is completed in 16 hrs at a constant temp of 50°. The 97% yield is acet dissolved, w pptd and vacuum dried. Post polymerization nitration of the polymer is accomplished by adding 200ml of 100% nitric acid to 22.0g of the polymer. After soln of the polymer the excess acid is vacuum distd. The 97% yield is then acet dissolved and repptd in chlf

The postnitrated polymer has a Q_c of 3067 cal/g (Ref liq H_2O at 25°) an impact sensy of 90cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 7 mins using a 1.3g sample wt with KI-Starch indicator paper (Ref NG, 10 mins, no color) and a rel visc of 1.2 centipoises using a 1% acet soln at 25°

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I and Contract No as 53-618-C (15 Sept 1953), 27 2) Ibid, Report No **1162** (28 Sept 1956), 184

The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and N,N'-Bis (2 Hydroxyethyl) Oxamide.



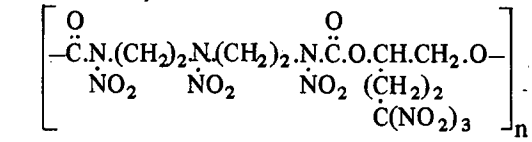
mw $(556.38)_n$, N 25.18%, OB to CO_2 –46.01%, amorph solid, mp 65–75°. Sol in formic acid and dimethylformamide. The initial polymer is prepd by dropwise addition of a soln of the diisocyanate in abs dimethylformamide to a soln of an equiv amt of the diol together with 5×10^{-4} mole of ferric acetylacetonate catalyst in abs dimethylformamide, and stirring the mixt for 4 hours at 70° until polymerization is complete. To 15g of the acet-methanol-eth washed and dried product is added 250ml of 100% nitric acid. The temp is maintained at 50–60° for 1 hr and then the acid soln is drowned in 2 liters of ice w to ppt the postnitrated polymer

The postnitrated polymer has a Q_c of 2631 cal/g (Ref Liq H_2O at 25°), an impact sensy of 47cm at the 50% point using a BM machine with

a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of failure in 8 mins using a 1.3g sample with KI-Starch paper (Ref NC, 10 mins, no color), and a rel visc of 1.05 centipoises (1% soln in dimethylformamide) at 25°

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers and Their Application To Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I, Contract NO as 53-618-C (15 Sept 1953) 2) Ibid, Report No **807** (14 April 1954), 20 & 21

The Postnitrated Polyurethane Polymer of 3-Nitraza-1,5-Pentane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

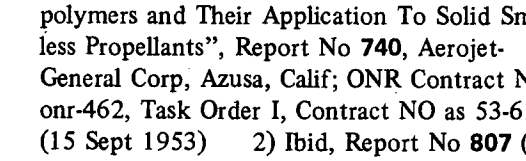


mw $(548.74)_n$, N 23.82%, OB to CO_2 −39.36%, amorph solid, mp 75–85°. Sol in acet. The initial polymer is prepd by dropwise addition of the diisocyanate in abs dioxane to a dioxane soln of an equiv amt of the diol plus 5×10^{-4} mole of ferric acetylacetonate catalyst, over a period of 30 mins while maintaining the temp at 40–50°. Polymerization at 50° requires 43 hrs to complete. After acet soln and w pptn, the yield is vacuum dried. Post polymerization nitration is accomplished by soln of the polymer in 100% nitric acid at 0° in the ratio of 1 g polymer to 10ml acid. The nitration is completed upon soln of the polymer in acid. The excess nitric acid is removed at RT by vacuum distn, the polymer is dissolved in acet and pptd in methylene chloride

The postnitrated polymer has a Q_c of 2601 cal/g (Ref liq H_2O at 25°), an impact sensy of 30cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 5 min to failure using KI-Starch paper with 1.3g sample (Ref NC, 10 mins, no color); a 1% soln in acet has a rel visc of 1.38 centipoises at 25°

Refs: 1) P.J. Blatz et al, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Ca; ONR Contract N7 onr-462, Task Order I, Contract NO as 53-618-C (15 Sept 1953) 2) Ibid, Report No **772** (30 Dec 1953), 20

The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and 2-Nitro-2-Methyl-1,3-Propanediol.

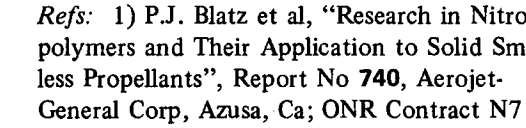


mw $(425.32)_n$, N 23.06%, OB to CO_2 −58.31%, amorph solid, mp 70–80°. Sol in acet. The initial polymer is prepd by dropwise addition of a soln of the diisocyanate in dimethylformamide to a dimethylformamide soln of an equiv wt of diol plus 1×10^{-4} mole ferric acetylacetonate catalyst over a period of 15 mins. Polymerization is completed in 136 hrs at 50°. After dilution with dimethylformamide, the polymer is pptd in w and vacuum dried. Post polymerization nitration is accomplished by soln of the polymer in 100% nitric acid at 0° in the ratio of 1 g polymer to 15ml acid. Nitration is completed on soln of the polymer. The excess acid is vacuum distd at RT, the polymer is dissolved in acet and pptd in methylene chloride

The postnitrated polymer has a Q_c of 2994 cal/g (Ref liq H_2O at 25°), an impact sensy of 83cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 10 mins to failure using KI-Starch paper and a 1.3g sample (Ref NC, 10 mins, no color), and a rel visc at 25° of a 1% soln in acet of 1.20 centipoises

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application to Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7-onr 462, Task Order I, Contract NO as 53-618-C (15 Sept 1953) 2) Ibid, Report No **772** (30 Dec 1953), 20 & 21

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

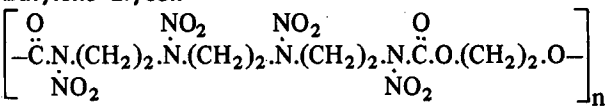


mw $(544.37)_n$, N 25.74%, OB to CO_2 −41.15%, amorph solid, mp 65–75°. Sol in dimethylformamide and acet. The initial polymer is prepd by cautious mixing of equiv amts of the monomers plus $5x10^{-4}$ mole of ferric acetylacetonate catalyst in abs dimethylformamide, while maintaining the temp at 50–60°. Polymerization is completed in 100 hrs at 50°. Post polymerization nitration of the acet washed and vacuum dried polymer is accomplished by adding to 20g of the polymer 250ml of 100% nitric acid at 0°. As soon as the polymer is completely dissolved in the acid the excess acid is removed by vacuum distn. The postnitrated polymer is dissolved in acet and pptd in methylene chloride

The postnitrated polymer has a Q_c of 2596 cal/g (Ref liq H_2O at 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 30cm), and a rel visc of 1.8 centipoises using a 1% dimethylformamide soln at 25°

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I and Contract NO as 53-618-C (30 Dec 1953), 17–19 2) Ibid, Report No **1162** (28 Sept 1956), 184

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate with Ethylene Glycol.

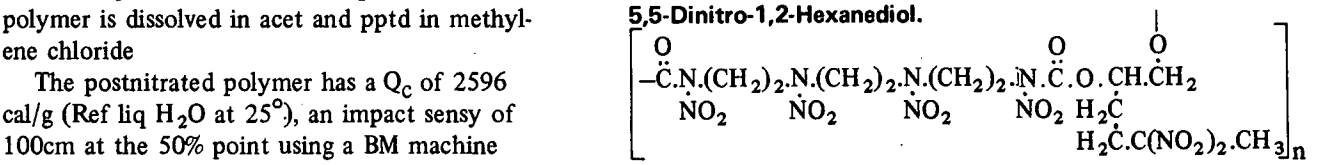


mw $(440.36)_n$, N 25.45%, OB to CO_2 −58.13%, amorph solid, mp 60–65°. Sol in dimethylformamide. The initial polymer is prepd by adding dropwise to a mixt contg purified ethylene glycol and ferric acetylacetone catalyst in abs dimethylformamide, a soln of the diisocyanate in a mixt of 20ml abs dimethylformamide and 20ml abs acet. During the diisocyanate addition and for 100 hrs afterward, the reaction is kept at 100°. The 86% yield of polymer is acet washed and vacuum dried. Post polymerization nitration is accomplished by dissolving the polymer in cold 100% nitric acid. Immediate ice-w pptn and w washing with vacuum drying produces a yield of 92%

The polymer has a Q_c of 2979cal/g (Ref liq H_2O at 25°). Impact sensy is 75cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I, Contract No as-53-618-C (Dec 1953), 16

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate with 5,5-Dinitro-1,2-Hexanediol.

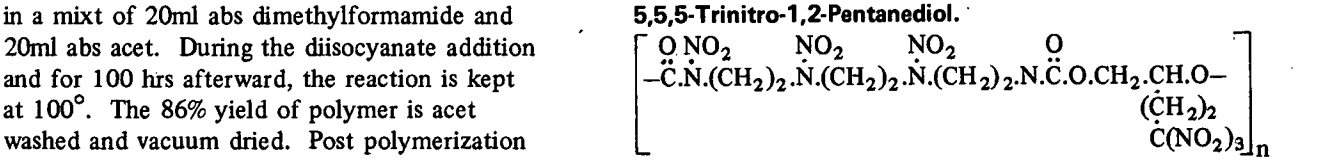


mw $(586.46)_n$, N 23.89%, OB to CO_2 −62.75%, amorph solid, mp 85–95°. Sol in acet and dimethylformamide. The initial polymer is prepd by reacting equiv quantities of diol and diisocyanate in dioxane using 10^{-3} mole of ferric acetylacetonate catalyst at 50°. The polymerization requires 186 hrs at 50°. After w pptn and vacuum drying the 97% yield is nitrated using cold 100% nitric acid. After soln of the polymer, the product is pptd in ice-w, w washed and vacuum dried to produce a 93% yield

The postnitrated polymer has a Q_c of 3148 cal/g (Ref liq H_2O at 25°) and an impact sensy of 90cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif; ONR N7-onr-462, Task Order I, Contract NO as-53-618-C (Dec 1953), 17

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.



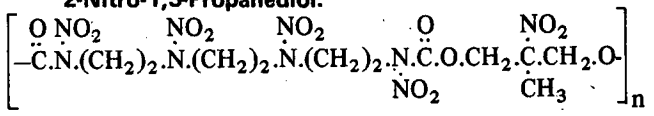
mw $(617.43)_n$, N 24.96%, OB to CO_2 −45.35%, amorph solid, mp 70–80°. Sol in acet, butyrolactone and dimethylformamide. The initial

polymer is prepd by combining equiv amts of the monomers in abs dioxane soln together with $1x10^{-3}$ mole of ferric acetylacetonate catalyst and maintaining the soln at 50° for 192 hrs. The polymer is then diluted with acet and pptd in w. Post polymerization nitration is accomplished by adding 400ml of 100% nitric acid at 0° to 25g of the dried polymer. When the polymer is completely dissolved, the excess acid is removed by distn at reduced press. The anhyd dioxane-acet soln is then pptd in methylene chloride and dried

The postnitrated polymer has a Q_c of 2712 cal/g (Ref liq H_2O at 25°), an impact sensy of 82cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of failure in 3 mins using KI-Starch paper with a 1.3g sample (NC, 10 mins, no color), and a rel visc in acet of 1.23 centipoises using a 1% soln at 25°

Refs: 1) P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **740**, Aerojet-General Corp, Azusa, Calif; ONR N7 onr-462, Task Order I, Contract NO as 53-618-C (15 Sept 1953) 2) Ibid, Report No **807** (13 April 1954), 19 & 20

The Postnitrated Polyurethane Polymer of 3,6-Dinitraza-1,5-Octane Diisocyanate and 2-Methyl-2-Nitro-1,3-Propanediol.

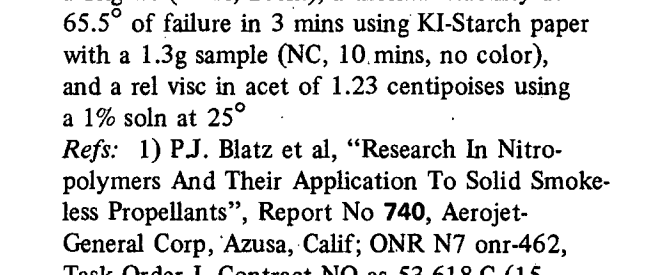


mw $(513.40)_n$, N 24.56%, OB to CO_2 −60.77%, amorph solid, mp 55–65°. Sol in dimethylformamide. The initial polymer is prepd by dissolving equiv quantities of diol and diisocyanate in dioxane with 10^{-3} mole of ferric acetylacetonate catalyst and maintaining the temp at 50° for 200 hrs. Post polymerization nitration of the polymer is accomplished by dissolving the dried polymer in cold 100% nitric acid at 0° (15g/150ml). Upon soln the excess acid is vacuum distd at RT, the product is dissolved in dimethylformamide and pptd in methylene chloride

The postnitrated polymer has a Q_c of 3102 cal/g (Ref liq H_2O at 25°), an impact sensy of 50cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), and a 65.5° thermal stability using KI-Starch paper of 12 mins to failure using a 1.3g sample (Ref NC 10 mins, no color)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I, Contract NO as 53-618-C (Dec 1953), 19

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate with N,N′-Bis (2-Hydroxyethyl) Oxamide.



mw $(644.46)_n$, N 26.09%, OB to CO_2 −49.65%, amorph solid, mp 65–70°. Sol in acet and dimethylformamide. The initial polymer is prepd by heating the monomers to 100° together with a small amt of ferric acetylacetonate catalyst (0.0001 mole/equiv monomer wt) in a solvent mixt consisting of 2/1/40 of dioxane/dimethylformamide/acet. After soln of the reactants the mixt is kept at 50° for 186 hrs. The vacuum-dried polymer is then nitrated with cold 100% nitric acid. The reaction is allowed to proceed for one hr at 50°. The postnitrated polymer is then pptd in ice-w, w washed and vacuum dried. Yield rel to original monomers is 61%

The polymer has a Q_c of 2799 cal/g (Ref liq H_2O at 25°). Impact sensy is 90cm at the 50% point using a 2kg wt in a BM machine (RDX, 28cm)

Ref: P.J. Blatz et al, "Research In Nitropolymers And Their Application To Solid Smokeless Propellants", Report No **772**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I, Contract NO as 53-618-C (Dec 1953), 15

Addl References on Nitropolymers.

A) L.T. Carleton et al, "Research In Nitro Poly-

mers and Their Application To Solid Smokeless Propellants", Report No **515**, Aerojet Engrg Corp, Azusa, Calif; ONR Contract N7-onr-462 (15 June 1951)
B) M.B. Frankel et al, "Explosives Research", Report No **538**, Aerojet Engrg Corp, Azusa, Calif; ONR Contract N7 onr-46208 (11 Sept 1951)
C) L.T. Carleton & M.B. Frankel, "Explosives Research", Report No **660**, Aerojet Engrg Corp, Azusa, Calif; ONR Contract N7 onr-46208 (11 Dec 1952)
D) J.R. Fischer et al, "Explosives Research", Report No **1224**, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-46208 (21 Feb 1957)

Written by **H. L. HERMAN**

Nitrosomethanoxime (Methylnitrosolic Acid, Methylnitrosolsäure in Ger). $(ON.CH:N.OH)_2$, mw 148.1, N 37.83%, OB to CO_2 −21.6%, yel needles; mp, decomps explosively ca 76°

Was prepd by Wieland and Hess (Ref 2) by acidifying its K salt with mineral or acetic acids, but it proved to be very unstable. It is sl sol in warm alc, from which it can be crystd

K salt. $KCHO_2N_2$; indigo-blue needles from aq alc; mp, decomps explosively ca 194° with a loud report. Was prepd (Ref 2) by adding alc K hydroxide to a mixt of hydroxylamine hydrochloride and formamidoxime (Ref 1) in methanol at 50–60°. Sol in w, sl sol in alc. Explds on heating or impact

Ag salt. $AgCHO_2N_2$; reddish-brown ppt; mp, explds at 102°. Insol in w and organic solvents, sol in amm hydroxide imparting a violet coloration

Refs: 1) Beil **2**, 91–2 2) H. Wieland & H. Hess, Ber **42**, 4179 (1909)

Nitrostarch (Nitrate d'amidon in Fr; Nitrostaerke or Staerkenitrat in Ger)

Nitrostarch (NS) is a nitrate ester (more properly a mixt of several nitrate esters) of starch, which is a plant-product polysaccharide of the general formula $(C_6H_{10}O_5)_n$. The general molecular formula for NS is $[C_6H_7(OH)_x(ONO_2)_y]_n$ where x + y = 3. The following empirical relation, similar to that used for NC (see Vol **2**, C100-R), can be employed to obtain y as a function of N, the measured nitrogen content (in %) of NS:

$$y = 162N / (1400 - 45N)$$

For example, NS of 13.5% N contains, on the average, about 2.75 nitrate groups and about 0.25 OH group per saccharide unit and consequently consists primarily of a mixt of di- and tri- nitrates

According to Hackel and Urbański (Ref 12), the solubility of Nitrostarch is dependent on its N content. Nitrostarch containing 8.0–12.8% N dissolves completely in eth-alc, but products with a N content of over 12.8% are only partially soluble. For 13.1% N, the solubility amounts to about 78%

Nitrostarch characterized by a N content below 8.0% is scarcely soluble in eth-alc. Thus the solubility of a 6.4% N-product is only 8.4%

Nitrostarch dissolves in alc more easily than NC, and at a N content of 10.0–11.5% is wholly soluble in ethyl alc. Incomplete dissolution indicates Nitrostarch of higher or lower N percentage. A product containing 12.1% N has a solubility of 32.5%

Nitrostarch of 6.4 or higher % N dissolves completely in acet

X-ray diffraction studies by Kolaczkowska & Urbański (Ref 13) suggest that during nitration starch passes thru a hydrolysis stage according to:

$$\text{Starch} \xrightarrow{HNO_3} \text{soluble starch} \rightarrow \text{Nitrostarch}$$

This view is also supported by viscosity data, which show that the starch molecule is strongly degraded during nitration. The viscosity of NS solns is appreciably lower than the viscosity of corresponding NC solns. Consequently NS cannot be used in lacquer or smokeless powder production. For a thorough discussion of NS solubility and degradation see Ref 26, pp 422–26

Nitrostarch is still used extensively by the Trojan Powder Company as the *sensitizer* in their "non-headache" Dynamites, where it replaces the NG/EGDN mixts used by other Dynamite manufacturers. It was used in WWI in *Trojan Explosive* and in *Grenite*. The former was used as the bursting charge for hand grenades, rifle grenades, and mortar shells, and the latter only for grenades (Ref 21a). According to Urbański (Ref 26, p 420), it was still used in Hungary during WWII for filling hand grenades. It is also

the major constituent of **NSX**, a Nitrostarch Demolition Explosive (Ref 30)

Historical.

Extensive historical reviews of NS are given by Caesar (Ref 21a) and by Urbański (Ref 26, pp 418–20). For the early history of NS, which parallels that of NC, we quote Urbański:

"Braconnot, who first nitrated cellulose, was also the first to nitrate starch, in 1833 (Ref 1). He dissolved potato meal in conc nitric acid, and then preceipitated the nitration product by adding water. These experiments were repeated by Pelouze (Ref 2) and Buijs Ballot (Ref 3), whereas in an experiment of Rheinsch (Ref 4) the starch was nitrated like cellulose in modern methods, by means of a mixture of nitric and sulphuric acids. For a long time nitrostarch was not distinguished from nitrocellulose. Eventually, attention was drawn to their difference by Béchamp (Ref 5). By reduction of starch nitrate he recovered the initial carbohydrate, ie, starch in a form that differed from the non-nitrated original starch by its solubility in water. (In accordance with our knowledge it was most probably dextrin). Béchamp (Ref 6) tried to apply various methods for isolating nitrostarch dissolved in nitric acid. He used both water and sulphuric acid, and obtained nitrostarch with different nitrogen contents, and has observed that the product separated by means of sulphuric acid was the less stable, readily undergoing spontaneous decomposition. Mühlhäuser (Ref 7) expressed a far-sighted view that the low stability of this nitrostarch was due to partial sulphonation brought about by sulphuric acid

The most extensive of the researches carried out in the nineteenth century were those of Mühlhäuser (Ref 7) who dissolved starch in a ten-fold quantity of nitric acid, sp gr 1.50, and precipitated the product with thirty times as much sulphuric acid. In this way he introduced 13.5% N, but the nitration product was unstable

Experimenting with a still stronger nitric acid, sp gr 1.52, Will and Lenze (Ref 8) prepared nitrostarch characterized by a nitrogen content of 14.04%. They established that it is possible to produce nitrostarch of high nitrogen percentage and adequate stability providing it is subjected to a stabilization boil in ethyl alcohol

Moreover, Will and Lenze established that starch can be nitrated in a manner resembling cellulose nitration, by means of a mixture of nitric and sulphuric acid, to obtain a product containing 13.9% N. The same method was tried by Sapozhnikov (Ref 11). However, he did not wholly confirm the results published by Will and Lenze, since the maximum nitrogen content in his product was 13.5%

Starch nitrated by Brown and Millar (Ref 10) by dissolution in nitric acid and subsequent precipitation with the help of sulphuric acid, was stabilized by washing in ether and chloroform

Soluble starch was nitrated by Syniewski (Ref 9). The most extensive published researches devoted to the preparation, purification and properties of nitrostarch are those of Hackel and T. Urbański (Ref 12)"

US production of NS began in 1888 under the name of *Volney Powder.* Improved NS stability was achieved by Hough, who operated two plants in New Jersey for the production of NS. Later (1905 to 1907) Dupont and Eastern Dynamite Corp experimented with NS expls. At about that time Trojan Powder Co became interested in NS. It soon became and still is the largest manufacturer of NS. Numerous patents (from 1918 to 1945) have been issued to W.O. Snelling (of Trojan Powder Co) for the prepn, stabilization and use of NS (Ref 21a)

At present Trojan Powder Co is the only large-scale producer of NS. Some NS was manufactured in Hungary and Poland between the two World Wars but its production is now discontinued (Ref 26, p 420)

Preparation.

Nitrostarch can be prepared by dissolving starch in an excess of nitric acid and pouring this solution into an excess of sulfuric acid to precipitate NS as an amorphous powder. This method is uneconomical and hard to control. Consequently it is not used commercially

The usual preparative methods employ mixed acids. The N content of the NS depends on the composition of the mixed acid and on the mixed acid-to-starch ratio. This is illustrated in the triangular diagram of Fig 1 obtained by Hackel and Urbański (Ref 12). Starch was nitrated for one hour and 50 mins at 10–12°. The acid compn is given in mole %. The region of mixts between the curve AAA'A' and the HNO_3–

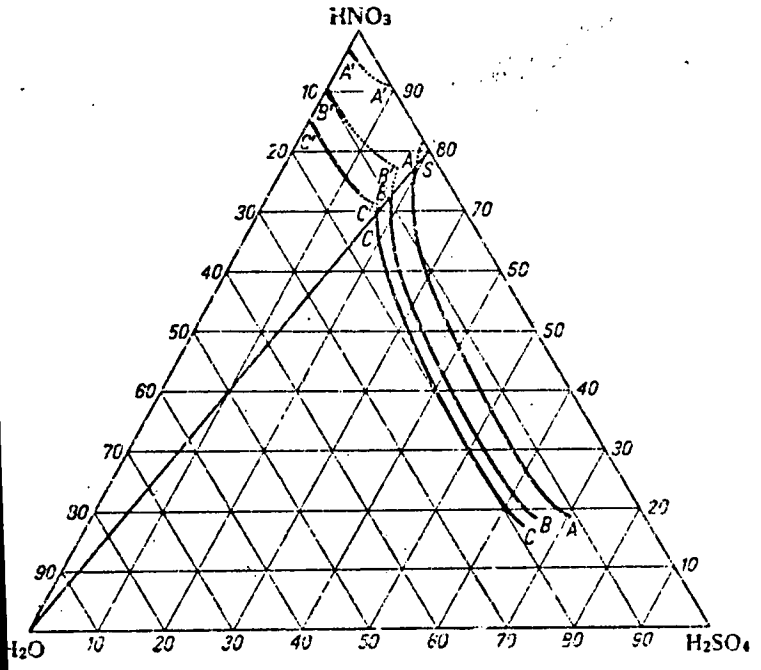


Fig 1. Triangular Diagram for the Nitration of Starch

H_2SO_4 axis corresponds to nitration to a N content of more than 12.75% N. In the area limited by AA–BB and A′A′–B′B′ respectively, the products contain 11.1–12.75% N. Between BB–CC and B′B′–C′C′ respectively, products of 9.15–11.1% N are obtd. To the left of the line CC lies an area corresponding to nitrating acids that give non-homogeneous, low-grade nitrated, oxidized or hydrolyzed products. The outlines of the curves AA, BB, CC, resemble those for NC and also those for nitronium ion NO_2^+ concns

Comparison of the Sapozhnikov graph for NC with the graph by Hackel and Urbański shows that in the latter the curve has a minimum which corresponds approx to a mixed acid whose nitric acid-to-sulfuric acid weight ratio is about 6 (mole ratio is about 9) (See article on *Nitration* in this Vol)

According to Izraelashvili (Ref 18a) high NO_2^+ concn favors production of high N-content NS

Kunz & Toth (Ref 22) found that nitration time for NS varies linearly with temp (Fig 2). Above 14°C nitration is very rapid

Nitrostarch can also be prepared via nitration with nitric and phosphoric acids (Ref 12); N_2O_5 dissolved in nitric acid (Ref 14); N_2O_5 dissolved in chloroform (Ref 18); or nitric acid with P_2O_5 (Ref 23)

Details on commercial production of NS are scarce. Davis (Ref 17) describes a mixed acid consisting of 38% HNO_3 and 62% H_2SO_4, with a 4 to 1 acid-to-starch ratio, and a nitration temp of 38–40°. He states that after nitration the contents are drowned in water and the NS is separated by filtration

A two-stage nitration at 5° is claimed to improve NS stability (Ref 15)

Stabilization.

Stabilization of NS is frequently kept as a trade secret, although there have been some recent publications (Refs 23, 24, 25, 27 & 28). Early studies (Ref 12) suggest that NS made using nitric acid is more stable than that made with mixed acid – possibly because starch sulfates are formed with the latter

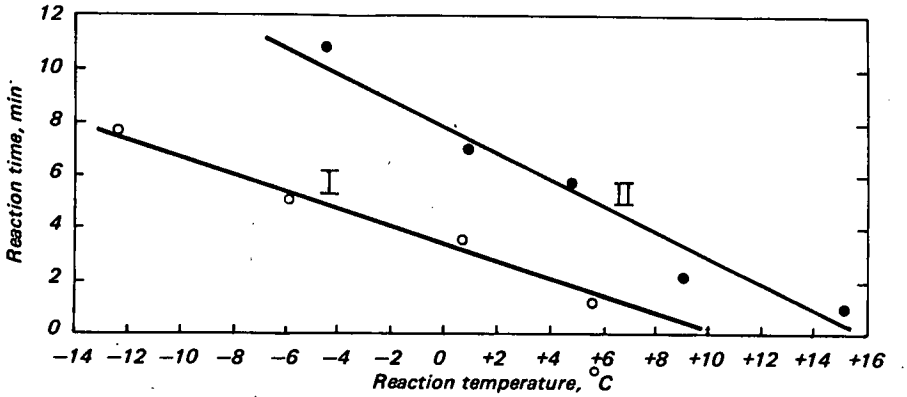


Fig 2. Reaction time of nitration of starch as a function of temperature
(I) 35.0% HNO_3, 57.5% H_2SO_4, 7.5% H_2O,
(II) 33.4% HNO_3, 60.75% H_2SO_4, 5.81% H_2O

Usually, prolonged boiling in acid water and then in alkaline water is used to stabilize NS. However, there are claims that boiling with alkaline water decreases NS stability (Ref 28). However, in a previous publication (Ref 27) these same authors claim that kier-boiling or prolonged boiling in water or in dilute alkaline soln improves stability. Addition of substances such as epichlorohydrin that swell the NS and aid water penetration is claimed to improve stability (Ref 16)

Explosive Properties.

Smolenski & Strzondala (Ref 20) obtained the following heats of combustion and heats of formation for NS:

Table 1
NITROSTARCH PRODUCED BY MEANS OF MIXED ACID

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2575.8	702.4
11.02	2510.6	668.3
12.87	2276.7	555.5
13.24	2217.9	541.0

Table 2
NITROSTARCH PRODUCED BY MEANS OF NITRIC ACID ALONE

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2580.7	696.5
12.20	2378.4	576.3
12.87	2309.0	523.3
13.34	2273.3	504.5

Differences in heats of formation of the two kinds of Nitrostarch are regarded by these authors as related to the presence of sulfuric esters in the Nitrostarches prepared by means of mixed acids

Expl properties of NS obtained by Hackel & Urbański (Ref 12a) are summarized in the following tabulation:

Table 3
EXPLOSIVE PROPERTIES OF NITROSTARCH (AFTER HACKEL & T. URBANSKI)

Nitrogen content %	Rate of detonation, m/sec (in a pipe of diameter 34/28 mm), d = 0.88, initiation by		Lead block test cm^3	Sensitiveness to shock; 8% explosions caused by a 5-kg weight falling from a height of cm
	No 8 detonator	10g of picric acid		
13.4	6190	–	430	21
13.1	5740	–	395	23
12.8	5300	–	375	–
12.4	4950	–	360	36
12.1	4480	–	320	38
11.6	3880	–	300	70
11.0	3020	–	260	100
10.5	2880	–	230	100
9.4	1500	3200	160	100
8.9	1000	3000	125	100
7.7	does not detonate		35	does not explode

Le Roux (Ref 19) examined the expl properties of Nitrostarch of 13.52% N. At a density of 0.90g/cc, a charge of 30mm diam in a cardboard tube detonated at the rate of 4970m/sec. The relative lead block expansion was 117% of Picric Acid

Cook (Ref 21) presents a thermo-hydrodynamic calcn of the detonation parameters and detonation products of two NS expls containing 25/1.5/73.5 NS/Al/AN-SN dope and 27.5/3/69.5 NS/Al/AN-SN dope

Urbański (Ref 26, p 426) states NS burns readily in a manner similar to NC

Merzhanov and coworkers (Ref 29) studied the ignition of NS (and other expls) in a hot gas stream and found that the critical expln temp decreases with increasing O content of the gas

Explosive Compositions Containing NS.

Davis (Ref 17) gives the following compn for *Trojan Explosive:* 23-27/31-35/36-40/1.5-2.5/0.5-1.5/0.5-1.5/0.2-0.4% NS/AN/SN/charcoal/heavy hydrocarbon/antacid/diphenylamine. For *Grenite* he shows 97/1.5/1.5% NS/petroleum oil/gum arabic. He also gives examples of early Trojan NS Dynamites as follows: 30-39/0-20/37-58/0-5/0.5-0.75/2-5/1.0-1.5% NS/AN-TNT mixt/SN/carbonaceous matter/paraffin oil/sulfur/Ca carbonate

The Nitrostarch Demolition Explosive NSX consists of: 49/40/7/3/1% NS (12.5% N)/Ba nitrate/MNN/paranitroaniline/oil (Ref 30)

Several more recent NS expls are described below:

G.L. Griffith & D.G. Samuel, USP 2860041 (1958) & CA **53**, 3697 (1959). Provides a process for preparing blasting expls that are relatively nonsensitive and nonhazardous in handling and manufacturing, but which acquire full sensitiveness by the time the expl is to be used. This is accomplished thru incorporation into a mixt containing a damp, nitrated hydrocarbon such as *Nitrostarch* and the other normal ingredients of blasting Dynamites up to about 5% of an organic hydrophylic but not hygroscopic latent sensitizer (water absorber) such as locust-bean extract, gum karaya, or Na carboxymethylcellulose. This absorbs the water from the damp NS to sensitize the mixt and in so doing forms a gelatinous layer on the particles which aids in preventing penetration of external water

G.L. Griffith & F.W. Wells, USP 3083127 (1963) & CA **58**, 13704 (1963). Higher detonation velocity, better cratering and improved ease of initiation are claimed when NS replaces TNT in the following slurry expl: 10-30% NS/35-75% AN + SN/10-40% H_2O plus conventional fuels and thickeners

F.B. Wells & W.H. Rinkenbach, USP 3180773 (1965) & CA **63**, 2844 (1965). Bone meal imparts improved water resistance to the following NS Dynamite: 25% dry NS/51.6% AN/20.8% SN/2% commercial ground bone meal/0.3% ZnO/0.3% mineral oil

G.L. Griffith, USP 3300348 & CA **66**, 67518 (1967). Nonsegregating expl co-nitrates having relatively low impact sensitivities and higher rates of detonation and higher initiation sensitivities than mechanical mixts of the individual nitrates are claimed which are particularly useful as sensitizing expls. These are provided by nitration, preferably with a mixt of HNO_3 and sufficient H_2SO_4 to inhibit soln of the nitric esters in the nitration medium, of a mixt of a commercial starch, preferably corn starch, and a polyol or polyol derivative such as pentaerythritol (preferred), its hydroxyesters, dipentaerythritol and higher pentaerythritols, mannitol, sorbitol, erythritol, trimethylolpropane, and neopentyl glycol. The materials may be nitrated consecutively or simultaneously

G.L. Griffith & W.L. Schwoyer, USP 3457128 (1969) & CA **71**, 72517 (1969). Particulate self-explosive nitrated materials, such as Nitrostarch, PETN, TNT, and their mixts, can be made relatively safe to handle and transport thru formation of a uniform nongelled aq slurry containing 10–50% water and 0.5–10% partially hydrolyzed polyacrylamide suspending agent having 0.1–50% free acid, and ≧ 50% unhydrolyzed amide groups, and a mw of 1,000,000–25,000,000. Such slurries are especially useful for transporting expl sensitizers used in aq slurry blasting agents. Thus, a mixt was prepd by stirring together 66% dry *Nitrostarch*, 39.8% water, and 0.2% Polyhall 295 (a commercial partially hydrolyzed polyacrylamide of mw 3,000,000–8,000,000 containing 15–30% amide groups hydrolyzed to acid groups). This slurry showed no separation after 2 months' storage at 50–80°F, after which 50 parts of it was blended with dry AN 50, flake Al 30, and water 11 parts

to produce an expl blasting slurry which, when tested in a bore hole, detonated readily and produced good rock breakage

Written by **J. ROTH**

Refs: 1) H. Braconnot, AnnChimPhys **52**, 29 (1833); Ann **7**, 249 (1833) 2) J.H. Pelouze, CR **7**, 713 (1838) 3) C.H.D. Buijs Ballot, Ann **45**, 47 (1843) 4) H. Rhenisch, ReportPharm **3**, 6 (1849) 5) A. Béchamp, CR **41**, 817 (1855); AnnPhysChim **48**, 349 & 458 (1856) 6) A. Béchamp, AnnPhysChim **64**, 311 (1862) 7) O. Mühlhäuser, DinglersPolytJ **284**, 140 (1892) 8) W. Will & F. Lenze, Ber **31**, 87 (1898) 9) W. Syniewski, Ber **31**, 1791 (1898) 10) H.T. Brown & J.H. Miller, JCS **75**, 308 (1899); JSCI **18**, 159 (1899) 11) A. Sapozhnikov, ZhRussKhimObshch **35**, 26 (1903) 12) J. Hackel & T. Urbański, SS **28**, 35 (1933) & CA **28**, 1865 (1934) 12a) J. Hackel & T. Urbanski, SS **30**, 98 (1935) 13) M. Kolachkowska & T. Urbański, RocznikiChem **15**, 339 & CA **30**, 1253 (1938) 14) T. Urbański & Z. Janiszewski, Ibid **17**, 384 (1937) & CA **31**, 8927 (1937) 15) "Nitrokemia" Ipartelek, HungP 118102 (1938), quoted in Urbański **2** (1965) 16) HungP 121180 (1939); A. Kunz, GerP 691154 (1939) & CA **34**, 4907 (1940) 17) Davis (1943), 273–276 18) G.V. Caesar & M. Goldfrank, JACS **68**, 372 (1946); et al, Ibid **69**, 617 (1947); et al, Ibid, **70**, 424 (1948) 18a) Sh. Izraelashvili, Nature **166**, 686 (1950) 19) A. Le Roux, MP **33**, 211 (1951) & CA **47**, 10229 (1953) 20) D. Smolenski & J. Strzondala, ZeszytyNaukPolitechn, Wroclaw No 4, Chem No 1, 49 (1954) & CA **49**, 15436 (1955) 21) Cook (1958), 309 21a) G.V. Caesar, *Starch Nitrate,* in Adv in CarbohydrateChem **13**, (1958) 22) A. Kunz & I. Toth, ActaChemAcadSciHung **13**, 385 & CA **52**, 11755 (1958) 23) A. Mustafa et al, CanadJChem **40**, 2072 (1962) & CA **58**, 654 (1963) 24) A. Mustafa & A.F. Dawoud, Explosivst **11**, 168 (1963) & CA **60**, 359 (1964) 25) A. Mustafa & A.F. Dawoud, Explosivst **12**, 227 (1964) & CA **62**, 7985 (1965) 26) Urbański **2** (1965) 27) A. Mustafa & A.F. Dawoud, Explosivst **14**, 241 (1966) & CA **66**, 67478 (1967) 28) A. Mustafa et al, Staerke **19**, 358 (1967) & CA **67**, 118357 (1967) 29) Yu. Grigor'ev et al, FizForeniyaVzryva **3**, 512 (1967) & CA **69**, 45000 (1968) 30) Anon, "Explosives Series, Properties of Explosives of Military Interest", EngDesHndb **AMCP 706-177** (1971), 246–48

Nitrosyl Chloride. NOCl, mw 65.47, N 21.40%; very corrosive, reddish-yel gas; mp −59.6°, bp −5.38°, decompd by w, sol in fuming sulfuric acid. Critical temp 167°, crit press 92.4 atm (Ref 4)

Can be prepd from Na nitrite and hydrochloric acid; $NaNO_2+2HCl=NOCl+NaCl+H_2O$ (Ref 1)

NOCl is a powerful oxidizing agent, and causes explns when mixed with reducing substances. For instance, an expln occurs when it is mixed with an equal quantity of hydrogen. When powdered As or Sb is introduced into gaseous NOCl, spontaneous combustion occurs. An expl reaction was reported when it was sealed in a tube with a residue of acet in the presence of Pt catalyst (Ref 2)

NOCl is intensely irritating to the eyes, skin and mucous membranes. Inhalation can cause pulmonary edema and hemorrhage (Ref 3)

Refs: 1) J.R. Morton & H.W. Wilcox, InorgSynth **4** (1953), 48 2) Anon, C&EN **35** (43), 60 (1957) 3) Merck (1968), 743-L 4) C.B. Colburn, Ed, "Developments in Inorganic Chemistry", Vol **2**, 141–155, Elsevier (1973) 5) Sax (1975), 975-L

Nitrosyl Fluoride. NOF, mw 49.01, N 28.58%; colorl gas, often bluish because of impurities; mp −132.5°, bp −59.9°; d solid, 1.71g/cc; d liq at −59°, 1.326g/cc. Sol in w with blue color evolving NO, HNO_3 and HF

Can be prepd by treating nitrosyl chloride with Ag fluoride (Ref 1), or by the combination of nitric oxide and fluorine (Ref 2)

NOF reacts violently with B, Si, red P, Sb and As even under cold conditions, and on heating with some organic compds (Ref 6). It reacts vigorously with glass and corrodes quartz (Ref 5). When mixed, even at low temps, with the relatively inactive OF_2, it explds (Ref 4). It can be kept in quartz ampules if cooled in liq oxygen

NOF is highly irritating to the skin, eyes and mucous membranes (Ref 5).

Refs: 1) O. Ruff & K. Stauber, ZAnorgChem

47, 190 (1905) 2) O. Ruff, W. Menzel & W. Neumann, ZAnorgChem **208**, 293 (1932) 3) Mellor **8** (1946), 612 4) Sidgwick, Chem-Elems **1** (1950), 701 5) Merck (1968), 743-L 6) Anon, "Fire Protection Guide on Hazardous Materials", NFPA, Boston, Mass (1973), 491M-180 7) Sax (1975), 975-L

Nitrosyl Perchlorate. $NOClO_4$, mw 129.47, N 10.82%; white cryst, decomps on heating, hygroscopic, d 2.169g/cc, unstable

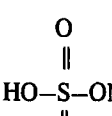
First prepd by Hofmann and Zedtwitz (Ref 1) by passing a mixt of nitric oxide and nitrogen dioxide into 72% perchloric acid. The acid was then evapd at 140°, and on cooling the hydrate, $NOClO_4.H_2O$, crystd out. The product was dehydrated in vacuo over phosphorous pentoxide.

When heated below 100° it decomps (Ref 2) according to the equation: $2NOClO_4 \rightarrow 2ClO_2 + N_2O_5 + \frac{1}{2}O_2$. At higher temp the decompn follows a different course: $2NOClO_4 \rightarrow Cl_2 + N_2O_4 + 3O_2$. It is strongly endothermic with $\Delta Hf = -41.79 \pm 0.08$kcal/mole

It reacts with w with the evolution of nitrogen oxides. With methanol it forms methyl nitrite, while ethanol, ether or acet react with ignitions and explns. Violent explns occur with primary aromatic amines, probably because of the formation of diazonium perchlorates (Ref 3)

Refs: 1) K.A. Hoffman & A. vonZedtwitz, Ber **42**, 2031 (1909) 2) A. vonZedtwitz, "Beiträge zur Kenntnis der Ueberchlorsäure, Insbesondere des Dihydrates", Dissertation, Munchen (1911) 3) A. Hantzsch & K. Berger, ZAnorgChem **190**, 321 & 333 (1930) 4) Mellor **8** (1946), 453 5) K. Cruse et al, ZAnorgChem **259**, 154; **260**, 295 (1949) 6) Sidgwick, ChemElems **2** (1950), 1235 7) Hackh's (1972), 461-R 8) Anon, "Fire Protection Guide on Hazardous Materials", NFPA, Boston, Mass (1973), 491M-180

Nitrosylsulfuric Acid (Nitroso, Nitrosyl Sulfate, Nitrosulfuric Acid, Nitroxylsulfuric Acid, Nitrosulfonic Acid, Nitrosyl Hydrogen Sulfate, Nitro Acid Sulfite). HNO_5S, NO_2HSO_3, $HNOSO_4$, $ONOSO_3H$, mw 127.08, N 11.02%, colorl prisms; mp, decomps 73.5°. In moist air the crysts decomp with the formation of sulfuric and nitric acids, and above 50°, nitric oxide and nitrogen dioxide are evolved. Decomps violently with w with formation of sulfuric acid and nitrogen oxides. Sol in sulfuric acid contg not more than 30% w, otherwise it is decompd by the w in the acid



Formed as an intermediate in the Pb chamber process for sulfuric acid by the reaction of sulfur dioxide, nitrogen trioxide, oxygen and w *(chamber crystals)* (Refs 1 & 2). Can be prepd from Ag acid sulfate and nitrosyl bromide (Ref 4)

In the expl industry, it is constantly necessary to deal with nitrosylsulfuric acid, because it forms during the nitration of organic compds as a result of the partial oxidation of the compds by nitric acid. For example, in the manuf of TNT, a small amt forms during the mononitration:

$$C_6H_5CH_3 + 18H_2SO_4 + 18HNO_3 \rightarrow 18HNOSO_4 + 7CO_2 + 22H_2O$$

Larger amts form during dinitration, and still larger amts, reaching 15–18% of the total acidity, during trinitration

In the nitration of glycerin to NG, the reaction proceeds as follows:

$$C_3H_5(OH)_3 + 7H_2SO_4 + 7HNO_3 \rightarrow 7HNOSO_4 + 3CO_2 + 11H_2O,$$

and in the nitration of cellulose to NC, or of starch to Nitrostarch:

$$C_6H_{10}O_5 + 12H_2SO_4 + 12HNO_3 \rightarrow 12HNOSO_4 + 6CO_2 + 17H_2O$$

Nitrosylsulfuric acid is highly toxic, and a strong irritant to skin and mucous membranes (Refs 10 & 11)

Refs: 1) A. Clémont & J. Désormes, AnnChim-Phys [1] **59**, 329 (1806) 2) G. Lunge, JCS **47**, 470 (1885) 3) G.A. Elliot et al, JCS **1926**, 1219 & CA **20**, 3142 (1926) 4) E. Berl et al, ZAnorgChem **209**, 264–66 (1932) 5) Mellor **8** (1946), 696–702 6) Thorpe **8** (1947), 532 7) Partington (1950), 558 8) Urbański **1** (1964), 9, 53, 102 9) Merck (1968), 743-R 10) CondChemDict (1971), 626-L 11) Sax (1975), 975-L

Nitrous Fumes. This term includes any nitrogen oxide fumes produced in the manuf of nitric

acid or in processes in which it is used. The exact compn of the fumes or vapor depends upon such factors as temp, humidity, and the material the acid acts upon

The oxides of nitrogen are somewhat sol in w, reacting with it in the presence of oxygen to form nitric and nitrous acids. This is the action that takes place deep in the respiratory system. The acids formed are irritants, causing congestion of the throat and bronchi, and edema of the lungs. The acids are neutralized by the alkalies present in the tissues, with the formation of nitrates and nitrites. The latter may cause some arterial dilation, fall in blood press, headache and dizziness, and there may be some formation of methemoglobin. However, the nitrite effect is of secondary importance

Because of their relatively low solubility in w, the nitrogen oxides are only slightly irritating to the mucous membranes of the upper respiratory tract. Their warning power is therefore low, and dangerous amts of the fumes may be breathed before the individual notices any real discomfort. Higher concns (60 to 150ppm) cause immediate irritation of the nose and throat, with coughing and burning in the throat and chest. These symptoms often clear up on breathing fresh air, and the individual may feel well for several hours. Some 6 to 24 hours after exposure, he develops a sensation of tightness and burning in the chest, shortness of breath, sleeplessness and restlessness. Dyspnea and air hunger may increase rapidly, with development of cyanosis and loss of consciousness, followed by death. In cases which recover from the pulmonary edema, there is usually no permanent disability, but pneumonia may develop later. Concns of 100–150ppm are dangerous for short exposures of 30 to 60 minutes. Concns of 200–700ppm may be fatal after even very short exposures

Continued exposure to low concns of the fumes, insufficient to cause pulmonary edema, is said to result in chronic irritation of the respiratory tract, with cough, headache, loss of appetite, dyspepsia, corrosion of the teeth and gradual loss of strength

Exposure to nitrous fumes is always potentially serious, and persons so exposed should be kept under close observation for at least 48 hours (Refs 1, 2, 3, 5 & 6)

Renaud and Gilbert (Ref 4) developed indicator test paper to detect dangerous levels of nitrous fumes in expl plants

Refs: 1) T.M. Legge, ChemAge **1**, 465–7 (1919) & CA **14**, 775–6 (1920) 2) A. Koelsch, ZAngChem **33**, [1], 1–5 (1920) & CA **14**, 2033 (1920) 3) W.F. vonOettingen, US PubHealthBull No 272, 34 pp (1941) 4) R. Renaud & R. Gilbert, MP **32**, 529–39 (1950) 5) Merck (1968), 735-R & 739-L 6) Sax (1975), 961-L, 961-R & 967-R

Nitroxydialkylnitramines. See Hydroxydialkylamines, Nitrated Derivatives in Vol **7**, H239-L

Nitrylchloride (Nitroxyl Chloride). NO_2Cl, mw 81.47; corrosive, toxic colorl gas; mp $-145°$; bp $-14.3°$, decomps above 120°; vap d at 100°, 2.81g/ℓ; liq d at 0°, 1.37g/cc; at 16°, 1.33g/cc (Ref 11)

The most important processes for the practical production of nitryl chloride are those in which chlorosulfonic acid and practically anhydr nitric acid are used as starting materials; $HSO_3Cl+HNO_3 \rightarrow H_2SO_4+NO_2Cl$. The chlorosulfonic acid is added dropwise either at RT or with cooling to $-10°$ to 100% nitric acid or to mixts of concd nitric and sulfuric acids. A continuous current of almost pure nitryl chloride gas is evolved (Refs 1, 3, 4, 5, 6, 8 & 9). Further purification can be achieved by the passage of ozonized O_2 thru the liquefied gas (Ref 9). Very pure nitryl chloride is obtained on slow vac distn of anhydr nitric acid on to chlorosulfonic acid in an app consisting entirely of glass, followed by fractional distn (Ref 7)

The gas or liq may attack organic matter with expl violence (Ref 11). Instances of violent reactions with ammonia, sulfur trioxide, stannic bromide and iodide are documented (Ref 12)

Nitryl chloride was proposed for use as a nitrating agent for paraffin hydrocarbons (Ref 2)

Refs: 1) K. Dachlauer (to I.G. Farbenind AG), GerP 509405 (1929) 2) W. Steinkopf & M. Kühnel, Ber **75B**, 1323 (1942) & CA **37**, 4687 (1943) 3) M. Kühnel, GerP 739533 (1943) 4) H. Petri, ZAnorgChem **257**, 180 (1948) 5) R.A. Ogg, Jr & M.K. Wilson, JChemPhys **18**, 900 (1950) 6) H. Shechter et al, JACS **74**, 3052 (1952) 7) F. Seel & J. Nogradi, ZAnorg-

Chem **269**, 188 (1952) 8) R. Kaplan & H. Shechter, InorgSynth **4**, 52 (1953) 9) J. Ville, MP **37**, 343 (1955) 10) M.J. Collis, JCS **1958**, 438 11) Merck (1968), 744-R 12) Anon, "Fire Protection Guide on Hazardous Materials", NFPA, Boston, Mass (1973), 491M-181

Nitryl Fluoride (Nitroxyl Fluoride). NO_2F, mw 65.01; colorl, fuming gas; mp $-166.0°$, bp $-72.4°$; d (solid) 1.924g/cc, liq at $-72°$, 1.796g/cc

Originally prepd by the spontaneous combustion of nitric oxide in an atm of fluorine; $4NO+F_2 \rightarrow N_2+2NO_2F$ (Ref 1). More easily prepd by mixing nitrogen dioxide with fluorine; $2NO_2+F_2 \rightarrow 2NO_2F$ (Ref 2)

Nitryl fluoride spontaneously ignites I_2, Se, P (red & white), As, Sb, B, Si, Th and Mo. On mild warming attacks Pb, Bi, Cr, Mn, Fe, Ni, W, S and charcoal. On contact, alc is converted to ethyl nitrate and benz to NB. It attacks mucous membranes instantly (Ref 5)

Refs: 1) H. Moissan & P. Lebeau, CR **140**, 1573 & 1621 (1905) 2) O. Ruff, W. Menzel & W. Neumann, ZAnorgChem **208**, 298 (1932) 3) Mellor **8** (1946), 623 4) Sidgwick, Chem-Elems **1** (1950), 702 5) Merck (1968), 744-R

Nitryl Perchlorate (Nitroxyl Perchlorate). NO_2ClO_4, mw 145.47, white cryst; mp, decomps rapidly at $120°$; deflagrates on rapid heating

Can be prepd by the action of conc nitric acid on perchloric acid; $NO_2.OH+HClO_4 \rightarrow NO_2.ClO_4+H_2O$

Nitryl perchlorate reacts with organic matter with a violence ranging from slight explns to sharp detonations accompanied by fire. Incidents have been reported with acet, benz & eth (Ref 2)

Refs: 1) Partington (1950), 543 2) Anon, "Fire Protection Guide on Hazardous Materials", NFPA, Boston, Mass (1973), M491-181 & 2

Nizol. An expl patented by Schweiz of Sprengstoff-Fabrik AG, Dottikon (SwissP 226852), contg m-dinitrobenzene made more sensitive to initiation by the addition of 30% PETN. It was castable because of the low mp, about $80°$, of m-DNB

Ref: Stettbacher (1948), 72

NK. Abbrev for *Nobelkrut.* A series of double-base proplnts manufd by the AB Bofors Nobelkrut of Sweden. See under Bofors Propellants in Vol **2**, B220-L

Nobel, Alfred Bernard (1833–1896). Swedish inventor and philanthropist who revolutionized the expls industry. Between 1863 and 1865, in spite of an expln which killed his youngest brother and four other persons, he successfully developed a detonator, based on MF, to make possible the industrial use of NG. This was quickly followed by the development of Dynamite (see Vol **5**, D1585 ff), in which the admixture of kieselguhr, while reducing the expl force of NG by one-fourth, provided a blasting material which was reasonably safe in manuf and use. From its first patenting in 1867, Dynamite enjoyed a world-wide success, and in 1875 Nobel introduced the still more powerful Blasting Gelatine (see Vol **5**, 1599 ff), in which the NG was gelatinized with collodion cotton. Finally, in 1888 he contributed one of the first smokeless powders for military purposes. This was Ballistite (see Vol **2**, B8–B9), a mixt of collodion cotton, NG, benz, and (initially) camphor, which was first used by the government of Italy

In spite of many battles over patent rights, these inventions earned Nobel a considerable fortune, which was increased from his large holdings in the Baku (Russia) petroleum industry. He died in 1896 in San Remo, Italy, leaving a vast fortune, a major part of which established the world-famous prizes for chemistry, physics, physiology or medicine, literature of an idealistic tendency, and the promotion of world peace

A detailed listing of Nobel's inventions, arranged chronologically, follows:

1863: An expl prepd by dissolving NG in ethyl or methyl nitrate, followed by mixing with BkPdr, NC and other materials

1863: Initiation of NG charges by a detonator incorporating gunpowder

1865: Initiation of NG charges with a modern

detonator (blasting cap) contg MF

1866-67: Invention of kieselguhr Dynamite, and application of MF caps for its initiation

1869: Invention of Straight Dynamite (see Vol 5, D1596-R to D1598-R)

1873: Improvement of AN blasting powder, invented in 1867

1875: Invention of Blasting Gelatine and Gelatine-Dynamite

1879: Invention of Extra Dynamite or Ammonia Gelatin Dynamite, a combination of AN and Blasting Gelatine (see Vol **1**, A295-R, Vol **5**, D1604-L and Vol **6**, E500-L). In this expl, the AN was rendered non-hygroscopic (Ref 3, p 335)

1879: Expls suitable for mining or military purposes, contg NG, NC and Nitrosugar, mixed with nitrates, chlorates or perchlorates of alkali or alkaline earth metals

1884: Expls consisting of combustible liqs, such as petroleum, mixed with nitrates or other oxidizing salts. To this could be added various quantities of expls, such as NG

1885: A liq expl consisting of 1p of goudron (Fr for tar or pitch) dissolved in 2p of NG. This soln was mixed just before use with 2p of oleic acid

1885: Addition to NG of materials having a tendency to lower its fp

1885: Expls contg AN with other materials

1886-87: Expls suitable for charging shells or torpedoes, consisting of compressed gaseous expl mixts with or without liq or solid expls or combustibles

1887: Safety expls contg Cu nitrateammine, $Cu(NO_3)_2.4NH_3$, either alone or in mixt with combustibles

1887: Improvements in detonator manuf, described in FrP 184129 of 1887 (Ref 1, pp 198–99)

1887: Smokeless powders prepd by gelatinizing with a vol solvent, NC's prepd from such materials as corozzo, coconut shells, etc, together with Nitrostarch or Nitrodextrin

1888: Invention of Ballistite, the first successful smokeless powder contg NG, described in BritP 1471 of 1888 (Ref 1, p 51)

1888: An expl for use in detonators contg 2p collodion cotton dissolved in 12p acet, to which was added 1p NG, 4p K picrate and 8p K chlorate (Ref 1, p 199)

1888: An expl prepd by mixing Ba nitrate, charcoal and Amm picrate or amorph P

1888: An expl consisting of 3p Ba nitrate and 1p AN, together with a small quant of dextrin or gum as binder

1888-89: A cordeau détonant contg Blasting Gelatine with 15–20% camphor, as well as K chlorate, K ferrocyanide and NC

1891: A smokeless powder prepd by carefully blending pulped NC (70 to 99p) with liq nitroaromatic compds (30 to 1p), heating the mass and pressing it in the form of plates, which were cut into sections and granulated in the manner practiced with BkPdr. This was one of the first "solventless" methods of proplnt prepn (Ref 1, p 5)

1894: A cordeau détonant contg a compn prepd by thoroughly mixing NG or Nitrosugar with NC, mononitronaphthalene, dinitrobenzene, di- or trinitrotoluene, K dichromate & K ferricyanide (FrP 237447 of 1894) (Ref 1, pp 158–159)

1894: Smokeless powders prepd by blending NC and Nitromannite, with or without dinitrobenzene (DNB). **No 1:** NC 60, Nitromannite 40; **No 2:** NC 60, Nitromannite 20, DNB 20; **No 3:** NC 50, Nitromannite 30 & DNB 20% (Ref 1, p 580)

1896: A safety mining expl contg AN as the main ingredient, together with K permanganate and a small quantity (1–3%) of NG (Ref 1, p 5)

1897: A safety mining expl contg K chlorate 40.0, Na bicarbonate 33.3 & dextrin 26.7%

1896-97: A progressive burning smokeless powder, patented by Nobel shortly before his death, consisted of a core of rapid burning powder, such as Ballistite, surrounded by a coating of a slow burning compn

There were many other expl compns patented after Nobel's death by the numerous companies established by him thruout the world. Some are given below:

Nobel-Ardeer Powder. A Dynamite manufd in the early twentieth century by Nobel's Explosive Co, Ardeer, Scotland. It contd NG 31–34, kieselguhr 11–14, Epsom salt 47–51, K nitrate 4–6, soda 0.5 & Amm carbonate 0.5% (Ref 1, p 30)

Nobelit. One of the permissible Gelatine-Dynamites manufd by the Nobel Explosive Co. It contd NG 28.0, collodion cotton 0.7, AN 39.7, dextrin 2.5, potato flour 10.0, vegetable oil

0.5, woodmeal 1.0 & Na chloride 17.6%

Nobel's Carbonite. A dynamite manufd at the end of the 19th century in England by Nobel's Explosives, Ltd. It contd NG 25 to 27, K nitrate 28 to 32, Ba nitrate 3.5 to 4.5, wheat flour or woodmeal 31.2 to 37.8, & moisture 3.9 to 8.4%. To this were added Na bicarbonate or Ca carbonate 0.5 and benz 0.5% (Ref 1, p 114)

Nobel's Gelignite. A Dynamite manufd in England between 1897 and 1898, contg NG 54 to 63, collodion cotton 3 to 5, K nitrate 26 to 34 & woodmeal 6 to 9% (Ref 1, p 340)

Refs: 1) Daniel (1902), 573–76 2) VanGelder & Schlatter (1927), 316, 318–25 3) Davis (1943), 332 4) J. Erik Jorpes, JChemEduc **37**, [7], 328–34 (1960) 5) E. Bergengren, "Alfred Nobel: The Man and His Work", Nelson & Sons, Ltd, London (1963)

Nobel's Mortar (Mortero probeta de Nobel in Spanish). A device for testing the strength of expls

Historical. Shortly after the invention of gunpowder (BkPdr), it was recognized that a test had to be developed to evaluate its properties. As it was first used only as a proplnt and not as a HE, it was sufficient to test it solely for burning rate. One of the first devices to test the strength of BkPdr was described by Bourne in 1578 (Ref 1). It consisted of a small metal cylinder closed at the top with a heavy lid, one side of which was attached to a hinge, the other side being connected to a ratchet. When a charge of BkPdr was fired inside the cylinder, the resulting press raised the lid to a certain angle, and the ratchet prevented it from falling back. The angle was measured and related to the power of the particular batch of BkPdr

A better instrument was devised in 1627 by Curtenbach. It consisted of a small mortar with a heavy cylindrical shot positioned at its mouth. When a charge was fired, the shot travelled at a 45° angle along a stretched wire, provided with a series of catches to stop the shot at the highest position it attained. This device can be considered to be the prototype of the modern Ballistic Mortar (See Vol **1**, VII). The same device was described in 1647 by Nye in his "Art of Gunnery". However, he advised firing the shot into clay in order to detn the depth to which it was buried. This design was adopted by the French Government in a device called the "Mortar Éprouvette". The next improvement was that of Robbins, who in 1742 invented the "Ballistic Pendulum" (See Vol **1**, VII–VIII), by means of which the actual velocity of a projectile could be measured

Nobel's mortar, which can be considered as an improvement over that of Curtenbach, consisted of an iron block provided with a cylindrical cavity, 25cm deep and 10cm in diameter. A 10g sample of expl was weighed into a wooden shell, 6cm deep and 3cm in external diameter, which was then inserted into the cavity. A length of safety fuse with a detonator at its lower end was then inserted in the charge. The shot, consisting of an iron cylinder slightly smaller than 10cm in diameter, which weighed exactly 15kg, was then inserted in the cavity. This cylinder was provided with a channel parallel to its axis, thru which the safety fuse ran to the outside of the app. After the gun was positioned at a 45° angle, the fuse was ignited, and the shot was fired. The distance traveled was then compared to that obtained with 10g of a standard expl (Ref 3)

Barnett (Ref 2) gives the following distances obtained for some Brit expls with Nobel's mortar: Blasting Gelatine, 240m; Gelignite, 168m; Gelatine Dynamite, 188m; Dynamite No 1, 132m; and Brit "Permitted" Expls, 80–120m

Note: In order to avoid having to recover the shot after each test, the gun was sometimes mounted as a pendulum, and the shot fired into a sand bank a few feet away. In this case, the recoil was measured in a manner similar to that of a Ballistic Pendulum

Refs: 1) Marshall **1** (1917), 27–8 2) Barnett (1919), 181–82 3) A. Pérez Ara (1945), 120–21

Nobel's Patent Blasting Oil. Name under which NG was known in the USA at the time of its introduction in the 1860's

Ref: VanGelder & Schlatter (1927), 324

Nobel's Powder-Dynamite (La Poudre-Dynamite de Nobel in Fr). Smokeless powds similar to Ballistite manufd by the Nobel Co. One compn

was prepd by mixing 4–5p of NC with 20p of NG. To this were added 4p of camphor, 20p of Nitrostarch (12.5% N), and 40p of Nitrodextrin (12.5% N). The mixt was blended at 60°, passed thru heated rolls several times, and the resulting thin sheets cut to desired dimensions. This proplnt, manufd at the end of the last century, was an example of early solventless powders. One of the varieties of "Powder-Dynamites" was known in Germany under the name **"RGP 88 Pulver"**, and was used in cannons of various caliber
Ref: Daniel (1902), 581–2

Nobel's Safety Powder. The name given to Dynamite at the time of its invention
Ref: Davis (1943), 332

Nobel, Sir Andrew (1832–1915). British artillery officer who did important work in ordnance and expls. He invented a chronoscope in 1862, and modified the press gauges existing at that time, creating a model which, with some modification, is still used. This gauge, patented in 1868, was called a "Crusher Gauge", and was designed to estimate the press developed on an expln. It consisted of a heavy-walled cylinder, closed at one end and fitted at the opposite end with a steel piston. A copper cylinder of known dimensions was placed inside the app behind the piston. The ensemble was then screwed into the wall of a gun barrel, or placed in the breech behind the charge. On firing, the press of the gases developed pushed the piston against the copper cylinder, causing its deformation (compression), the greater the press, the shorter its length. Calibration of the copper cylinder under known press loads allowed for an estimate of the press developed in a gun to be made
Refs: 1) Marshall **2** (1917), 445 2) Colver (1938), 603–5

Nobel's 704. See under British Military Explosives and Propellants in Vol **2**, B301-R

Nobel's Wetterdynamit I. One of the older permissible Dynamites contg NG 30, Na nitrate 31, flour 30, woodmeal 6, naphthalene 2 & Al 1%
Refs: 1) Marshall **2** (1917), 492 2) PATR **2510** (1958), Ger 122-R

Nobelit (Nobelite). A type of permissible Gelatine-Dynamites used before and after WWI. Two examples are given in the following table:

Table 1

Compn (%) and some properties	Nobelite	Nobelite 19
NG (gelatinized with NC)	28.7	26.0
DNT	–	2.0
Dextrin	2.5	–
Woodmeal	1.0	1.0
Potato flour	10.0	–
Vegetable oil	0.5	–
Amm nitrate	39.7	34.0
Amm chloride	17.6	32.0
Satd soln of Ca nitrate	–	5.0
Oxygen Balance, %	–	5.0
Density, g/cc	–	1.7
Velocity of Detonation, m/sec	–	3750
Trauzl test, cc	270	220

Refs: 1) Naoûm, Expls (1927), 150 2) Naoûm, NG (1928), 407 3) PATR **2510** (1958), Ger 122-R

Nobelita Antigrisú Gelatinizada (Span). See under Spanish Permissible Explosives in Vol **3**, C455-L

Nobélite (Fr). A plastic expl manufd before and after WWII by the Société Nobel Francaise. It contained NG 20, collodion cotton 1.6, AN 60, liq DNT 14, woodflour 4.3, and Na bicarbonate 0.1%. Its c.u.p. (coefficient d'utilisation practique) was 78 vs 100 for PA, and it was difficult to detonate
Refs: 1) Pepin Lehalleur (1935), 342 2) L. Médard, MP **32**, 217 (1950)

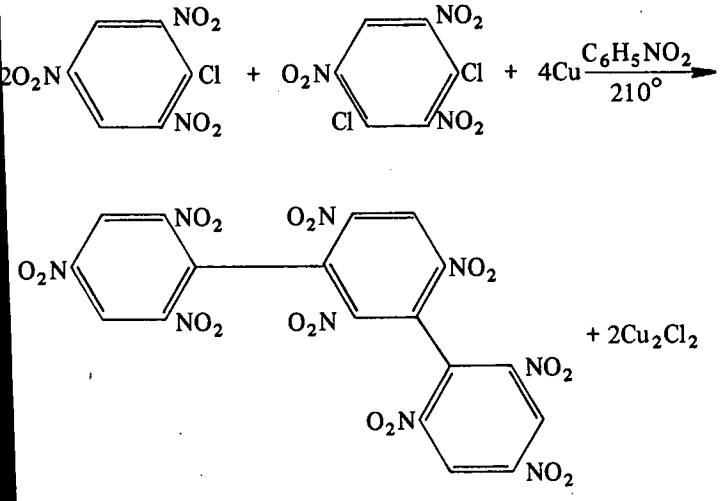
No-Fire Level. The max level of electric energy input that will in no case, within a specified time, initiate an expl-actuated device
Ref: K.O. Brauer, "Handbook of Pyrotechnics", Chemical Publishing Co, NY (1974), 387

NOL No 130 Primer Mixture. See under Lead Styphnate, Basic in Vol **5**, D1278-L

Nombre de Moisson (Fr). See Moisson Number in this Vol

NONA (Nonanitroterphenyl; 2,2′,2″,4,4′,4″, 6,6′,6″-Nonanitroterphenyl). $C_{18}H_5N_9O_{18}$, mw 635.31, N 18.85%, OB to CO_2 −51.63%, light yel monocl cryst, mp 440–50° decompn, d 1.78g/cc

NONA was prepd in a mixed Ullman reaction using picryl chloride, 1,3-dichloro-2,4,6-trinitrobenzene and electrolytic Cu dust;



Thirty g (0.12 mole) of thoroughly dried picryl chloride was dissolved in 50ml of anhydr nitrobenzene in a 500ml 3-neck round bottom flask fitted with a mechanical stirrer and an air cooled condenser. The soln is heated to reflux on a heating mantle. From a dropping funnel fitted with a mechanical stirrer, a slurry of 5.6g (0.02 mole) of 1,3-dichloro-2,4,6-trinitrobenzene and 13g of electrolytic Cu dust was added dropwise while stirring vigorously during a 15 minute period. Reflux was continued for an additional ten minutes and the soln was filtered while still hot. The inorganic residue on the filter was washed with several small portions of hot nitrobenzene. The filtrate and washings were concd on an oil bath under reduced press to a thick syrup. A vol of 350ml of toluene was added, the mixt was refluxed for 15 minutes and filtered hot. The dark brown residue (ca 8g) was suspended in 350ml of toluene, and the mixt was refluxed again for 15 minutes and filtered while hot. The residue on the filter was a brown powdery solid which weighed 5.5g after drying in air. It was not further investigated. The combined filtrates and washings were filtered thru a 3″ pad of silicic acid on a 90mm sintered glass funnel, and the adsorbent pad was washed with toluene until a bright yel band had moved near the bottom of the filter. The filtrate was evapd to dryness, the residue added to 300ml of toluene, and the mixt refluxed for 15 minutes and filtered. The product recovered on the funnel was a tan crystn material which weighed 2.4g after drying. It was purified in two portions by chromatography on silicic acid–Celite 535 with a yield of 2.0g of a light yel crystn solid which melted on a hot bar between 440°–450°. All analytical and test samples were recrystd from either acet-n-hexane mixts or acetonitrile and dried in an Abderhalden drying app over refluxing nitrobenzene for at least 4 hours. The product was identified as 2,2′,2″,4,4′,4″,6,6′,6″-nonanitroterphenyl by elemental analysis and X-ray molecular wt detn

Note: The elemental analyses were difficult to perform due to the tendency of the compd to expld in the combustion tube (Ref 1)

NONA has an impact sensitivity of 39cm vs 32cm for Tetryl and 160cm for TNT. Its vacuum stability at 260° is 0.4cc/g/hr

NONA combines exceptional heat stability with a very low vap press, making it attractive as a booster expl in space applications

Refs: 1) J.C. Dacons, "Heat Resistant Explosives VIII; 2,2′,4,4′,6,6′-Hexanitrobiphenyl (HNB) & 2,2′,2″,4,4′,4″,6,6′,6″,-Nonanitroterphenyl" (Confid), Navord Rept **6904** (15 June 1960) (declassified 15 June 1972) 2) Anon, "2,2′,2″,4,4′,4″,6,6′,6″,-Nonanitroterphenyl (NONA)", Summary Rept Contr No NOw 60-0745-C, American Cyanamid Co, New Castle, Pa (Oct 1964 to Apr 1965) (Confid-material not used in above article) 3) M.J. Kamlet, "Perspectives and Prospects for Research in High Energy Chemistry in 1966–75; I. Heat Resistant Explosives" (U), **NOLTR 65-220** (1966) (Contents Confid–material not used in above article)

Nonaqueous Titration Methods. See under Nitrogen Determination in Energetic Materials in this Vol

Noncased Charges. These are contained in one or more combustible bags instead of a cartridge case. Guns utilizing these charges must provide for obturation against rearward escape of gases by features built into the gun breech. Variations include the following: (1) *Complete proplnt charge in one bag.* This arrangement can be used where the resulting size and shape is suitable for handling and loading. One or more elements of igniter material (usually BkPdr), formed as end pads or as a central core, are fixed within the proplnt bag to augment the primer flame in effecting thorough ignition of the entire mass of proplnt. The propellant bag (sometimes termed cartridge bag) constitutes one unit of separate loading ammo, in which the projectile, proplnt and primer are separately inserted into the gun. (2) *Proplnt charge in two or more bags:* (a) This arrangement is used in separate loading ammo either to divide the proplnt into portions more easily handled in gun loading, or to provide a basic charge and increments for zone firing. An ignition charge may be included in the basic charge only, or in the increment charges also, as may be necessary for satisfactory ignition; (b) Separately bagged (or wrapped) basic charge and increments are also utilized as components of semifixed ammo for zone firing of muzzle-loading mortars. In this use the separate portions of the complete charge are attached to the fins or fin shaft of the projectile, with the increments readily removable in the field to reduce the range from the maximum to the zone desired. A primer cartridge is carried in the rear of the fin shaft of the projectile. (3) *Grain arrangement.* Generally, whether cased or bagged, proplnt charges composed of the commonly used shapes of grain are assembled with the grains in random positions. However, where large rod-shaped grains are used in a package of large length-to-diameter ratio, improvement in compactness, rigidity and uniformity can be obtained by orderly arrangement of grains, end to end, with axes parallel to the axis of the container. A charge thus arranged is termed a *stacked charge*

Also see Vol **1**, A385-L under Semi-fixed Ammunition & Separate-loaded Ammunition, and Vol **2**, B167-L under Black Powder or Gunpowder. Combustible and Consumable Cartridge Cases are discussed in Vol **3**, C420-R ff

Ref: Anon, "Guns-General", EngDesHdbk **AMCP 706-250** (1964), pp 5-5 to 5-6

Nonideal Detonation. See under Detonation, Ideal and Nonideal in Vol **4**, D389-R to D390-R

Non-Permissible (Amer) or Non-Permitted (Brit) Explosives. See under Commercial or Industrial Explosives in Vol **3**, C435-R to C437-R, and Coal Mining Explosives, Testing for Permissibility in Vol **3**, C368-R ff

Nord 5210 (SS.11 and AS.11). A Fr line-of-sight wire-guided battlefield missile that can be fired from aircraft, vehicles and ships. The SS.11 is a surface-to-surface version, and the AS.11 is a similar air-to-surface version

The operator acquires the target by means of a magnifying optical device. As soon as the missile enters his field of vision after launch, the operator commands it to his line of sight by means of a joy-stick. The signals are transmitted over wires trailed from the missile. Tracer flares are installed on the rear of the missile for visual reference. When installed in a helicopter or ship, the simple sighting device used for land vehicles is replaced by a special stabilized sight

The missile has an overall length of 120cm, a launching wt of 29.9kg, an average cruising speed of 360–584km/hour, and a range of 500–3000m. It is propelled by a two-stage solid proplnt rocket motor

Since 1962, the SS.11B1 version, using transistorized firing equipment, has been in production. It is available with a variety of different warheads, including an inert type for practice. The Type 140AC anti-tank warhead is capable of perforating 60cm of armor plate, the Type 140AP02 expl warhead (2.6kg of expl) will penetrate a 1 cm thick armored steel plate at a 3000m range and expld about 2.1m behind the point of impact, and the Type 140AP59 high-fragmentation antipersonnel type with contact fuze

This missile is used by some 18 countries, including the USA where it is designated AGM-22A

Nord SS.12. A spin-stabilized, wire-guided surface-to-surface missile system derived from the Nord SS.11. The principal change is the incorporation of a much larger warhead (29.9kg of HE) which makes it effective against fortifications as well as tanks, ships and other vehicles. Available warheads include the Type OP.3C which can pierce

more than 40mm of armor and expld on the other side

The missile has an overall length of 187cm, a launch wt of 75kg, an avg speed of 190m/sec, and a range of 6000m

Refs: 1) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 139–40 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 327 3) R.T. Pretty & D.H.R. Archer, "Jane's Weapon Systems", Franklin Watts, NY (1974/75), 21

Nordenfelt and Meurling Powder. A proplnt, patented in Engl in 1884, prepd as follows: Cotton or other cellulosic material, was transformed into a material resembling hydrocellulose thru treatment with hydrochloric acid. It was then dried, pulverized, and mixed with S disd in carbon disulfide. After evapn of the CS_2, the material was treated with a concd soln of K nitrate, granulated and dried

Ref: Daniel (1902), 583

Normal Powder (Normalpulver). A Swedish proplnt invented by E. Schenker and manufd at the turn of the century by the Aktiebolaget Svenska Krutfaktorierna at Landskrona and at Annestof. The formulation for use in the Swedish Army rifle contained Guncotton 96.2, sol cotton 1.8, resin, a stabilizer and other materials 2.0%. These proplnts were very stable, nearly hygroscopic, and produced much lower temps than corresponding double-base powders such as Cordite, Ballistite, etc. As a result, gun barrel life was lengthened

Normal Powders were also subsequently manufd in Switzerland, Denmark, England, Belgium and Australia

These proplnts gave very satisfactory performance. They developed a muzzle velocity of 1640 ft/sec and a press of 1750 atm, when used in 84cm field guns with a 600g charge and a 6.7kg projectile. In the 7.5mm rifle, with a 2g charge and a 13.8g bullet, a muzzle velocity of 2035 ft/sec and a press of 2200 atm were attained

Refs: 1) P.G. Sanford, "Nitroexplosives", London (1896), 186–7 2) Daniel (1902), 584 3) Brunswig, Props (1926), 134 4) Thorpe **4** (1940), 515

Norrbin, J.H. (1835–1907). A Swedish inventor, who, in collaboration with C.J. Ohlsson, introduced the first AN blasting powder, called *Ammoniakkrut* (see Vol **1**, A306-R to A307-L)

Norris Powder. A low-freezing mining expl invented in 1901 by an American, Norris. It was much less sensitive to impact and friction than contemporary Dynamites. It contained NG 70, mononitrobenzene 15, and "Huile empyromatique" 15%. The latter ingredient consisted of an oily substance obtained on distn of wood tar. This expl could be used for underwater blasting

Ref: Daniel (1902), 586–7

Norsabite. An AN coal mining expl of the Favier type contg a small amt of calcium silicide as sensitizer; AN 68, TNT 12, NaCl 17 & Ca silicide 3%. Power by BalPend is 2.64″ vs 3.27″ for standard Brit 60% Gelignite

Ref: Marshall **3** (1932), 119

Nougat Method. A method of charging large caliber shells and mines by making successive layers of rough fragments of expl, which are cemented in place by liq expl. A layer of fragments from 1″ to 2″ thick is placed on the bottom of a container and molten expl run in until the fragments are just submerged. When this layer has solidified the process is repeated until the container is full. By employing this method contraction cavities do not occur, but it is naturally a comparatively slow process

In the case of small caliber shells, etc, it is usually possible to fill them completely with fragments, heat the whole until its temp exceeds the mp of the fusible ingredient, which is then added, and the whole allowed to cool

The process provides a useful means of making a composite expl in that the fragments may be a totally different compd from that used to cement them together. Such a process can be used as a means of prepg an expl contg a high percentage of infusible constituents which may either be nitro-compds or oxidizers

Refs: 1) Chemische Fabrik Griesheim, GerP 69897 (1892) (TNT–Picric Acid composite) 2) Colver (1938), 320, 458, 697

Novit (Swed). An underwater expl consisting of TNT 50 and Hexanitrodiphenylamine (HNDPhA) 50%, invented prior to WWI. Its properties were: loading d, 1.65–1.68g/cc; relative brisance, 103% (TNT 100%); $Q_e \approx$ 1000cal/g (TNT 950); power by Trauzl Pb block test, 315cc (TNT 290cc); and vel of deton ≈ 7200m/sec (TNT 6800)

A similar mixt was used in Ger during WWI for loading torpedoes and mines (the name used for HNDPhA was *Hexyl)*

At the time of WWI some pulverized Al was incorporated in the Novit formulation and this considerably increased its efficiency, especially for underwater applications. A similar expl contg TNT 55.7, HNDPhA 27.9 & Al 16.4%, was used in Ger for torpedoes and mines. The Japanese used compns similar to Novit under the names "Seigata" and "Type 97 Explosive"

Refs: 1) Stettbacher (1933), 294 (listed in the index under Torpedominenfüllmittel) 2) A. Stettbacher, Protar **9** (1943), 38 & 41 3) Bebie (1943), 112 4) Anon, "Allied & Enemy Explosives", Aberdeen Proving Ground, Md (1946), 107

Novo-Astralit (New Astralite). Russ pre-WWI mining expl contg AN 80.8, TNT 16.0, potato meal 3.0 & sawdust 0.2%

Ref: Anon, SS **12**, 428 (1917)

Novo-Nobelits (New Nobelites). Russ pre-WWI coal mining expls contg NG (gelatinized with collodion cotton) 11.5–12, AN 47–50, Na nitrate 4–3, glycerin 3.5–4, potato meal 6, Na chloride 22–20, & talcum 6%

Ref: Anon, SS **12**, 410 (1917)

NOX. Code name for 1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane

Nozzle Theory of Detonation. See Detonation (and Explosion), Nozzle Theory or Expanding Jet Theory of Jones in Vol **4**, D460-R

NPMn 95/5 (Fr). A booster expl mixt of 95/5 PETN/mononitronaphthalene, compressed to a d of 1.6g/cc, was used to determine the vel of deton of ethylenediaminedinitrate (Ref 1). It was called *Mélange NPMn 95/5* by L. Médard (Ref 2) who used it at a d of 1.6g/cc in 30mm cartridges having charge wts of from 10 to 50g. He claimed that it possessed the same initiating efficiency as straight PETN, but was easier to compress and did not break on handling. Médard also recommended its use as a booster expl in lieu of PA or Tetryl (Ref 3)

Refs: 1) A. LeRoux, MP **32**, 123 (1950) 2) L. Médard, MP **33**, 339 (1951) 3) Ibid, MP **34**, 102 (footnote) (1952)

NS (Nitrate of Soda). Brit for Na nitrate

NS (Nitrate of Soda) Gelignites. Brit NG expls of the Gelignite type contg Na nitrate which were cheaper than those contg K nitrate. See under Gelignite in Vol **6**, G57-R to G58-R

Ref: Taylor & Gay (1958), 25

NSDI and NSDII. Span solventless (sin disolvente) double-base propInts intended for use in large cal guns

Ref: Vivas, Feigenspan & Ladreda **3** (1948), 405

NSX. Designation for Nitrostarch Demolition Explosive. See under Nitrostarch in this Vol

NT (Explosif) (Nitrate d'ammoniaque-Tolite). A Fr military expl consisting of AN 70 & TNT 30%. This castable compn corresponds to the US 70/30 Amatol

Refs: 1) Anon, Ordn Sergeant (Aug 1943), 16 2) Anon, "Handbook of Foreign Explosives", **FSTC 381-5042**, US Army Foreign Science and Technology Center (Oct 1965), 130 & 229

NTMX (Explosif) (Nitrate d'ammoniaque-Trinitrometaxylene). A Fr military expl consisting of AN 78 & Trinitroxylene 22%, used as a bursting charge in projectiles

Ref: Anon, "Handbook of Foreign Explosives", **FSTC 381-5042**, US Army Foreign Science and Technology Center (Oct 1965), 131 & 229

NTN. A liq expl consisting of a mixt of Nitromethane 51.7, Tetranitromethane 33.2, and 1-Nitropropane 15.1% by wt. A clear, light yel homogeneous liq between −58° and 100°; d 1.269−0.0014T (T in °C)g/cc. Impact sensitivity (50% height, NOL 2.5kg wt), 31.4cm vs 320cm for TNT. It is insensitive to electric sparks, non-reactive in air, and insol in w. Its sensitivity and stability meet military requirements

Ref: A. vonEgidy et al, "A New Liquid Explosive, NTN", **UCRL-5861**, Lawrence Radiation Laboratory, Univ of Calif, Livermore (1960)

NUCLEAR ACTIVATION ANALYSIS AND DETECTION

Nuclear activation analysis (NAA) is a method for qualitatively and quantitatively detg elemental compn by means of nuclear transmutations. The method involves the irradiation or bombardment of samples with nuclear particles or high-energy electromagnetic radiation for the specific purpose of creating radioactive isotopes from the stable or naturally-occurring elements present. From the numbers, types and quantities of radioactive elements or *radionuclides,* it is possible to deduce information about the elemental compn of the original sample

NAA has been most frequently associated with the nuclear reactor as a tool because of the availability of intense beams of neutrons at thermal energies (0.025ev) from such facilities. Many elements have a reasonably large probability (cross-section) for thermal neutron capture. This can result in a radioactive product from the $A(n, \gamma)A'$ reaction where A is the stable element, n is a thermal neutron, A′ is the radioactive product of one atomic mass unit greater than A, and γ is the prompt gamma ray resulting from the reaction. A′ is usually a beta and/or gamma emitter of reasonably long half-life. Where access to a nuclear reactor has been convenient, *thermal neutron activation analysis* has proven to be an extremely valuable nondestructive analytical tool and in many cases, the only method for performing specific analyses at high sensitivities

NAA based upon fast neutron-induced reactions has also been intensively utilized. This technique is applied to systems which produce radionuclides by the general reaction $A(n, q)B$, where A is again the stable element, n is a fast or high-energy neutron, q is a nuclear particle (not a γ-ray), and B is the radioactive product, usually (but not always) of an atomic mass different from A. Thus, such reactions as (n, p), (n, 2n), (n, α), (n, n′), (n, d) and (n, t) are included in this category. The *thresholds* for these particle-particle reactions, i.e., the energies required to induce the reactions, with few exceptions, are in the 1 MeV and higher regions. The greatest amt of work with fast neutrons has been in the 14 MeV range. This has resulted from the commercial development of small, low cost particle accelerators, called *neutron generators,* utilizing the $t(d, n)\alpha$ reaction. In these devices, deuterium (d) ions are accelerated into metal targets satd with tritium (t) gas. The result is a beam of neutrons with an average energy of 14.7 MeV, and α particles (He ions) as a product. Activation products formed from these high energy neutrons are usually produced in much lower yields and possess much shorter half-lives than those from the (n, γ) thermal neutron reaction. However, using such neutrons in combination with rapid transfer sample systems and *gamma-ray spectrometry,* elemental analysis on a wide range of elements, in particular the lighter ones, can be performed on a routine basis

An additional source of neutrons for NAA, other than reactors or accelerators, are radioactive isotopes, which either in combination with other stable elements or by their own decay, emit neutrons. The advantage and attraction of these encapsulated sources are their small size and wt, and complete absence of operational or maintenance problems. The most widely utilized of such sources is californium-252 (^{252}Cf) which decays by spontaneous fission and emits neutrons in copious amts per unit wt. ^{252}Cf is made by bombarding plutonium-239 (^{239}Pu) in a very high intensity nuclear reactor. Elements of higher atomic number are built up by successive neutron captures. Thirteen successive neutrons must be added to each nucleus of ^{239}Pu to convert it to ^{252}Cf. The important nuclear properties of this new man-made element are:

Effective half-life	2.65 yrs
Average neutron energy	2.35 MeV
Neutron emission rate	2.34×10^{12} neutrons/sec/gram
Decay heat	38.5 watts/gram

Individual sources of ^{252}Cf are currently available in quantities up to 10–50mgs of the element. Such sources, when contained in a suitable hydrogenous moderator, can provide thermal neutron outputs adequate for the activation analysis of many elements in the fraction of a percent wt range

The measurement of the prompt gamma ray following neutron capture in the *(n, γ)* reaction with thermal neutrons is an alternate method of NAA and is extensively used. In this method the gamma-ray intensity is dependent only on the neutron capture cross-section and not upon the half-life of the product nucleus. The gamma-rays to be detected are termed *prompt* in that they are emitted within 10^{-15}sec of the time of neutron capture; thus *prompt NAA* is generally more difficult to perform because the γ-ray detector must also be shielded from the source of neutrons. *Prompt NAA* is particularly useful in process control and measurement applications with flowing or continuous streams of material, or for high volume inspection where nondestructiveness and speed of analysis are important factors

Other types of NAA involve activation with charged particles and with high energy photons (γ-rays). However, as of this writing, these have had no applications to energetic materials and are merely mentioned here

A detailed technical treatment of the general practice and subject matter of NAA is not within the scope of this Encyclopedia. Some excellent comprehensive refs in the field are: R.C. Koch, "Activation Analysis Handbook", Academic Press, NY (1960); Paul Kruger, "Principles of Activation Analysis", J. Wiley, NY (1971); G.J. Lutz et al, Eds, "Activation Analysis: A Bibliography Through 1971", NBS Technical Note **467**, US Dept of Commerce, National Bureau of Standards, Washington, DC 20234 (Aug 1972); S.S. Nargolwalla and E.P. Przybylowicz, "Activation Analysis with Neutron Generators", J. Wiley, NY (1973)

The remainder of this article will be devoted to specific applications of NAA to energetic materials and processes. Areas of interest will include: 1) Elemental Analysis, 2) Determination of Pellet Weight in Primers, 3) Determination of Gunpowder Residues in Forensic Investigations, 4) Detection of Explosives in Buried Mines, 5) Detection of Hidden Explosives in Baggage, and 6) Explosives Safety in Neutron Activation Analysis

1) Elemental Analysis

Total Nitrogen Content

Almost all expls and proplnts, particularly those of organic compn, contain nitrogen, usually in high proportions. Fast neutron activation analysis (FNAA) is used routinely at PicArsn (Ref 13) as a rapid non-destructive method for total nitrogen content of energetic materials, as a measure of purity and for process control applications. The method is based on the $^{14}N(n, 2n)\ ^{13}N$ reaction with the radioassay of the 10min positron annihilation radiation (0.511 MeV) from ^{13}N. The source of fast (14.7 MeV) neutrons is a Kaman Nuclear model A711 sealed tube neutron generator. A physical layout (not to scale) of the laboratory facility is shown in Fig 1:

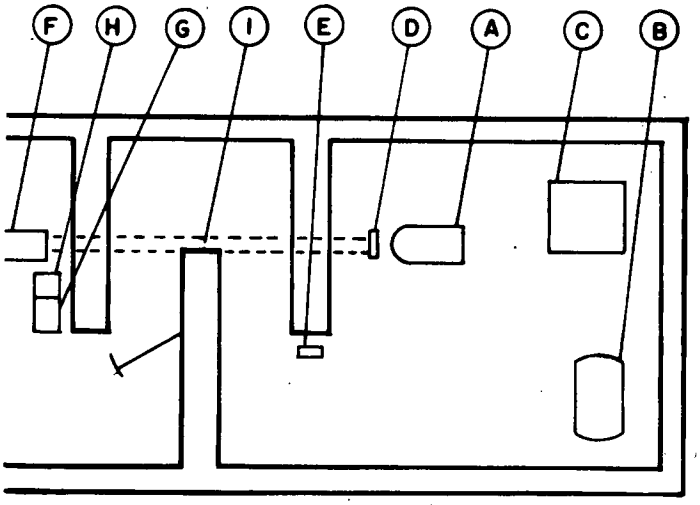


FIG.1 NEUTRON GENERATOR FACILITY

A. SEALED TUBE NEUTRON GENERATOR
B. 200 KV POWER SUPPLY
C. CLOSED-LOOP REFRIGERATION SYSTEM
D. DUAL-AXIS SAMPLE ROTATOR ASSEMBLY
E. PROTON RECOIL NEUTRON FLUX MONITOR
F. SAMPLE LOAD STATION AND DUAL CRYSTAL COUNTING ASSEMBLY
G. CONTROL CONSOLE FOR NEUTRON GENERATOR
H. PROGRAMMED TIMER FOR SAMPLE TRANSFER SYSTEM
I. POLYETHYLENE SAMPLE TRANSFER TUBING

The concrete block walls of the cell housing the generator tube and associated components are 1.7 meters thick. The facility also includes a Kaman Nuclear dual-axis rotator assembly for simultaneous transfer and irradiation of reference and unknown sample, and a dual Na iodide (NaI) scintillation detector system designed for simultaneous counting of activated samples. Automatic transfer of samples between load station to the rotator assembly in front of the target, and back to the count station, is accomplished pneumatically by means of two 1.2cm (i.d.) polyethylene tubes which loop down at both ends of the system and pass underneath the concrete shielding thru a pipe duct. Total one-way traverse distance for the samples is approx 9 meters. In performing quantitative analysis for a particular element by neutron activation, the usual approach is to compare the count rates of an unknown sample with that of a reference standard of known compn irradiated under identical conditions

Based on extensive work on FNAA as applied to gross elemental analysis in the percent range, the conditions for optimum precision and accuracy are as follows: (a) Reference standard and sample to be analyzed should be as similar as possible in compn to minimize interferences from activation of other elements; (b) Reference standard and sample should be as similar as possible with respect to wt, volume and density to minimize geometry counting errors and to eliminate the need for gamma and neutron self-shielding corrections; (c) Simultaneous irradiation of both reference and sample to eliminate neutron flux correction; and (d) Dual-axis rotation of reference and sample during irradiation to insure a uniform neutron dose to both

Using the above conditions, some representative results are given in Table 1 for total nitrogen content assay of "pure" homogeneous high energy compds by FNAA

Included are four samples of NC of different degrees of nitration and one sample each of the high expls TNT (2,4,6-trinitrotoluene) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane). The NC samples were supplied from plant production lots and the listed nitrogen contents under 'Chemical Analysis' were determined by a nitrometer technique; these values are usually precise to within a few hundredths of 1%. The

Table 1

Total Nitrogen Content in "Pure" Explosives by High Precision FNAA

Sample	% Nitrogen Chemical Analysis	% Nitrogen FNAA[b]
Nitrocellulose	12.60	12.57 ± 0.05
Nitrocellulose	12.18	12.12 ± 0.10
Nitrocellulose	13.11	13.03 ± 0.07
Nitrocellulose	13.23	13.23 ± 0.06
TNT	18.50[a]	18.50 ± 0.06
HMX	37.84[a]	37.78 ± 0.06

[a]theoretical value for pure compound

[b]values listed are the mean of at least four determinations ± 1σ (std. dev. from the mean)

TNT and HMX were from highly purified laboratory samples and the nitrogen contents listed are calcd values for the pure compds. Precision and accuracy as indicated by the FNAA data for these compds are excellent and most likely represent the optimum that can be achieved by this technique

For the analyses given in Table 1, samples were contained in special polyethylene vials specifically designed to fit the Kaman Nuclear dual-axis rotator assembly. These vials are 4.5cm long and 1.0cm o.d. with an internal volume of 2.3cu cm. When filled, a vial contains approx 0.5g of NC and 2.3g of TNT or HMX. A 12.60% NC was used as the reference standard for all samples of this material; TNT and HMX were compared against "pure" samples of each other, respectively

NC samples were irradiated for 3 min and TNT and HMX for 1 min at a 14 MeV neutron flux of approx 10^8n/cm^{2}sec. Simultaneous counting was performed by means of a matched dual 7.6x7.6cm flat NaI crystal detector assembly in conjunction with a Kaman Nuclear programmed timer system for automatic sample transfer. A one-min count time was usually sufficient to exceed 10^4counts. The signal from each de-

tector was fed to an individual single-channel pulse height analyzer and only the 0.511 MeV photopeak was counted using a 20% window

Neutron activation is also used routinely for the assay of binary mixts contg two compds of different nitrogen content. This method has been applied extensively to Octol compns which contain varying proportions of TNT and HMX. The mixture is normally manufd by dispersing finely-divided crystalline HMX in hot molten TNT and cast loading the melt into ammo items. The finished product is designed to contain a specific HMX content in the 60–80% by wt range. Because HMX is not soluble in the molten TNT, nonuniformity of compn can result and hence the need for quality control by chem analysis

The conventional assay technique is an extraction procedure whereby a 5g sample of Octol is treated with hot benz to remove the TNT and the insoluble HMX is determined gravimetrically. Analysis time per sample is approx 3 hrs and each sample is assayed in duplicate. For this particular product, in addition to a decrease in analysis time, a non-destructive method is especially desirable because of other physical tests that are also required on each sample

By FNAA, the total nitrogen content of a sample is first detd and then related to compn of the mixture. Since Octols contain no ingredients other than "pure" TNT (18.50% N) and "pure" HMX (37.84%), the following linear relationship is derived from the calcd nitrogen content of each ingredient:

$$\%HMX = 5.171 \cdot N - 95.66$$

where N is the nitrogen content of the mixt in % by wt

For Octol containing 60–80% HMX, a 0.2% change in nitrogen content is equivalent to approx a 1% change in HMX content. Determination of HMX content, by a non-destructive method, to an accuracy of ± 1% or better, is considered adequate for plant-grade material. At PicArsn (Ref 13), various FNAA techniques were examined with regard to accuracy and precision for the assay of Octol samples. These included: (a) Dual-axis rotation of sample and standard during irradiation followed by sequential counting, ie, counting sample and standard in succession and correcting for decay; (b) Dual-axis rotation of sample and standard with simultaneous counting of both; and (c) Single-axis rotation of standard and one or more unknown samples with sequential counting

For single-axis rotation, a special lucite wheel is used designed to hold up to 12 small polyethylene vials contg expl. The wheel is manually mounted in front of the accelerator target before irradiation, and manually removed after irradiation for counting the samples

In Table 2, results are given comparing the three above FNAA techniques for total nitrogen and corresponding HMX content of three synthetic Octol samples containing 70, 60 and 80% HMX respectively. Chemical analysis by extraction is also included as another basis for comparison. An 80/20 Octol (80% HMX) was used as the reference standard for the activation assays

Table 2

Comparison of various FNAA techniques for assay of synthetic Octol samples

Sample	Calculated	Nitrogen,[a] %			Chemical analysis HMX,[b] %	
		Dual-axis rotation, sequential counting	Dual-axis rotation, simultaneous counting	Single-axis rotation, sequential counting		
70/30	32.03	32.16 ± 0.09 (70.65 ± 0.47)	32.07 ± 0.16 (70.18 ± 0.82)	32.35 ± 0.14 (71.58 ± 0.70)	70.59 70.70	(70.65)
60/40	30.11	30.19 ± 0.09 (60.42 ± 0.49)	30.19 ± 0.11 (60.42 ± 0.60)	30.27 ± 0.17 (60.88 ± 0.87)	59.13 60.63	(59.88)
80/20	33.98	34.03 ± 0.13 (80.28 ± 0.70)	33.94 ± 0.14 (79.82 ± 0.75)	34.22 ± 0.16 (81.27 ± 0.85)	79.99 80.68	(80.33)

[a] Mean of six determinations of each sample ± 1σ(standard deviation from the mean); Value in parenthesis is corresponding %HMX ± 1σ

[b] Two determinations on each sample, mean given in parenthesis

Analysis by dual-axis rotation yields the best results; agreement with calcd values for total nitrogen is 0.1% or less in all cases. The corresponding average absolute errors in HMX content for the three samples are 0.45 and 0.26%, respectively, for sequential and simultaneous counting as compared to 0.31% for chem analysis. Differences between the two modes of counting for dual-axis rotation are not considered significant and the choice of counting arrangement is arbitrary for ^{13}N radioassay in these samples

Predictably, analysis by single-axis rotation is not comparable in accuracy to dual-axis rotation. The mean absolute error was 0.24 and 1.24% for the total nitrogen and HMX content, respectively. Dual-axis rotation by means of the Kaman assembly, however, despite its undeniably greater accuracy and precision, is limited to only one sample and reference standard per irradiation. It is the preferred method where speed is not essential – but when the number of samples to be analyzed is large, multiple sample irradiation on the lucite wheel with single-axis rotation is used. The precision of this latter technique for six plant samples of Octol is shown in Table 2a. In this series each irradiation consisted of six Octol samples, an 80/20 Octol reference standard and a blank vial mounted on the lucite wheel. The FNAA results are again compared with chem analysis for HMX content. The mean 1σ precision for 10 determinations on each of the six samples is ± 1.30% HMX and the average difference between FNAA and chem analysis is 1.05% HMX:

Table 2a

Precision of single-axis rotation FNAA for assay of Octol Plant samples

Sample	FNAA[a]		Chemical analysis[b]
	N, %	HMX, %	HMX, %
1	30.11 ± 0.29	60.02 ± 1.42	59.04, 59.07 (59.06)
2	30.60 ± 0.22	62.56 ± 1.15	60.36, 60.35 (60.36)
3	31.94 ± 0.33	70.02 ± 0.94	70.25, 70.29 (70.27)
4	31.97 ± 0.44	70.16 ± 1.87	70.06, 70.14 (70.10)
5	32.23 ± 0.25	71.00 ± 1.27	69.24, 69.81 (69.88)
6	32.29 ± 0.22	71.28 ± 1.14	69.40, 69.79 (69.60)

[a] Mean of 10 determinations on each sample ±1σ(standard deviation from the mean)
[b] Two determinations on each sample, mean given in parenthesis

In the most recent work at PicArsn on total nitrogen content assay by FNAA, a special triple-axis rotator assembly was designed and fabricated to achieve both high precision and the capability for simultaneous irradiation of multi-samples (Ref 22). The overall diameter is 15cm and the device contains eight sample cavities designed for snap-cap polyethylene vials, 2.3cm long by 0.9cm o.d. The entire rotator is made of Delrin thermoplastic and polyethylene. Seven samples and a standard are rotated around the target of the neutron generator, their own axes, as well as traversing the neutron beam (Fig 2).

The samples rotate around the target at 100rpm by means of an external motor and pulley assembly, and traverse the neutron beam from 1 to 11cm from the target

Nitrogen analyses with this special rotator assembly are given in Table 3 for apparently "pure" samples of Ammonium Nitrate (AN), TNT and a 70/30 Octol (HMX/TNT) compn.

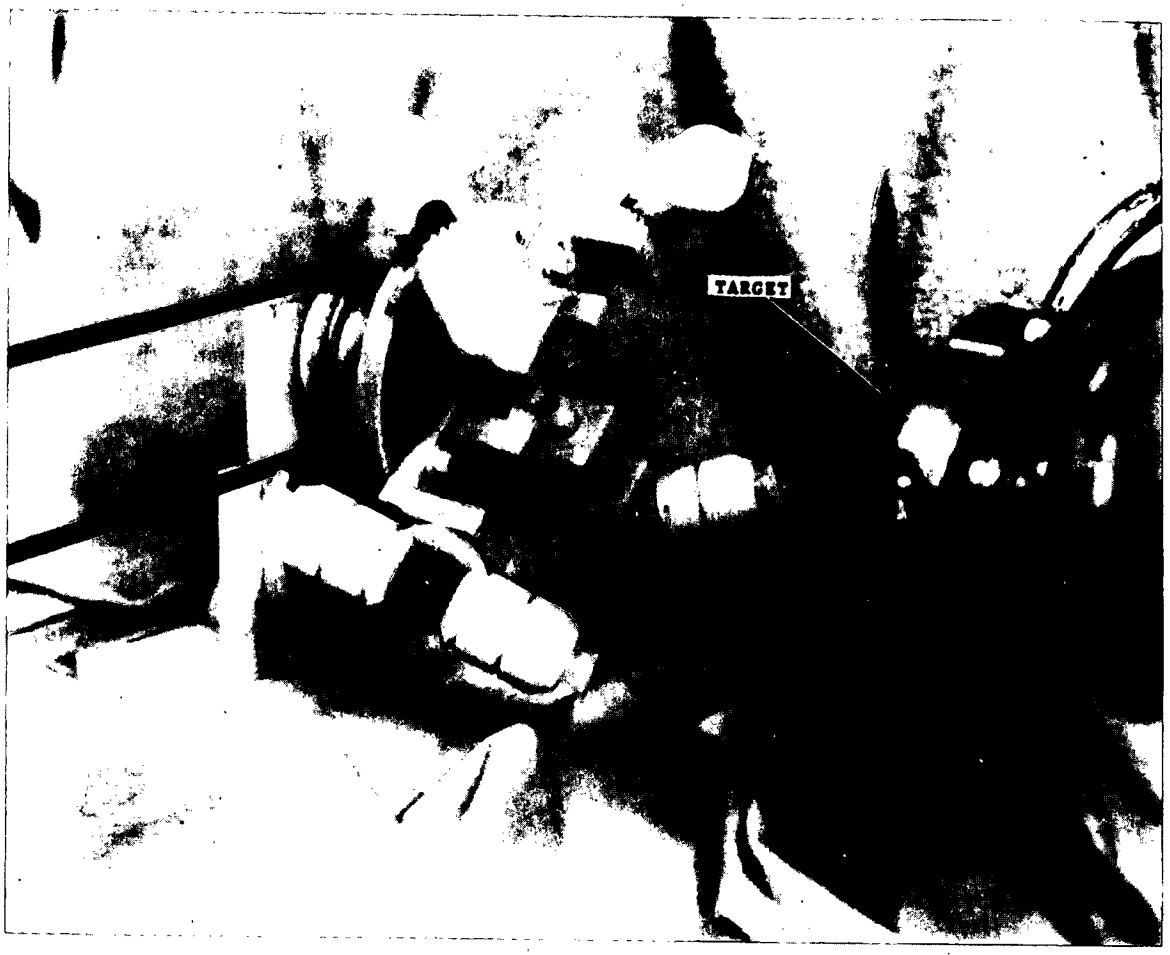


Fig 2. Triple-Axis Rotator for Fast Neutron Activation of Explosives

Table 3

Fast Neutron Activation Analysis for Nitrogen in Explosives by Triple-Axis Rotation

Sample	%N Calculated	%N, determined at different positions[a]			
		1	2	3	4
Ammonium Nitrate	34.98	34.95 ± 0.09	34.95 ± 0.09	34.97 ± 0.09	34.97 ± 0.08
TNT	18.50	18.56 ± 0.07	18.51 ± 0.07	18.50 ± 0.06	18.52 ± 0.05
Octol 70/30	32.03	32.04 ± 0.09	32.04 ± 0.05	32.00 ± 0.11	32.04 ± 0.10

[a] Mean of six determinations at each position $\pm 1\sigma$

To establish the equivalence of all eight sample positions with regard to neutron dose, a sample of each material was irradiated simultaneously at four different alternative positions along with a ref standard of the same compn. Each of the three expls was assayed six times at each designated position; the mean and standard deviation is given for each set of six determinations

The results in Table 3 demonstrate that the triple-axis multi-sample rotator will give a precision equal to that of a two-sample dual-axis rotator (as presented in Table 1) with the advantage that seven samples and a ref standard can be irradiated simultaneously and counted sequentially. This system is useful when many research or production samples of organic expls need be analyzed for purity. The 10 min half-life of ^{13}N is sufficiently long for all eight sample vials to be manually transferred from the irradiation room to the nuclear counting system and sequentially radioassayed at one-min count times

Aluminum and Chlorine in Composite Propellants

At the White Sands Missile Range, NAA has been developed as a non-destructive method for determination of Al and/or chlorine in solid composite proplnts for quality control purposes (Ref 21). The compn of the proplnts of interest contain approx 70% Ammonium Perchlorate (AP), 15% Al, 15% binder, and other minor additives. X-ray fluorescence methods had previously been developed for this assay but these were sensitive to matrix effects and particle size

For the analysis of aluminum, the $^{27}Al(n,p)^{27}Mg$ reaction with 141 MeV neutrons, and for chlorine, the $^{37}Cl(n,\gamma)^{38}Cl$ reaction with thermal neutrons, gave the best results. It was found possible to produce a useful mixt of 14 MeV and thermal neutrons, so that both Al and Cl could be determined simultaneously from a single irradiation. This was accomplished using a Texas-Nuclear Model 9505 150-kv neutron generator which had a max output of approx 10^{11} neutrons/sec, and which gave a 14 MeV flux as high as 10^9 neutrons/cm^2-sec at 3cm from the target. For this work, samples were irradiated inside a 30cm cubic polyethylene box, with a 15cm cubic cavity and 7.5cm wall thickness. The samples were about 10cm from the target and were subjected to fluxes of approx 10^8 neutrons/cm^2-sec for 14 MeV neutrons, and 10^7 neutrons/cm^2-sec for thermal neutrons. The polyethylene box served to moderate a portion of the fast neutrons down to slow or thermal levels

Al was determined by counting the ^{27}Mg activation product, with a half-life of 9.5 min, and its two emitted γ-rays of 0.842 and 1.013 MeV energies. Cl was assayed by counting ^{38}Cl, 37.3 min half-life, and γ-rays of 1.60 and 2.17 MeV. Specific conditions and a discussion of interfering reactions can be found in the original ref. Determination of each element by this NAA method was judged to be sufficiently accurate for quality control purposes with a precision of better than ± 1%

Phosphorus in Composite Propellants

Rison et al (Ref 4) of the Naval Ordnance Station at Indian Head, Md have described a rapid sensitive method to determine small amts of P in a composite proplnt using FNAA. In this case, the proplnt consisted of 60% AP, 20% Al and 20% binder. The small amts of P to be determined were known to be in the binder phase and existed at concns in the proplnt in the order of 0.05% by wt

A Kaman Nuclear, Model 1001, 200-kv Neutron Generator was the source of fast neutrons. The $^{31}P(n,\alpha)^{28}Al$ reaction gave the best sensitivity for P with a product half-life of 2.3 min and a γ-photopeak of 1.78 MeV. The only serious interference is from the Al in the matrix which yields the same activation product from the reaction $^{27}Al(n,\gamma)^{28}Al$. This interference can be eliminated in two ways, (a) by chem separation of the P from the Al by extracting the proplnt with pentane, and (b) thru spectrum stripping by first subtracting the counts due to Al using a different nuclear reaction $^{27}Al(n,p)^{27}Mg$. In this latter case, ^{27}Mg has a half-life of 9.5 min with a main γ-energy peak of 0.84 MeV. For a given neutron flux, the ratio of $^{27}Mg/^{28}Al$ is constant. When the amt of Al present has been determined by counting ^{27}Mg, the amt of ^{28}Al can be calcd by dividing the ^{27}Mg activity by the ratio $^{27}Mg/^{28}Al$

Usually, 1g of proplnt is irradiated for 0.5 to 2 min depending on the flux level. Decay time is 45 sec. Counting time is 5 min for ^{28}Al under the 1.78 MeV peak. Because of its higher initial activity, ^{27}Mg (from Al activation) is counted 20–40 min after irradiation. The authors estimate an overall relative error of 5% for the

determination of P after chem separation, and a relative error of 15% after spectrum stripping

Sodium and Potassium in Solid Propellants

U.S. Navy researchers (Ref 11), using the water-pool nuclear reactor of the Naval Research Laboratory, developed a technique employing NAA and γ-ray spectrometry to determine trace amts of Na and K in solid rocket proplnts. It is believed that traces of alkali metals such as Na and K, when contained in such proplnts, cause the concn of free electrons in rocket motor exhaust plumes to increase considerably. The high concn of free electrons, in turn, results in attenuation and modulation of guidance and telemetry signals. Therefore, an accurate and precise technique is required to control the concn of Na and K during rocket proplnt manuf. NAA was selected because of its excellent sensitivity, precision, reasonable accuracy and non-destructiveness. The particular solid proplnt matrix studied in this work was composed of ingredients containing the elements H, O, N, Cl and Al

This NAA technique is based on the nuclear reactions $^{23}Na(n,\gamma)^{24}Na$ and $^{41}K(n,\gamma)^{42}K$. Half-lives of the activated products are 15.0 hrs and 12.4 hrs, respectively. For Na analysis, the samples were irradiated in a specially designed thermal column to suppress the fast neutron reaction of $^{27}Al(n,\alpha)^{24}Na$ which interferes with the reaction for Na. For K analysis, the proplnt samples were irradiated at a standard irradiation position of the reactor. For the Na irradiations, the neutron flux in the thermal column was in the order of 10^{10}, whereas for the K assays it was approx 10^{12} neutrons/cm^2-sec

A typical procedure for Na assay is: One gram proplnt samples sealed in polyethylene vials are irradiated for at least seven hrs in the thermal column. In order to minimize any thermal neutron flux gradient, the samples are rotated uniaxially at 60 rpm. Following irradiation, the samples are allowed to decay for approx 15 hrs to permit all short-lived radioisotopes to decay to insignificance. The 1.369 MeV γ-photopeak of each sample is then counted for 10 min with a 7.6cm x 7.6cm Na iodide scintillation detector coupled to a 400-channel pulse-height analyzer

For K assays, one gram samples are irradiated in one of the standard irradiation positions for four to five hrs and rotated uniaxially at 20 rpm. Following a decay period of at least 15 hrs, the 1.524 MeV γ-photopeak of ^{42}K is counted for 40 min with a Ge-Li solid state detector and a 4096-channel analyzer. This more sophisticated counting system is necessary to obtain the required resolution, since with a Na iodide detector, the 1.524 MeV peak of ^{42}K overlaps with the 1.369 MeV γ-peak of the ^{24}Na decay spectrum

The actual amt of Na and K in solid proplnt samples is calcd by comparing the sample activity with the activity of a ref sample with known concns of Na and K. In this case, the ref standards consisted of water samples doped with known amts of Na and K, with all other conditions being the same as for the proplnt samples

With the above NAA techniques, composite solid rocket proplnts containing approx 20% Al were analyzed for Na and K at levels as low as 1 ppm at a 95% confidence level (2σ) of approx ± 12% for Na and ± 20% for K

Aluminum, Chlorine and Manganese in Energetic Materials

At PicArsn, both thermal and fast NAA were compared for non-destructive gross element assay in selected materials used in ammo (Ref 14), specifically Al in aluminized high expls (eg, Minols), Cl in AP and Mn in manganese dioxide (as used in pyrotechnic flare compns). The nuclear data and reactions for the elements investigated are listed in Table 4:

Table 4
Nuclear Data for Elements Analyzed by Neutron Activation

	Neutron Energy	Reaction	Cross Section mb	Half-life	E, MeV
Al	Thermal	$^{27}Al(n,\gamma)^{28}Al$	215	2.3 min	1.78
	Fast	$^{27}Al(n,p)^{27}Mg$	80	9.5 min	0.84, 1.02
Cl	Thermal	$^{37}Cl(n,\gamma)^{38}Cl$	560	37 min	1.60, 2.17
	Fast	$^{37}Cl(n,p)^{37}S$	30	5.1 min	3.09
Mn	Thermal	$^{55}Mn(n,\gamma)^{56}Mn$	13,000	2.6 hr	0.85, 1.81, 2.11
	Fast	$^{55}Mn(n,\alpha)^{52}V$	50	3.8 min	1.43

For the thermal neutron activations, a 10mg Californium-252 (^{252}Cf) source was utilized in a special assembly constructed from a "Neutron Howitzer" (Trademark of Reactor Experiments, Inc). The assembly is a 6-cu ft cylindrical Lucite tank filled with distilled water and containing three access ports (Fig 3). The large spherical container on the right is the shielded storage cask for the ^{252}Cf neutron source when not in use

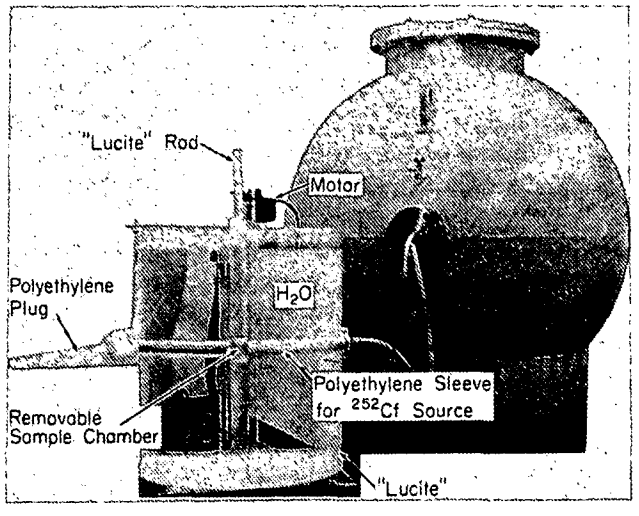


Fig 3 - Picatinny Arsenal Thermal Neutron Activation Analysis Facility

Polyethylene vials containing samples up to 10g are placed in a removable hollow polyethylene sample chamber, which is attached to the end of a solid Lucite rod. The rod is inserted into the vertical port of the tank (moderator), and is rotated by a motor mounted on top to provide a uniform neutron dose on the sample(s). The ^{252}Cf source is remotely inserted into the moderator thru one of the horizontal ports which contains a polyethylene sleeve as a guide. With this arrangement, the ^{252}Cf source and sample are 2.5cm apart, and the measured thermal neutron flux on the sample is approx 1 x 10^8 neutrons/cm^2-sec. The other horizontal port is available for other activation or beam expts

For fast neutron activations, the samples were irradiated with a Kaman nuclear neutron generator (Model A711) under conditions similar to those described in this article under the section on total nitrogen content analysis. The samples were rotated on dual-axes during irradiation

For both methods, the counting rate of an unknown was compared with that of a simultaneously irradiated known sample to eliminate correcting for neutron and gamma self-shielding. A 7.6cm x 7.6cm Na iodide scintillation well detector was used for integral counting of all gamma rays from each sample; a low-energy threshold was selected just below the photopeak of the lowest energy gamma ray. Accuracy and precision of analysis for each element (Table 5) are about equal for both types of activation, and the results, in general, are comparable to what can be expected from wet chem or other destructive instrumental assay methods. For the expts summarized in Table 5, Al and Mn were analyzed in Al_2O_3 and $MnSO_4$, respectively, as inert simulants for expls containing these elements:

Table 5
Accuracy, Precision and Conditions for Thermal and Fast NAA for Al, Cl and Mn

Element	Matrix[a]	% Element: Calculated	% Element: Measured[b] Thermal[c]	% Element: Measured[b] Fast[d]
Al	Al_2O_3	52.91	52.10 ±0.33[e]	52.58 ±0.30[f]
Cl	NH_4ClO_4	30.17	30.33 ±0.13[g]	30.12 ±0.30[h]
Mn	$MnSO_4$	32.51	32.65 ±0.37[i]	32.70 ±0.41[j]

[a] ~1.5 g of sample of each material
[b] Mean of 15 or more replicate runs ±1 σ; 1-min count
[c] ~10-mg ^{252}Cf source; ~1 x 10^8 n/(cm^2-sec)
[d] D,T generator; ~1 x 10^8 n/(cm^2-sec)
[e] 5-min irradiation, 1-min decay
[f] 10-min irradiation, 5-min decay
[g] 30-min irradiation, 5 min decay
[h] 20-min irradiation, 5-min decay
[i] 1-min irradiation, 1-min decay
[j] 3-min irradiation, 1-min decay

Titanium in Gun Powder Residues

The reduction of gun erosion by the use of additives to the gun powder has been studied at the US Naval Ordnance Station (NOS), Indian Head, Md. During the investigation of one of the additives, namely titanium dioxide (TiO_2) or *Swedish additive*, it was necessary to determine small amts of Ti in gun powder residues taken from the gun after firing. As only very small amts of Ti were expected in the samples, the very sensitive technique of NAA was used for the analysis (Ref 2)

Thermal neutron activation was selected for the radioassay via the $^{50}Ti(n,\gamma)^{51}Ti$ reaction. Since the half-life of ^{51}Ti was 5.8 min, non-destructive NAA by gamma-ray spectrometry was used in lieu of chem sepn of Ti

Gunpowder residues containing Ti were obtained after a gun firing by wiping the barrel with small pieces of wet cotton cloth. These pieces of cloth, containing the powder residue, were then irradiated together with clean pieces of the same size serving as blanks, and with a standard sample of TiO_2. Irradiations were performed in the Naval Research Laboratory reactor. The samples were packed in polyethylene bags, placed into polyethylene transfer "rabbits", and irradiated in the pneumatic transfer system of the reactor. In this way they could be transferred after irradiation to the counting location in about 1 to 2 min

^{51}Ti was identified and counted by measuring the 0.32 MeV gamma-rays with a 4.45 x 5.08cm Na iodide detector and a single-channel analyzer. Counting started usually 2 min after the end of an irradiation, and was carried out for about 60 min (about 10 half-lives), after which all the ^{51}Ti activity had disappeared. The amt of Ti in the cloth samples was obtained by comparing the activities with that of the standard sample

From the amts of TiO_2 added to the powder charge, from the length of the gun barrel, and from the width of cotton cloth pieces, it was calcd that approx 400mg TiO_2 should be found on the cloth pieces after a gun firing, assuming even distribution of TiO_2 in the barrel. The sensitivity for TiO_2 detection by the NAA method was calcd as 0.3mg. Within this limit, based on the NAA results obtained, no TiO_2 was detected in the gun barrel. The NOS workers concluded, therefore, that the material is "cleaned out" after each gun firing, ie, there is no TiO_2 in the residue

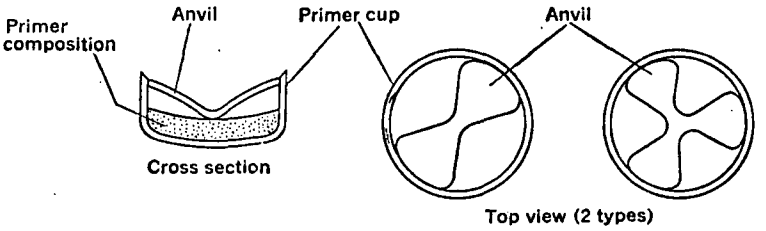
2) Determination of Pellet Weight in Primers

Malfunctions of small arms ammo using the M34 primer have been related to inadequate control of pellet wt in the primer, with low pellet weight causing hangfires in the weapon. At the Army Mechanics and Materials Research Center (AMMRC), Watertown, Mass, NAA was investigated for 100% inspection of pellet wt in such primers (Refs 5 & 6)

Fig 4 is a sketch showing the components of typical primer caps for small arms cartridges. Wt specifications, in grains for the components of the M34 primer, with the various ranges and tolerances allowed in its manuf are as follows:

Entire unit	5.430–0.520
Cup (Copper)	3.5 ± 0.15
Anvil (Copper)	1.07 ± 0.07
Disk (paper)	Negligible
Pellet Weight (individual)	0.600–0.120
Pellet Weight (av of 5)	0.580–0.80

Fig 4 Components of Primer Cap for Small Arms Cartridges



Specifications for the primer pellet compn (FA-956) used in M34 primers are: Pb Styphnate 37 ± 5%, Tetracene 4 ± 1%, Ba nitrate 32 ± 5%, Sb sulfide 15 ± 2%, Al pdr 7 ± 1%, PETN 5 ± 1%, and light gum soln as a binder (concn unspecified)

Two NAA methods were developed by AMMRC for non-destructive determination of pellet wt, both utilizing 14 MeV neutrons. In one method, total oxygen in the primer is determined via the $^{16}O(n,p)^{16}N$ reaction. Oxygen is present in the average pellet mix in a concn of 26.53% from the compds Ba nitrate, Pb Styphnate, Tetracene and PETN. Activation with fast neutrons yields ^{16}N with a half-life of 7.2 sec and a 6.1 MeV gamma ray; ^{16}N decomps back to the original ^{16}O. Total oxygen in a pellet was determined by irradiating a primer and a lucite standard under identical conditions (Ref 6), and counting both reference and sample simultaneously with two 12.7cm x 12.7cm NaI detectors. The gamma radiation from ^{16}N was counted in an energy window from 4.85–8.0 MeV. From the measured oxygen content, pellet wt of a primer is calcd from the assumption that 0.159 grains of O are equivalent to 0.600 grains of primer pellet (based on the average oxygen concn of 26.53% in the pellet mix)

The other method for quality assurance inspection of pellet wt in the primer eliminates the need for a comparator oxygen-containing standard. Here, the Cu in the cup-anvil combination in the primer is used as an internal standard by comparing the 0.511 MeV positron annihilation radiation from ^{62}Cu produced by the $^{63}Cu(n,2n)^{62}Cu$ reaction to the 6.1 MeV γ from ^{16}N produced by oxygen activation. In this case the actual determination of pellet wt is not required; the ratio of Cu to O, which should be fixed for a properly loaded primer, after necessary corrections, is a measure of the pellet wt, and rejection or acceptance can be based on the ratio

To determine the Cu/O ratio, the outputs from the two linear amplifiers (one for each 12.7cm x 12.7cm NaI detector) were combined in a sum invert amplifier, the output of which was split and connected to two separate single-channel analyzers. The energy window of one analyzer was set from 0.45–0.60 MeV to count the ^{62}Cu, and the other was set from 4.85–8.0 MeV to count the ^{16}N. The primer was irradiated, transferred, and dropped in place between the two detectors for simultaneous counting of each energy band. The output of each single-channel analyzer was fed to an individual timer-scaler combination. The calcns for this method are somewhat more complex than for the case where a standard comparator of the same isotope is used. In the energy range set on the analyzer for Cu, there is a real contribution due to Compton (scattered) radiation from the oxygen. This is a function of the oxygen concn and must be determined by analyzing a sample containing oxygen as the only element activated by 14 MeV neutrons,

eg, a CHO compd, to obtain the ratio of the O count in the 4.85–8.0 MeV window to the Compton count due to O in the 0.45–0.6 MeV window. Also, since the ^{62}Cu and ^{16}N have markedly different half-lives, 9.8 min and 7.2 sec respectively, it is necessary to correct the counts in each window back to N_0, which can be the counts either at the time when irradiation stops or when counting starts

Table 6 shows results obtained on some special primers prepared at Frankford Arsenal containing various pellet wts as specified in the last column. The Cu/O ratios with and without Compton corrections are shown:

reflects the variation in cup and anvil wt as well as pellet wt. In the case of the lowest pellet wts, the ratios do not check as well as with primers having larger pellet wts, partly because of poorer statistics and partly because the effect of variations in cup and anvil wt will be a greater proportion of the total ratio

In both the standard oxygen analytical procedure and the Cu/O ratio method, the primer was counted for 20 sec following a 25 sec irradiation and a 4.5 sec transfer from completion of irradiation to start of count

Table 7 shows some typical results for production primers from East Acton, Illinois,

Table 6

Determination of Pellet Weight and of the Copper/Oxygen Ratio for Special Primers* (from Ref 6)

14 MeV Neutron Activation Analysis (Weight in Grains)

Primer Designation	Oxygen	Pellet Weight Based on Corr. O Weight**	Ratio		Specified Weight*
			Cu-Comp 0 / O	Cu / O	
B-1	0.084	0.260	5.9574	7.4493	0.26
B-2	.069	.204	5.8339	7.3259	.26
B-4	.085	.264	4.7959	6.2878	.26
C-1	.119	.394	4.6093	6.1012	.39
C-2	.115	.378	4.8203	6.3122	.39
C-3	.112	.366	4.5599	6.0518	.39
D-1	.170	.585	2.5408	4.0327	.54
D-2	.157	.535	2.8207	4.3126	.54
D-3	.159	.545	2.9183	4.4102	.54

*Original Special Primers supplied by Frankford Arsenal
**Correction made for oxygen in primer cup, anvil, and paper

The pellet wt as determined by analysis for oxygen has been corrected for oxygen in the cup, anvil, and paper. Because the correction is indeterminable for individual primers, the oxygen correction of 0.015 grain is based on the mean wt values for cup, anvil, and paper, and is the same in all cases despite the fact that there may be a variation in individual cases. The expected trends are observed, namely, the lighter the pellet, the higher the Cu/O ratio. Doubling the pellet wt does not quite halve the Compton corrected ratio. The agreement between primers based on ratios is not as good as the agreement based on oxygen analysis as expected, because the ratio

labelled WCC. The same information is reported as that in Table 6, with the addition of percentage deviations and the inclusion of primer unit wt. All the pellets fall within specification. The Cu/O ratios, both Compton corrected and uncorrected, essentially match the results of direct analysis, but there are discrepancies probably caused by the uncontrolled variances in other components of the primer such as the cup and anvil. In no case, however, is there a discrepancy in the ratios large enough to indicate pellet wt below specification, and so none of the primers tested in this group would be rejected on the basis of low pellet wt either by the Cu/O ratios

or by direct O analysis. The primer unit wts (column 8) are quite uniform indicating relatively good overall quality control:

Table 7

Determination of Pellet Weight and Copper/Oxygen Ratios for Production Primers (from Ref 6)

14 MeV Neutron Activation Analysis (Weight in Grains)

Primer Designation	Oxygen	Pellet Weight			Ratio		Primer Unit Weight		
		Based on Corr. O Weight*	% Dev. from Spec (0.600)**	% Dev. from Mean	$\frac{\text{Cu-Comp 0}}{\text{O}}$	$\frac{\text{Cu}}{\text{O}}$	Grains	% Dev. from Spec (5.430)**	% Dev. from Mean
WCC-1	0.168	0.576	− 4.00	+ 1.59	3.178	4.699	5.171	4.76	0.04
2	.169	.581	− 3.17	+ 2.47	3.161	4.653	5.126	5.60	0.83
3	.172	.594	− 1.00	+ 4.76	2.812	4.304	5.107	5.89	1.19
4	.173	.596	− 0.67	+ 5.11	2.642	4.133	5.163	4.92	0.12
5	.155	.530	−11.67	− 6.53	2.920	4.411	5.209	4.07	0.77
6	.160	.547	− 8.83	− 3.53	2.818	4.310	5.212	4.01	0.83
8	.170	.584	− 2.67	+ 3.00	2.599	4.091	5.136	5.41	0.64
9	.165	.565	− 5.83	− 0.35	2.679	4.171	5.226	3.76	1.10
10	.171	.588	− 2.00	+ 3.70	2.545	4.037	5.118	5.75	0.99
11	.151	.513	−14.50	−9.52	2.954	4.446	5.167	4.84	0.03
12	.164	.563	− 6.17	− 0.71	2.727	4.219	5.185	4.51	0.31
13	.165	.567	− 5.50	− 0.00	2.669	4.161	5.204	4.16	0.68

*Correction made for oxygen in cup, anvil and paper
**M34 specifications

This feasibility study shows that determination of pellet wt by fast neutron oxygen activation analysis can be used for quality assurance inspection of M34 primers. Either direct oxygen analysis, where a comparison standard (such as lucite) is used, or a ratio method, utilizing the Cu in the cup-anvil combination as an internal standard, can be applied. In general, the uniformity of production primers is quite satisfactory, as is usually the case where production procedures are standardized. It seems likely that the light pellet is one which has been improperly manufd and will probably be well below specifications in pellet wt. Production experience with such primers indicates that only one in $3x10^5$ primers is expected to show low pellet wt; therefore, one would not expect to find a reject in a small sampling. Nevertheless, detection and rejection of this one bad unit is critical for the prevention of weapon malfunctions and possible injuries to personnel

As of this writing, 100% inspection by NAA of small arms primers in an actual production loading plant has not been implemented, nor is it contemplated in the near future. Technical problems exist related to coupling the present state-of-the-art nuclear components with the high production rates for the primers, namely, tens of units per sec per automatic loading line. The high intensity of the neutron source and the complexity of the detection system required detracts from the utility of the method in a plant environment where simplicity and safety of operation are of paramount importance. Nevertheless, the technical feasibility of the method has been demonstrated by the AMMRC study and future developments in nuclear activation hardware may ultimately make this non-destructive inspection for production primers more viable

3) Determination of Gunpowder Residues in Forensic Investigations

In the field of forensic technology, there has long been a considerable need for detecting gunshot residues on the hands of an individual suspected of having fired a gun in a criminal act. The older technique for this purpose (Ref 8), variously referred to as the *paraffin test,* the *paraffin-glove test,* the *dermal nitrate test,* and the *diphenylamine test,* had been abundantly shown to be unreliable, was no longer accepted in most US courts, and was now seldom used by good crime investigation laboratories

This older method involved: (a) coating most of the back of the hand of a suspect in a shooting case (or of the victim in a questionable gunshot-suicide case) with molten paraffin, (b) reinforcing the paraffin "cast" or "glove" with a few layers of gauze as the cast is made thicker, (c) peeling off the cast after it has solidified, (d) pouring some diphenylamine-sulfuric acid soln on the concave inside surface of the cast (that had been in contact with the skin), and (e) examining for blue specks imbedded in the paraffin. Thus, the *dermal nitrate* test is a color test for unburned or partially burned gunpowder, ie, nitrocompds, which form a blue product with the acidic diphenylamine reagent

In practice, it happens that the *dermal nitrate* test is not highly sensitive in that it does not develop a detectable blue color with very tiny particles of gunpowder. Also, it can apparently be interfered with in some cases by other material that may be present on a subject's hand or in his perspiration, and the same color reaction can also be produced by various other nitrogen-containing compds, eg. fertilizers and urine

In 1959, H.C. Harrison and R. Gilroy of the University of Rhode Island (Ref 1) reported on an improved gunshot residue detection method which also employed qualitative color reactions, but not with any gunpowder present on the back of the firing hand of a suspect. Instead, the method entailed detection of traces of particular elements that originated as constituents of the cartridge primer, viz, Ba, Sb, and Pb. Unfortunately, when various forensic laboratories attempted to use the Harrison and Gilroy method, they obtained very poor results. The chief problem appeared to be related to the fact that the method was being used at the limit of its sensitivity, ie, the extremely small amts of these elements deposited on the back of the gunhand in a typical firing was very close to the limit of the chemical detection method

Early NAA Work at General Atomics Corp

In the early 1960's, with the advent of high neutron flux NAA as an extremely sensitive method for the quantitative detection of many elements, the nuclear activation technique began to be investigated for determination of gunshot residues. The original preliminary expts and much of the subsequent detailed investigations of this technique were performed at the General Atomics (GA) Corp, San Diego, Ca, by Vincent Guinn and his associates (Ref 8). The bulk of the material on determination of gunshot residues in this article is taken from the above

The initial exploratory expts at GA showed that the NAA approach worked quite well for the detection and measurement of Ba and Sb as primer residue elements. Since NAA sensitivity for Pb is rather poor, no effort was made to detect this third element. In these first expts, the backs of both hands of a police officer were first rinsed with very dil nitric acid (after first washing his hands with ordinary soap and water), and the acid rinsings saved for analysis for background handblanks. The officer then fired a 0.38 cal revolver once, with his right hand, and the rinsing procedure was repeated. He then fired the same gun three times in rapid succession, again using his right hand, and subsequently both his hands were rinsed with dil nitric acid. The various nitric acid rinsings were then each placed in a small polyethylene vial, sealed, and irradiated for 30 min in a 250Kw TRIGA Mark I reactor, at a thermal neutron flux of 1.8×10^{12} n/cm^2-sec. Because of the large amt of NaCl from perspiration present in the nitric acid rinses, it was observed that ^{24}Na and ^{38}Cl dominated the gamma-ray spectrum. As a result, activation products from other elements were masked out in using purely instrumental gamma-ray spectrometry with an NaI scintillation detector. Radioactive Sb and Ba were therefore quantitatively separated chemically from the rinsings. In this manner, by counting the recovered Sb from each rinse, it was found that gross Sb on the gun-hand increased from 0.12ug after one firing to 0.23ug after three firings, with a background handblank

before firing of 0.02ug and a reagent blank of 0.03ug. Similar results were obtained for Ba gunshot residues on the gunhand. Based on these encouraging results, more extensive investigations on use of NAA for this purpose were conducted by GA and other groups interested in forensic technology

Origin of Barium and Antimony in Primers

The origin of Ba and Sb in commercial cartridge primers is typically from $Ba(NO_3)_2$ and Sb_2S_3 as constituents from the primer mix. Specific chem compn of a commercial brand is usually "proprietary" and not readily available. The GA investigators, upon analyzing residues from the firing of five different commercial brands of 0.38 cal ammo for total Ba and Sb, observed that anywhere from 49 to 334ug of Ba and from 16 to 168ug of Sb were collected. Quantities of Cu, presumably from the primer caps, in the range of 0.4 to 64ug were also observed

The pertinent neutron activation data for the determination of Ba and Sb in gunshot residues by (n,γ) thermal neutron activation is given in Table 8

Na and Cl products will dominate the pulse-height gamma-ray spectrum. The radiochemical separation procedure for Ba and Sb from the activated sample as developed by GA is as follows:

"The activated sample is placed in a beaker, along with about 15ml of distd water, 3.5ml of concd HCl, 1 ml of concd HNO_3, about 100mg of NaCl (as holdback carrier), and small amts (1 ml each) of carrier solns of Ba^{+2}, Sb^{+3}, and Cu^{+2} (20.0mg each), and the mixt boiled for 10 mins – to dissolve any particles present, and equilibrate any ^{139}Ba, ^{122}Sb, and ^{64}Cu present with their respective nonradioactive carriers. After cooling, the soln is poured into a 50-ml centrifuge tube. One ml of concd sulfuric acid is added, and the soln is stirred to precipitate $BaSO_4$. The ppt is centrifuged, filtered on a preweighed filter paper, washed with water and then with ethanol, dried at 110°C for 15 mins, and weighed (thus determining the recovery of the Ba^{+2} carrier). Cellophane tape is then placed over the ppt, and the filter paper is carefully folded and placed in a 2-dram polyethylene vial – the sample then being counted for its ^{139}Ba activity in a well-type NaI scintillation detector, coupled

Table 8

Element	% Abundance	Thermal Neutron Cross Section, barns	Product Nuclide	Half-Life	Principal γ-photopeak, MeV
^{138}Ba	71.66	0.35	^{139}Ba	82.9 min	0.166
^{121}Sb	55.25	6.5	^{122}Sb	2.80 days	0.564

At a thermal neutron flux of 1.8×10^{12} n/cm^2-sec and a 1-hr irradiation, experimentally-determined sensitivities for Ba and Sb are 0.0048ug and 0.0032ug, respectively. These sensitivities are reported to be adequate for the general gunshot-residue detection problem

Radiochemical Separation Procedure for Barium and Antimony

As stated earlier, when gunshot residues are removed from the back of the hand of a person who has recently fired a gun, other material present on the skin, in particular considerable amts of Na chloride, are also removed, and that the activated

to a multichannel pulse-height analyzer. Copper is removed from the supernatant soln by adjusting the pH to 1.5–2.0 with NaOH soln, and extracting the Cu by shaking with 5ml of $CHCl_3$ soln of dithizone (400mg of dithizone in 100ml $CHCl_3$) in a 150ml separatory funnel. The lower ($CHCl_3$) phase is discarded. The Sb^{+3} in the supernatant soln left from the $BaSO_4$ pptn is pptd as Sb_2S_3, using about one gram of thioacetamide and heating. The ppt is centrifuged, dissolved in about 10ml of HCl soln, boiled for about 15 mins (to remove H_2S), cooled, and diluted to about 30ml. The free sulfur formed is centrifuged out. The supernate is transferred to a clean centrifuge tube, about 20ml of water and 2ml of chromous

chloride soln (oxorbent) are added and stirred, and the tube is placed in a boiling water bath for 30 mins. The soln is allowed to stand overnight to complete the pptn and settling of elemental Sb, which is then transferred by means of a transfer pipette to a 2-dram polyethylene vial and counted for its ^{122}Sb activity in a well-type NaI scintillation detector that is coupled to a multichannel pulse-height analyzer. The recovery of Sb carrier is determined by re-irradiation and comparing the resulting ^{122}Sb activity with that of a similarly activated and counted comparator standard"

With the development of high resolution lithium-drifted germanium (Ge-Li) detectors in the late 60's and early 70's, for gamma-ray spectrometry, direct instrumental analysis for activated gunshot residues became more feasible. At a flux of 1 x 10^{12} n/cm^2-sec for 3 hrs and counting directly with a 20 cm^3 Ge-Li detector connected to a 4096-channel analyzer, Borra et al (Ref 16) at the University of Pavia, Italy, report sensitivities for Ba and Sb as 0.05ug and 0.01ug, respectively. It should be noted, however, that these sensitivities are approx an order of magnitude lower, ie, poorer, than those obtained by GA's chem separation procedure

Paraffin Coating Method for the Removal of Gunshot Residues from Hands

Various methods were investigated by the GA group for removing gunshot residues from the hands after firing a gun, including swabbing or scrubbing with different materials moistened with a variety of solns. Although these were convenient to use, unfortunately each showed very high levels of induced activities when activated in a reactor. The studies also showed that a swabbing or scrubbing technique, in general, did not remove as much gunshot residue-material from the skin as did a paraffin coating. A paraffin coating procedure was therefore adopted by the GA workers as the regular hand-sampling method to be used in all subsequent gunshot-residue work. Although not so convenient to apply, paraffin has the advantage of being readily available commercially in high purity, at a very low cost. Only the barest traces of Ba and Sb are found in most batches, thus resulting in an essentially negligible paraffin blank correction

The application technique finally adopted by GA "consists of melting pure paraffin in a clean porcelain evaporating dish, holding the temperature at about 120°F, and then applying it to the desired region of the back of the hand, primarily the 'thumb-web' area, allowing the applied molten paraffin to cool and solidify, peeling it off, and placing all of the removed paraffin in a labelled polyethylene vial – ready for neutron activation. The person applying the paraffin is required to wash his hands carefully first, and then put on thin disposable plastic gloves, before proceeding. The molten paraffin is allowed to flow off of a small clean paint brush onto the skin – rather than using a brushing or scrubbing motion – so that material is not transferred back to the dish of molten paraffin with repeated dippings of the brush into the dish. Naturally, a reasonably clean laboratory area must be used, and all materials employed must be free of barium or antimony. Measurements have shown that a second application of paraffin to a hand area, after the first lift has been peeled off, does not remove any significant additional amount of Ba or Sb."

The "thumb-web" area, referred to in the above procedure is the V-shaped section formed by the surfaces on the back of thumb, the trigger finger and the area between the thumb and trigger finger. Controlled firing tests show that the bulk of the gunshot residues are deposited on this area of the back of the hand

A distinctly negative factor on the utility of this method is the effect of washing the hands after firing a gun. It appears that normal washing of the hands destroys the evidence of a person having recently fired a gun. The length of time that has passed between the firing of the gun, the apprehension of the suspect and the performance of the residue test on the hands is therefore critical for the successful application of this technique

Handblank Measurements

A highly important factor in the interpretation of gunshot residue analyses is the presence of either Ba, Sb or both on a person's hands from sources other than the firing of a gun, eg, from materials encountered in their normal occupation. An extensive investigation of such handblank measurements was conducted by GA involving

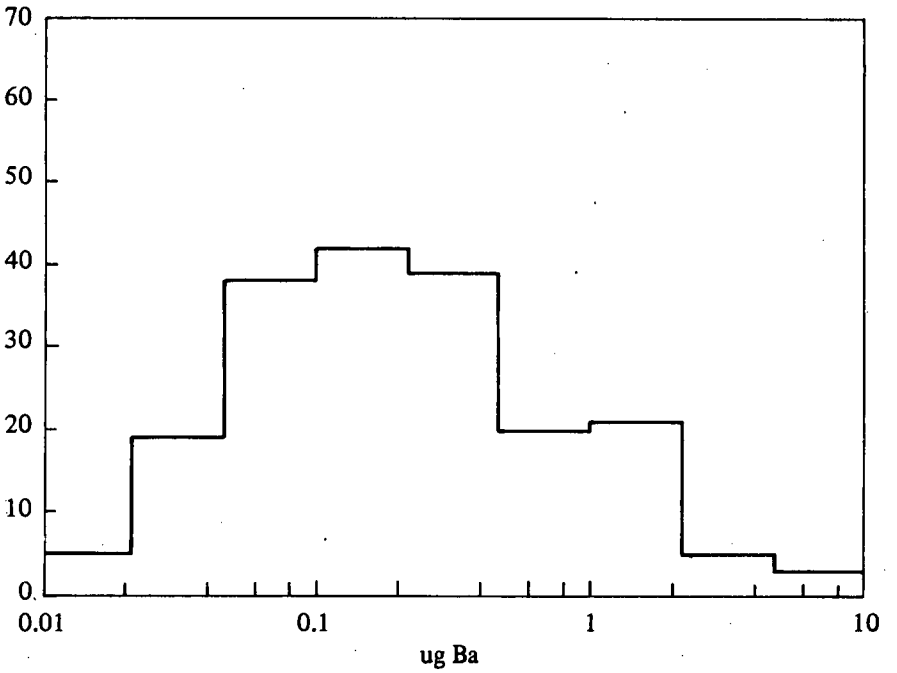


Fig 5 192-Barium handblank values from 97 persons in 30 different occupations (from Ref 8)

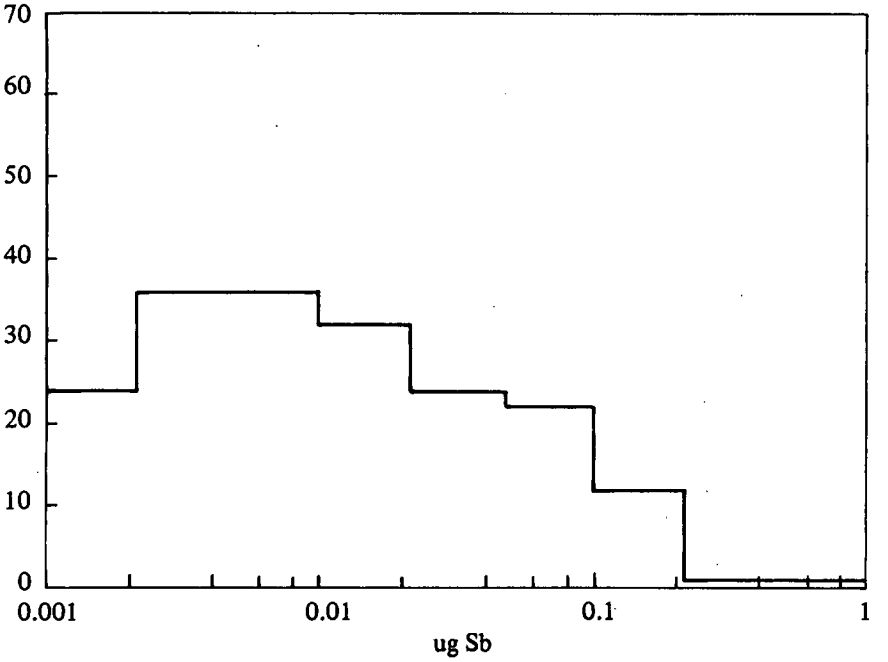


Fig 6 188-Antimony handblank values from 97 persons in 30 different occupations (from Ref 8)

97 persons in thirty different occupations. Both the left and the right hand of each person was treated and assayed. In Fig 5, the measured handblank values for Ba for 97 people are presented in a logarithmic distribution form. The values do approximate a log-normal distribution. Fig 6 shows the corresponding data for the Sb handblanks. In this case, the possible log-normal shape of the distribution histogram is compressed at the lower-Sb end, because of the fairly numerous lesser values encountered, and many of these values were at or below the limts of detection. From all the values obtained, the median Ba was 0.20ug, and the median Sb value was about 0.010ug. No apparent correlation exists between the corresponding Sb and Ba values from the same person

ratio is 16.5. In all of the test-firing data, this ratio is much smaller, ranging from 3.12 for a 0.38 cal revolver to 10.2 for a 9-mm automatic. These ratios are not sharply defined – not only because of the numerous variables included even with a given caliber and type of gun (eg, make and condition of gun, chamber-fired in the case of revolvers, brand of ammo, wind direction and velocity, cartridge to cartridge variability within a single brand of ammo, reproducibility of the hand-area sampling technique, etc), but also because in many cases they include varying amts of Ba and Sb already present on the hand before the test firing, ie, handblank material

For the 0.45 cal automatics and 0.38 cal revolvers, sufficient test firings were performed to warrant some statistical analysis and interpretation. Ba and Sb values from these firings are compared with the average handblank relationship in Figs 7 and 8. From the ∿190 handblank measurements, as depicted in Figs 5 and 6, only 9% of the Ba values are > 1.5ug and only 7% of the Sb values are > 0.1ug. In the case of the 32 firings of the 0.45 cal automatics (Fig 7), 66% of the Ba values are > 1.5ug and 94% of the Sb values are > 0.1ug. Thus, the degree of overlap between the gunshot-residue values in 0.45 cal automatic firings with handblank values is fairly small – particularly for Sb. In the case of the 79 firings of 0.38 cal revolvers (Fig 8), only 27%

Table 9

Gunshot Residue Results as Determined from Test Firings

Weapon	No of Test Firings	Ba, ug Low	Ba, ug High	Ba, ug Mean	Sb, ug Low	Sb, ug High	Sb, ug Mean	Factor X Av Handblank Value Ba	Factor X Av Handblank Value Sb
0.45 Cal Auto	32	0.216	15.4	3.60	0.068	3.12	0.598	6.9	19
0.44 Cal Rev	5	0.168	4.52	1.39	0.055	1.52	0.422	2.7	13
0.38 Cal Rev	79	0.168	12.7	1.31	0.045	4.17	0.421	2.5	13
0.25 Cal Auto	4	0.96	8.46	4.72	0.208	1.26	0.632	9	20
9mm Auto	5	1.37	15.4	7.47	0.056	2.05	0.732	14	23
0.22 Cal Auto	3	0.32	1.25	0.704	0.058	0.242	0.137	1.3	4.3
0.22 Cal Rev	16	0.21	0.82	0.391	0.05	0.24	0.082	0.75	2.6
Handblanks	190[a]			0.523			0.0316		

[a] – Total No of individual measurements

Results of Test Firings

In Table 9, the results of Ba and Sb values from gunshot residues determined by GA in 144 test firings are given. Seven different types of handguns were used including both automatic and revolver type weapons. One tentative conclusion that can be drawn from the relatively limited data is that larger-caliber guns generally seem to deposit more residue than do smaller-caliber guns

It is also of interest to compare the mean Ba/Sb ratios from the test firings of the various guns with mean Ba/Sb handblank or background ratios. From the ∿190 Ba and Sb handblank values, as shown in Figs 5 and 6, the mean Ba/Sb

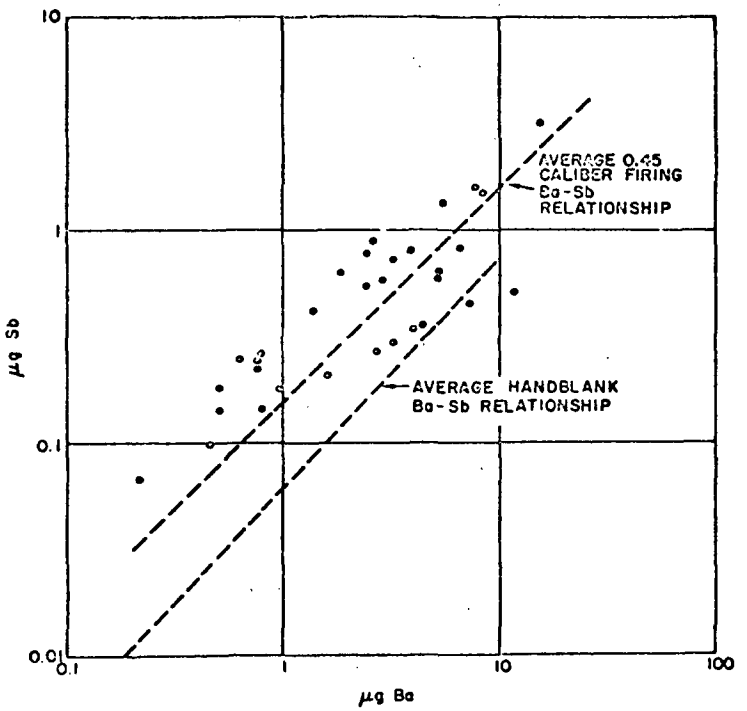


Fig 7 Ba and Sb Values from 32 Firings of 0.45 Cal Automatics (from Ref 8)

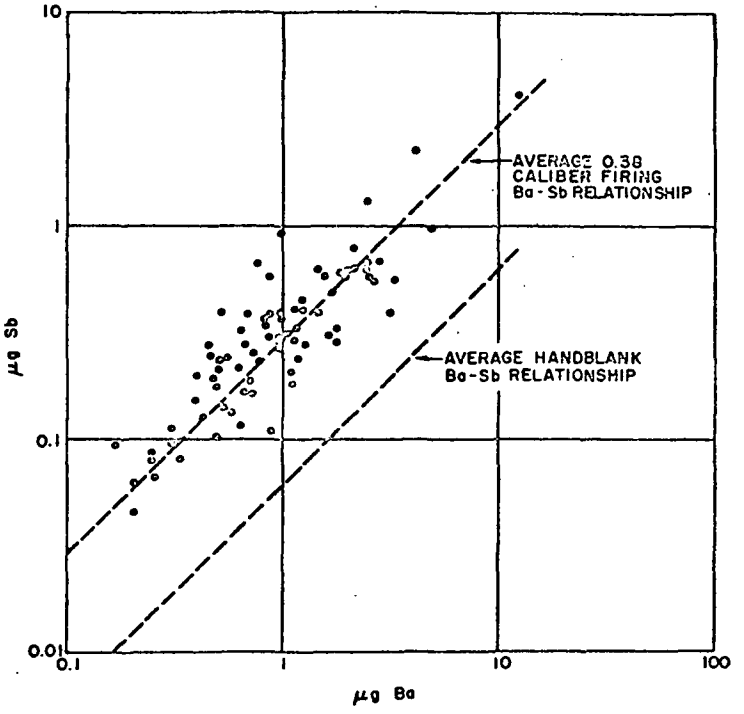


Fig 8 Ba and Sb Values from 79 Firings of 0.38 Cal Revolvers (from Ref 8)

Table 10

Degree of Overlap of Firing Values with Handblank Values (from Ref 8)

Type	No of Values	% of Ba Values > 1.5ug	% of Sb Values > 0.1ug
Handblanks	97 persons	9	7
0.45 automatics	32 firings	66	94
0.38 revolvers	79 firings	27	90
0.44 revolvers	5 firings	20	80
0.25 automatics	4 firings	75	100
9 mm automatics	5 firings	80	80
0.22 revolvers	16 firings	0	19
0.22 automatics	3 firings	0	67

of the Ba values are > 1.5ug, but 90% of the Sb values are > 0.1ug. Thus, in this case, the degree of overlap with Ba handblank values is considerable, but the degree of overlap with Sb handblank measurements is fairly small

The number of test firings with the other handgun types is too small to allow for much generalization. However, the degree of overlap of firing values with handblank values is summarized in Table 10 for all the weapon firings. It is evident from the table that, in almost every case, the Sb value provides a better distinction between a firing value and a handblank value than does the Ba value. It is also evident, at least from the above data, that it is very difficult to distinguish between a 0.22-cal firing (especially revolvers) and a handblank value

Although the bulk of the work done on analysis of gunshot-residues was directed to the firing of handguns, at GA some measurements were also made on residues deposited from the firing of rifles and shotguns. Ba and Sb residues were analyzed for on the cheeks as well as on the hands of individuals. In general, little residues of these elements are found on the cheeks, but significant quantities above handblank values are observed on the firing hand

Detection of Airborne Gunshot Residues

In addition to deducing whether or not an individual or suspect has fired a gun, in many criminal investigations the problem exists of determining where and when, or even *if* a weapon has been fired. Detection of gunshot residues on surfaces can pinpoint the location of the firing, but requires a systematic procedure covering many samples in suspect locations. These samples are inherently sensitive to contamination from accumulated dirt and dust lying on surfaces, and also can provide little or no time-of-firing information. At the Pennsylvania State University (Ref 17), a technique was developed to sample the gunshot residue left suspended in the air, followed by NAA to measure for traces of Ba and Sb. This method requires only one sample for suspected location, with external interference due mainly to the dust recently introduced into the air. Since the amt of residue remaining in the air is a function of time-after-firing, this technique also offers the potential of providing information as to the approx time the shot was fired

A special test facility was constructed from polyethylene sheeting forming a 11½'x11½'x8' room suspended from an Al frame (Fig 9). A glove box is attached to one side to allow for revolver firing without disturbing the still-room environment. A carriage allows the revolver to be fired in the test room and then withdrawn into the glove box for loading and unloading. The target is a bullet catcher constructed from a 30-gal drum packed with cotton filler. An exhaust fan on one side allows for a complete change in room air between tests

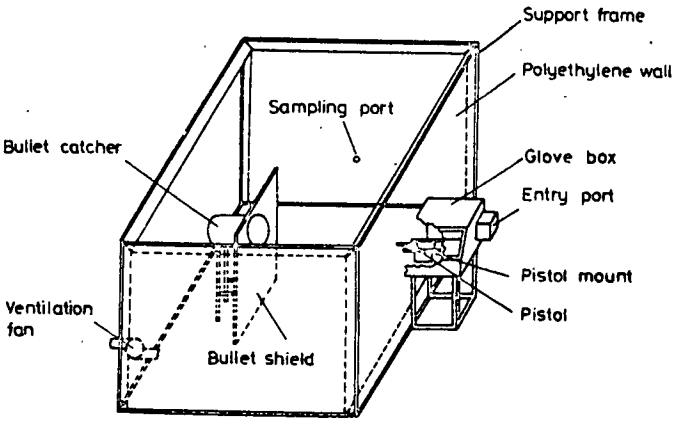


Fig 9 Air Gunshot Residue Test Facility (from Ref 17)

A Del Electronics, Model ESP-100A, electrostatic precipitator was used for sample collection. Cigarette smoke particles were found to give approx the same particle distribution pattern on the collection filter paper as the gunshot residue, and since the smoke stains the paper, this provided a rapid technique for optimizing operation conditions. With a flow rate of 15cfm and a corona current of 125 uA, the residue collects primarily on a narrow band across the sample paper. Samples were collected on Whatman No 1541 filter paper which lined the inside of the sample collection tube. The presence of this paper allowed air to flow only thru the center of the tube, so particle collection was made upon the filter paper exclusively. The filter paper samples were pelletized prior to neutron activation analysis

The NAA measurements on the paper samples were made at the Breazeale Nuclear Reactor Facility at the Pennsylvania State University with a TRIGA Mark III reactor at a flux of about 10^{13} n/cm^2-sec. Samples were irradiated from 2 to 20 min and counted for 2000 sec, after a 90 min decay time for Ba and a 60 hr decay for Sb. Analyses were performed instrumentally, without radiochemical separation, using a 35cm^3 coaxial Ge-Li detector and a 4096-channel pulse height analyzer. With these procedures, detection limits for Ba and Sb were 0.02ug and 0.001 ug, respectively. These sensitivities are comparable to those obtained by GA's radiochemical separation procedure, and are made possible by the use of the higher neutron output from the more powerful reactor and in combination with the higher resolution solid state detector

The results of test samples taken 4 hrs after firing, using the four major brands of 0.22 cal ammo available in the Eastern USA are shown in Table 11. These measurements demonstrate that

Table 11

Sb and Ba Collected by the Electrostatic Precipitator for Four Common Types of 0.22 Cal Ammunition (from Ref 17)

Ammunition	Micrograms in the maximum concentration region[a]	
	Sb[b]	Ba[b]
Western, .22 caliber T-22 standard vel	1.95 ± 0.75[c]	5.12 ± 2.26[c]
Remington Hi-Speed .22 caliber short	1.91	1.82
CCi .22 caliber	7.31	11.2
Imperial .22 caliber	17.6	21.0

[a]The region 1/2 to 4½ inches from the leading edge of the sample

[b]Sampling time of 30 min, sampling started 4 hrs after firing

[c]One standard deviation based on four test firings

Sb and Ba are present in the airborne gunshot residue expelled from all of the brands of 0.22 cal ammo. A chemical analysis of the primer of the Western brand gave a Ba to Sb ratio of 65, whereas the same ratio obtained from the data in Table 11 is 2.6. The authors conjecture that this additional Sb left in the air came from the vaporized bullet Pb which contains a large amt of Sb as a hardening agent

Fig 10 shows the variation of airborne gunshot residue collected at various times after one firing. Following a general initial exponential fall-off, the rate of decrease slows at 48 hrs after firing. This is expected, since at these long times after firing, only the submicron gunshot residue particles remain suspended in the air. Under the "still" room conditions of these expts, these particles can remain suspended from weeks to months after firing

The limiting sensitivity in this technique occurs in the analysis for Ba. Defining the limiting value as twice the standard deviation of the background in the 0.166MeV photopeak region, the least amt of Ba which can be detected is about 0.1 ug. Since the amt of Ba detected at 72 hrs is about 0.32ug, and since Ba and Sb losses out of

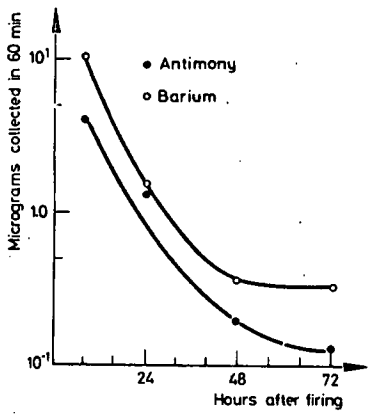


Fig 10 Airborne Sb and Ba Content in Electrostatic Precipitator Samples as a Function of Time of Firing (from Ref 17)

the air more than 48 hrs after firing are small (Fig 10), it appears that under test conditions the presence of gunshot residue could be detected well beyond 72 hrs

From the four hr test results, as given in Table 11, the variation of results with different 0.22 cal ammo is indicated. Thus it would be difficult to obtain precise time-of-firing information under field conditions. However a gross estimate of this time should be possible

Firing tests conducted with larger than 0.22 cal ammo showed that even greater sensitivity for detection of Ba and Sb in airborne gunshot residues can be obtained using these NAA techniques

Detection of Gunshot Residues on Floor Surfaces

In another study at the Pennsylvania State University (Ref 20), gunshot residues from firing tests were assayed in order to establish distribution patterns of Ba and Sb on surfaces below the flight path of the bullet

Test firings were conducted with handguns using two different indoor ranges; one had a gun to target distance of 2.5 meters while the second had a 12 meter separation between gun and target. The smaller facility maintained excellent control over climatic conditions, whereas no control was exercised with the large one. Both facilities utilized soft penetrating materials as targets. Thru the analysis (by NAA) of samples collected from various points around the gun and target, it was determined that the most desirable region to monitor was an approx one meter-wide area around the hypothetical line parallel to the trajectory of the bullet. Relatively large concns of residues were found on the tract compared with other areas farther from the trajectory

Moistened filter paper (Whatman No 541) was found to be optimum for collecting the residues from floor surfaces. The filter paper squares containing the powder residues were dried at 50° to remove moisture prior to reactor irradiation. Ba and Sb standards were also prepd to match the geometry of the test samples, and were irradiated under identical conditions

The dry filter paper samples contained in polyethylene vials were irradiated for 2 to 5 min at a thermal neutron flux of 10^{13}n/cm^2-sec using the pneumatic transfer system at the Penn State TRIGA Reactor. Samples from 0.22 cal ammo were usually irradiated for 5 min, while those from higher cal ammo required only a 2 min irradiation. The irradiated samples were transferred to clean counting vials and counted with a 2 min decay period. The short-lived isotopes of interest were ^{139}Ba (83.2 min), ^{122m}Sb (4.2 min) and ^{66}Cu (5.1 min). Instrumental radioassay was performed with a similar nuclear counting system as for the airborne gunshot residues (Ref 17) described above with the addition of a programmable computer coupled to the multichannel analyzer for data processing. Using these procedures, it was possible to detect Ba levels above 2 x 10^{-9}g/cm^2 and Sb levels above 1.5 x 10^{-9}g/cm^2 of floor surface

Handguns tested ranged from a 0.22 cal to a 0.45 cal revolver. More specific details of the firing expts and the range of results can be found in the original ref. However, Figs 11 and 12 illustrate some typical distribution patterns of Ba and Sb produced on the floor of the 2.5 meter long test facility from the firing of a 0.22 cal revolver. These are smooth curves drawn thru the analytical points to isolate areas of different concn levels

Firing tests with the other cal handguns indicated distinguishable differences in the overall distribution patterns of discharge residues from different handguns. This unique distribution pattern of residues deposited immediately below the flight path of the bullet results from the cloud of combustion products emitted thru the barrel of the weapon. The authors (Ref 20) propose the following mechanism:

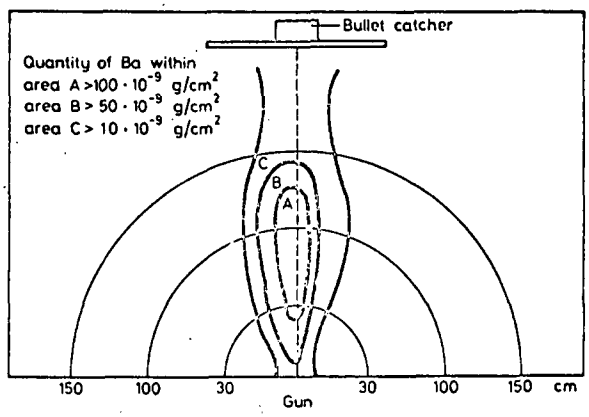


Fig 11 Distribution Pattern of Ba from the Discharge of a 0.22 Cal Revolver (from Ref 20)

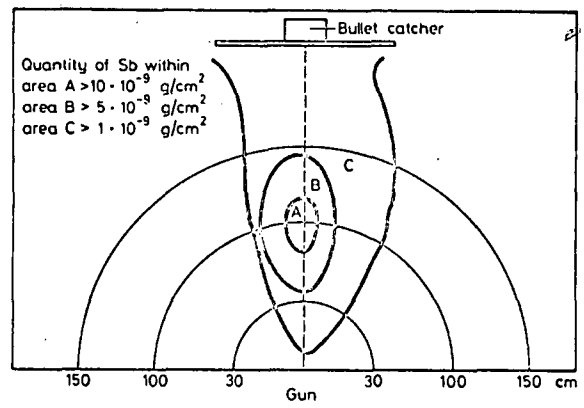


Fig 12 Distribution Pattern of Sb from the Discharge of a 0.22 Cal Revolver (from Ref 20)

. . . "When a projectile leaves the barrel of the gun at a high velocity, it sets up a wave front which extends out from the nose of the bullet. This condition creates an area of lower pressure immediately in its wake. In addition, due to the rifling action in the barrel of the gun, the projectile is discharged with a tangential velocity component. The combination of these two conditions creates a vortex in the wake of the bullet which carries with it some of the combustion products. Further, the continuous spinning of the bullet during its forward motion allows the spewing out of small amts of combustion products within its wake. When the bullet hits the target, the wave front collapses, depositing all the remaining residues around the target. While this seems to be the mechanism by which the residues are carried farther from the gun, the major contributions to the residue patterns generated in the immediate vicinity of the firearm are the emissions from the barrel of the gun."

"On the basis of the above mentioned mechanism, a number of variables characteristic of a firearm (barrel length, location of the emission ports, and possibly by the twist of the rifling grooves) can influence the amount and nature of the distribution of combustion products. In addition, the size of the projectile, its shape and velocity can influence the amount of residue carried within the wake of the bullet and its distribution along the trajectory. The experimental observations made during this study generally substantiate the dependence of gunshot residue patterns upon the above mentioned characteristics of the weapon and the bullet."

Nondestructive NAA can thus be used for the detection and measurement of Ba, Sb (and also Cu) from residue samples collected from the floor surface after the single firing of a handgun. By constructing a unique distribution pattern of these residues, it is possible to establish the flight path of the bullet and the proximity of the gun with respect to the target. The development of this information, particularly in the absence of a firearm, a bullet or an eyewitness, can be of considerable value in criminal investigations

Experiments with Tagged Ammunition

Because of the relatively high Ba and Sb handblank values found on persons in some occupations – which detracts from the reliability of the method for detecting gunshot residues on the hands of suspects – the idea was developed of deliberately tagging the gunpowder or primer material used in cartridges with low levels of very uncommon elements – using those that can be detected with extremely good sensitivity by NAA. As an aid to law enforcement, the approach here would have different US manufacturers of cartridges tag their gunpowder or primers with different combinations of these selected elements for each different type of cartridge. If technically and economically feasible, the use of tagged cartridges would offer several advantages: (a) the determination of whether or not a suspect had recently fired a gun

would be more conclusive, (b) the analysis could also identify the brand and caliber of the cartridge fired, and (c) a completely instrumental radioassay procedure or a simpler radiochemical separation method would be more possible

Rare earth elements, with relatively high thermal neutron activation cross-sections, have been tested or considered as tagging species for this purpose. At GA (Ref 8), preliminary expts were conducted with 0.38 cal ammo using dysprosium (Dy) and europium (Eu) deposited on the wall of the cartridge case and in the gunpowder, and Dy, holinium (Ho) and indium (In) in the primer. The amt of rare earth element used as a tag per round ranged from 1 to 100 ug. The results of expts were considered partially successful but inconclusive as to ultimate feasibility

A more extensive investigation of rare earth tracers for this application is reported by Pillay et al (Ref 9) in which the high purity oxides of Dy and Eu were added to commercial "Bullseye" gunpowder at a level of 0.1 wt% and loaded into 0.45 cal cartridge cases. Test firings were carried out at an indoor pistol range and gunshot residues were analyzed from paraffin casts taken from the web, palm and back of both the firing and nonfiring hands. Paraffin samples were irradiated in a reactor at a thermal neutron flux of 5×10^{12} n/cm^2-sec for 30 min and counted with a 3 x 3 in NaI scintillation detector both instrumentally, and also after radiochemical separation of the tracer elements

Firing test results with Dy as a tracer were inconclusive in that there was an insufficient lack of discrimination between levels found on the firing and nonfiring hands. However, levels of Eu were significantly higher on the web of the firing hand; the percentage of Eu recovered in an individual firing averaged 0.02%

The authors conclude that the use of Eu-labeled gunpowder can provide the basis for a rapid, simple instrumental gunshot residue test which can detect the firing of a weapon with a high degree of probability. The tagging of gunpowder with Eu can be developed into a method which is faster and less complicated than that based on the radiochemical separation of Ba and Sb with no reduction in sensitivity. An economic analysis based on a 0.1 wt% tagging level indicates the cost increase per box of cartridges at less than 2%

4) Detection of Explosives in Buried Mines

The use of nuclear techniques for the detection of buried expls (in mines) has been investigated by the US Army over the past 25 years. The basic approach is the use of a direct beam of highly penetrating radiation to irradiate the soil and the measurement of a reflected, scattered, induced or secondary signal to indicate the presence of a buried mine. A complete historical review and analysis of this work has been prepared by Coleman et al (Ref 18). A brief summary of the highlights of the overall effort is provided here

In the discussion that follows we refer to nuclear activation *detection* reactions in lieu of *analysis* reactions since the signals that are measured are not necessarily always from a radioactive product. Again, we will use standard nuclear physics notation in specifying nuclear reactions, namely:

target nucleus	[bombarding radiation,	product radiation(s)]	product nucleus

Thru 1967, emphasis was given to the use of neutrons as the bombarding source of radiation. Almost all possible neutron reactions were considered including moderation of fast neutrons by hydrogen in the expl, thermal capture reactions, elastic and inelastic scattering of neutrons and neutron activation reactions. These neutron reactions are listed as follows:

Fast neutron moderation:	$H(n,n')H$
Elastic scattering:	$^{12}C(n,n')^{12}C$, $^{14}N(n,n')^{14}N$
Inelastic scattering:	$^{12}C(n,n'\gamma)^{12}C$, $^{14}N(n,n'\gamma)^{14}N$, $^{16}O(n,n'\gamma)^{16}O$, $^{28}Si(n,n'\gamma)^{28}Si$
Thermal neutron capture:	$^{14}N(n,\gamma)^{15}N$
Fast neutron activation:	$^{14}N(n,2n)^{13}N$, $^{28}Si(n,p)^{28}Al$, $^{16}O(n,p)^{16}N$

Of these neutron interactions, those that produce prompt-γ rays were evaluated as the most feasible for mine detection. As discussed in the Introduction, we define a prompt γ-ray as one which is produced as a direct result of the primary neutron interaction, usually within nanoseconds of that initial event. Such reactions are obviously attractive because they can best satisfy the desired rapid sweep rate over a minefield. The three specific neutron-prompt gamma reactions that were intensively investigated by the US Army are listed below:

Nuclear Reaction	E_{γ}, MeV	Cross-Section, millibarns
$^{12}C(n,n'\gamma)^{12}C$	4.43	160
$^{28}Si(n,n'\gamma)^{28}Si$	1.78	Large
$^{14}N(n,\gamma)^{15}N$	10.83	80

The first two reactions, which entail inelastic scattering of fast neutrons, in combination formed the basis of a thoroughly studied detection scheme. This method is based upon an increase in the 4.43 MeV γ-ray signal from carbon when over a mine and a corresponding decrease in the 1.78 MeV γ-ray signal from silicon in the soil. The laboratory research model developed for this scheme used the ratio of the two γ-ray signals to indicate the presence of a mine buried in the soil. The third reaction is based on the measurement of the 10.83 MeV γ-rays from thermal neutron capture by nitrogen in expls

The chief obstacle in the neutron-prompt γ approach is that the specific γ-ray signal must be measured in the presence of a very high competing background signal. This background radiation is a combination of the signal emanating directly from the neutron source (either a neutron generator or an intense radioisotopic neutron emitter) to the detector and the host of prompt gammas produced from neutron interaction with all the other elements present in the soil, expl and detector components. The presence of this competing background places a stringent requirement on the resolution of the γ-ray detector, the complexity of the associated nuclear counting electronics and the amount of shielding required for the detector. When projected to an actual vehicle-mounted device, some of the laboratory model research mine detectors based on these schemes approximate fairly sophisticated nuclear physics laboratories on wheels. In addition, even with optimized laboratory research equipment, none of the prompt-γ schemes can detect mines efficiently beneath 2 or 3 inches of soil. The neutron-prompt γ approach is, therefore, considered as not feasible for mine detection with present available nuclear technology

Neutron activation reactions have also been considered for mine detection. Here a radioactive element is produced in the mine which in the process of decay, emits nuclear radiation, either alpha or beta particles or γ-rays or two of these or all three in combination. For buried mines the penetrating γ-rays are of most interest. In organic expls, the only elements capable of being so activated are nitrogen and oxygen. Using 14 MeV neutrons from a neutron generator, nitrogen via $^{14}N(n,2n)^{13}N$ produces ^{13}N with a half-life of 10 minutes and a γ-ray energy of 0.51 MeV; oxygen via $^{16}O(n,p)^{16}N$ produces ^{16}N with a half-life of 7.5 seconds and a 6.1 MeV γ-ray. Activation by fast neutrons of silicon in the soil, via $^{28}Si(n,p)^{28}Al$ to produce 2.3 minute ^{28}Al (E 1.78 MeV) has also been considered for mine detection. This last approach will obviously not serve to give a direct signal for the presence of expls but can indicate the presence of a void or disturbance in the natural soil terrain by a reduction in the 1.78 MeV γ-ray signal. However, the nuclear parameters – cross-section, half-lives, interfering reactions, personnel shielding and neutron source requirements, etc. – are such that none of the above activation schemes are feasible for detecting mines with any degree of efficiency approaching military requirements

In more recent years, γ-ray scattering techniques have been considered for buried mine detection. As an initial source of bombarding energy, γ-radiation is more attractive than neutrons because it is easily available in the form of relatively inexpensive long-lived radioisotopes. The more important ones (with their corresponding half-lives and principal γ-emissions are: americium-241 (458 yrs, 0.060 MeV), cesium-137 (30 yrs, 0.662 MeV), and cobalt-60 (5.2 yrs, 1.1, 1.3 MeV)

For γ-ray energies below 1 MeV (the range of interest) there are two principal modes of interaction with matter – Compton scattering and photoelectron absorption. Compton scattering is the elastic scattering of the γ photon by an orbital electron in which part of the incident γ-energy is imparted to the recoiling electron. The number of Compton scatters occurring in a given volume depends on the number of electrons present and is relatively independent of incident γ-energy. For the lower atomic number elements (excluding hydrogen), the number of electrons present is directly proportional to atomic wt. Thus Compton scattering on a per unit volume basis is a function of density and is independent of chem compn. The density of soils is widely variable and the density of expls falls within the normal range of soil

density variation. Therefore Compton scattering alone does not provide a means of detecting mines, although it may provide a means of detecting expls in a more homogeneous matrix

Photoelectron absorption is the total absorption of an incident photon by an orbital electron (predominantly the k electron), resulting in the freeing of that electron from its bound state. Photoelectric absorption is a strong function of gamma-ray energy (decreasing as roughly E^3) and of the atomic number (increasing roughly as Z^4 for the energy range of interest). Observing the number of photoabsorptions in a given volume therefore does provide a means of differentiating between soil, which has an average Z of approx 11, and expls, which have an average Z of approx 5. Unfortunately, photoelectric absorption cannot be detected directly as the photoelectrons produced are readily absorbed by the surrounding medium. However, while neither the Compton effect or the photoelectric effect by itself provides sufficient basis for the development of a viable expls detector, a combination of both effects will. While the fraction of total γ-rays Compton scattered in a volume of soil or expl is a constant, the total number of γ-rays available for Compton scattering is inversely proportional to the number of γ's photo-absorbed. Consequently, proportionally more γ's are scattered from a volume of expl than from a volume of soil. It is this increase in scattering that is detected, and this approach has been the basis for a number of devices designed to detect buried mines. However, soil penetration is relatively poor for the 60–100 keV γ-rays required in these devices, thus limiting their utility to shallow burial depths

As of this writing, the overall assessment of the feasibility of nuclear techniques for detecting buried mines is poor, for the reasons discussed above

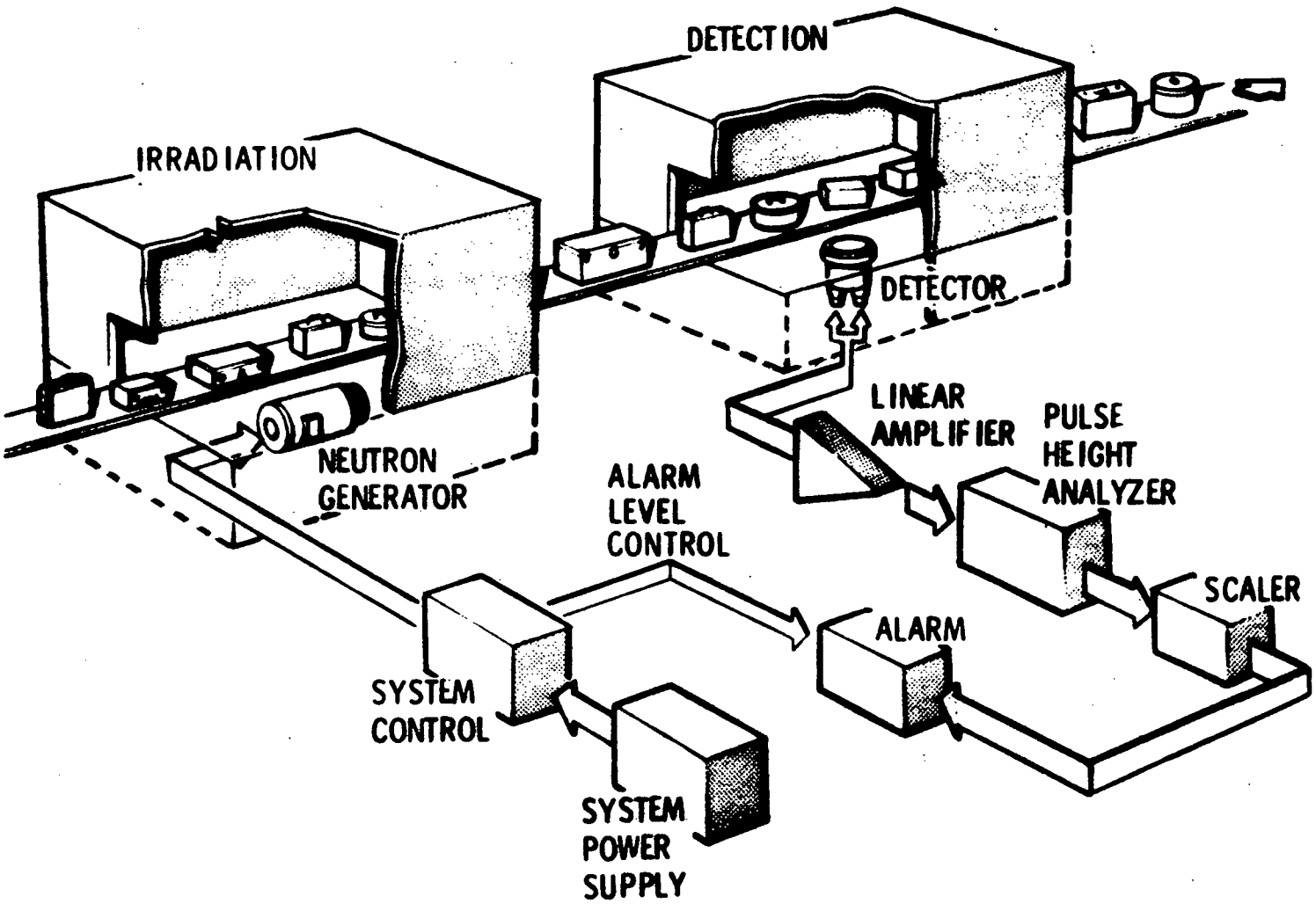
5) Detection of Hidden Explosives in Baggage

The increasing use of expls for terrorist and political blackmail activities, in particular the international "skyjacking" incidents of the early and middle 1970's, has resulted in a great interest in the development of efficient technological methods for detecting hidden expls, eg, in airline luggage. A technique that has received considerable attention for this purpose is the irradiation of luggage or suspect packages with fast neutrons followed by measurement of the γ-radiation from activated expl if present in the item. The approach is based on the same nuclear activation reaction discussed above under **Elemental Analysis** for total nitrogen content determination by FNAA, namely, the $^{14}N(n,2n)^{13}N$ reaction with 14 MeV neutrons, and counting of 0.511 MeV annihilation γ-rays emitted from the decay of ^{13}N. The potential success of the method is dependent on the premise that most expls contain nitrogen in varying amounts – in quantities greater than in the usual items found in passenger baggage. Mercury Fulminate has as little as 9.8 wt% of nitrogen and PETN as much as 56 wt%. A stick of straight Dynamite contains 15 wt% of nitrogen

As discussed previously, when an expl is irradiated with fast neutrons a ^{14}N nucleus captures the incident fast neutron and ejects two slow neutrons. The resulting nucleus, ^{13}N, is excited (radioactive) and decays with a 10 min half-life to stable ^{13}C. In this last transition, a positron, $\beta+$, is emitted. Because of its opposite charge, the $\beta+$ is strongly attracted by a nearby electron; in the resulting collision, both the positron and electron are annihilated and in the process of annihilation, the masses of the colliding particles are converted into two 0.511 MeV quanta of electromagnetic radiation. These γ-rays are what are detected to indicate the possible presence of an expl

Using the above neutron activation scheme, the North American Rockwell Corp (Los Angeles), under contract to the US Federal Aviation Administration (FAA), developed a full-scale operational system to test its feasibility for automatic inspection of airline luggage for the presence of expls (Ref 10). A block diagram of the activation concept employed in a baggage handling environment is illustrated in Fig 13. A conveyor belt transports luggage first past a neutron generator and then past a detector. The radiations detected are amplified, analyzed, and compared with a preset threshold. If the detected radiations surpass the threshold, a visual alarm is activated

A sealed-tube neutron generator, utilizing the deuterium-tritium reaction is the source of fast (14 MeV) neutrons, and a 8″ x 3″ NaI scintillation detector, with three optically coupled photomultipliers, is used to measure the γ-ray signal



N 199

Fig 13 Fast Neutron Activation System for Inspection of Airline Baggage for the Presence of Hidden Explosives (from Ref 10)

from each item of irradiated luggage. Both generator and detector stations have to be heavily shielded by a combination of concrete and lead. Shielding of the generator is necessary to protect the outside environment from harmful levels of radiation, and the detector must be shielded to maintain background levels as low as possible to maximize signal to noise ratio. The pulse height analyzer counting system isolates the desired 0.511 MeV γ-ray signal from other radiations

Typical demonstration expts with this system consist of filling handbags or suitcases with items customarily carried by passengers and placing these bags on the conveyor belt. Each bag is passed over the neutron generator and subjected to a total fast neutron fluence (integrated dose) of 10^8neutrons/cm^2. After approx a 25-sec delay, the bag passes under the scintillation detector, and the time-history of the radiation levels from the bag are recorded by the nuclear counting system. Integrated count times for a single bag are in the order of 2 sec

Next, the bags are opened and up to six sticks of straight Dynamite (or other type of expl, eg, Ammonium Nitrate) are placed inside, and the irradiation-count procedure is repeated. Typical results with sticks of 45% Gelex straight Dynamite, 1¼" x 8" cylindrical, approx 200g per stick, are shown in Table 12. (The designation "45% straight" refers to the expl strength of the Dynamite relative to blasting gelatine, rather than to its chem compn). Background counts are subtracted for the peak count rates given:

Table 12

Sensitivity of FNAA Method for Detecting Dynamite in Suitcases

No of Sticks	Peak Counts/Sec
1	35
2	65
3	100
4	130
5	160
6	190

The results in Table 12 are considered very conservative by the North American Rockwell authors, since they were not obtained under optimum conditions. Such conditions must take into account the type of luggage, conveyor belt speed, detector size, type of signal processing and activation geometry. None of these factors was optimized in the demonstration system. The authors project that the system as assembled could reliably detect a min of two sticks of straight Dynamite or one stick of Ammonium Nitrate

Another way of demonstrating currently achievable performance with the above system is shown in Table 13. Here, the peak counts/sec from a typical empty suitcase, leather attache case, and the leather attache case containing six sticks of Dynamite are compared to the background level. The attache case, in both cases, was also filled with common nitrogen-rich materials such as wool, vitamins B_1 and B_{12}, pills, rayon, saccharin, silk and other materials such as paper, cotton and brass:

Table 13

Count Rate of an Attache Case Filled with Dynamite vs Background Levels

Sample	Peak Counts/Sec
Room Background	170
Typical Empty Suitcase	220
Leather Attache Case (Filled)	260
Leather Attache Case (Filled) + 6 Sticks of Dynamite	340

From the data in Table 13 it is apparent that the signal from an item of luggage containing as many as six sticks of Dynamite is not sufficiently above the range of background levels to make the detection of smaller quantities of expl highly reliable. Materials, other than expls, which also contain nitrogen, will of course reduce detection reliability by increasing the false alarm rate. Any element which emits radiations similar to that of nitrogen, when activated with fast neutrons also represents a potential source of false alarms. Even elements which emit radiations with higher energy γ-rays than that of nitrogen represent a source of false alarms, since these higher energy γ-rays degrade to the 0.511 MeV level thru inelastic collisions (Compton scatter). The element most commonly found in baggage which is a likely source of false alarms is Cu – as present in articles containing brass. The interfering reaction here is ^{63}Cu(n,2n)^{62}Cu; the activated Cu product also decays by positron emission resulting in 0.511 MeV γ-rays, and its half-life is 9.7 min – almost identical to the 10 min half-life of ^{13}N

Although the North American Rockwell system was never optimized for max performance, the authors claim that sufficient demonstrations were run to verify feasibility. Four sticks of Dynamite were repeatedly detected in luggage with a probability of detection greater than 90%. Approx one false alarm per 1000 detections was noted which corresponds to better than 3σ false alarm rate. This false alarm rate, however, becomes much greater as one attempts to detect a smaller quantity of expl, ie, less than 4 sticks of Dynamite

Consideration has also been given to the possible harmful effects of the irradiation treatment on consumable materials present in luggage – either from induced radioactivity or radiation damage. For an integrated 14 MeV neutron dose of $10^8 n/cm^2$ on a suitcase, radiation induced by activating products such as foodstuffs, cosmetics, contraceptive devices, clothing and other personal items are assessed as being insignificant (Ref 12). Ordinary photographic film is also apparently visually undamaged when exposed to the neutron dose (Ref 10)

In 1972, the Lawrence Livermore Laboratory (LLL), also under Contract to the FAA, published a report (Ref 15) describing a more detailed statistical and exptl assessment of this same fast neutron activation method for inspecting baggage for the presence of expls. The LLL approach was directed towards a more quantitative evaluation of the nitrogen content background likely to be encountered in ordinary passenger luggage

Table 14

Comparison of % N by Weight in Some Materials Found in Typical Luggage and in Explosives (from Ref 15)

	wt % N
Cotton	0.0
Wool	16.0
Leather	18.0
Fur	16.0
Silk	18.4
Nylon	10.0
Rayon	0.0
Orlon, Acrilan	26.4
Dacron & similar polyesters	0.0
Dynamite	15-30
TNT	18.4
RDX	37.7
Ammonium Nitrate	35.0

items and its influence on the false alarm rate for a particular threshold setting. The compn of items most commonly contained in luggage was considered, the most important being clothing, typically made from natural and synthetic fibers in various combinations. The nitrogen content of common synthetic and organic fibers are compared to some standard commercial and military expls in Table 14 and it is seen that the N contents of some of these are in the same range as those of expls

In Table 15, the compn and N contents of specific items of clothing are given, and the LLL workers have also estimated the N content equivalency in terms of sticks of Dynamite (where one stick of Dynamite is taken to contain 20g of N)

From the data in Table 15, the LLL authors estimate that over half the suitcase population being processed at an airline terminal will contain the same amt of nitrogen, plus or minus a pair of shoes or a sweater. Then, a conservative estimate of the standard deviation of the nitrogen distribution may be put at 100g of N. This means that in order to have a false alarm rate of no more than 0.13%, or 3σ above the mean, the N threshold must be set at more than 300g above the average. With this threshold, an extra 300g of N is detected 50% of the time, and the added N content due to expls must go to 500g in order to be detected with 98% probability. This would represent as much N as in 25 sticks of Dynamite (at 20g per stick)

Exptl irradiations were performed at LLL to study and demonstrate the response of the fast neutron activation system to background nitrogen, and elemental interferences as applied to measuring gross nitrogen in a suitcase for the detection of hidden expls. The suitcases contained various clothing articles and nylon rods were used as mock Dynamite. A Kaman Nuclear A711 sealed tube generator with a total output of $4.5 \times 10^{10} n/sec$ was the source of 14 MeV neutrons. Suitcases were introduced by hanging them on a trolley which ran near the generator target. During irradiations the suitcase was stationary at a distance of 40cm from the neutron source. Irradiations were performed at full power for 60 sec, and the integrated neutron flux seen by the sample was $5.4 \times 10^8 n/cm^2$. The activated suitcase was then passed over two 2x8" NaI scintillation detectors, positioned side by

Table 15

Nitrogen Content and Dynamite Equivalency of Selected Items of Clothing
(from Ref 15)

Item	Composition	N Content g	N Content Equivalency as Sticks of Dynamite
Socks	¾ Orlon, ¼ Nylon	12.5	5/8
Sweater	Acrilan	105	5 1/4
Sweater	Orlon	104	5 1/4
Shirt	Orlon	75	3 3/4
Blazer	Wool	190	9 1/2
Jacket	Nylon	25	1 1/4
Shoes	Leather	164	8 1/5
Bodyshirt	Nylon	14.2	7/10
Pantyhose	Nylon	5	1/4
Nightwear	Nylon	31.2	1 1/2
Panties	Nylon	8.5	2/5
Slips	Nylon	14.1	7/10
Dresses	Nylon	25.5	1 1/4
Shorts	Nylon	22.7	1 1/8
Overcoat	Wool	218	10 4/5

side, and the outputs summed to produce a single pulse height spectrum in a multichannel analyzer counting system. Counts were taken for 200 sec after a delay of 120 sec from the end of the irradiation period

A typical γ-ray spectrum from an Al (the most popular fabrication material) suitcase is shown in Fig 14. The neutron-activated Al decay peaks are indicated in addition to the 511 keV peak from ^{13}N. Although not an interference in detecting the nitrogen γ-rays, the Al γ-rays mask higher energy γ's from Cu and other interfering elements which can also contribute to the nitrogen signal

Based on the initial statistical analysis and subsequent exptl verification, the following summary and conclusions are made in the LLL report:

"The feasibility of the fast neutron bulk activation detection system and of other bulk nitrogen measurement systems is in serious question. The nitrogen present in innocent, common, and completely legitimate materials to be found in suitcases varies sufficiently that the estimated minimum detectable amount of explosive in this system is around 25 to 50 sticks of '40% straight dynamite' (containing 20 grams of nitrogen per stick, although some types of '40% straight dynamite' contain as much as 50 grams of nitrogen per stick). This is a much greater amount than the desired minimum of 3 to 4 sticks. These limits are determined by the estimated variation in nitrogen content of the suitcase population and are independent of the nitrogen measurement technique itself"

"There are several activation techniques for measuring nitrogen in an unknown sample. One of them is to activate the sample with fast neutrons. The nitrogen is then activated in an n,2n reaction and subsequently decays with a 10 minute half-life. The annihilation gamma radiation of the positron decay product is detected. There are a great many elemental interferences to this technique. One elemental interference which is strong and seemingly indistinguishable from nitrogen in the presence of aluminum is copper. Copper is commonly found in a variety of items such as electric shavers, brass snaps, and zippers. To remove this interference, an associated technique such as x-ray radiography could be used to look for copper articles. Also high-maintenance, high-resolution germanium detectors might allow the weak higher energy copper gamma rays to be distinguished from the ever-present aluminum gamma rays"

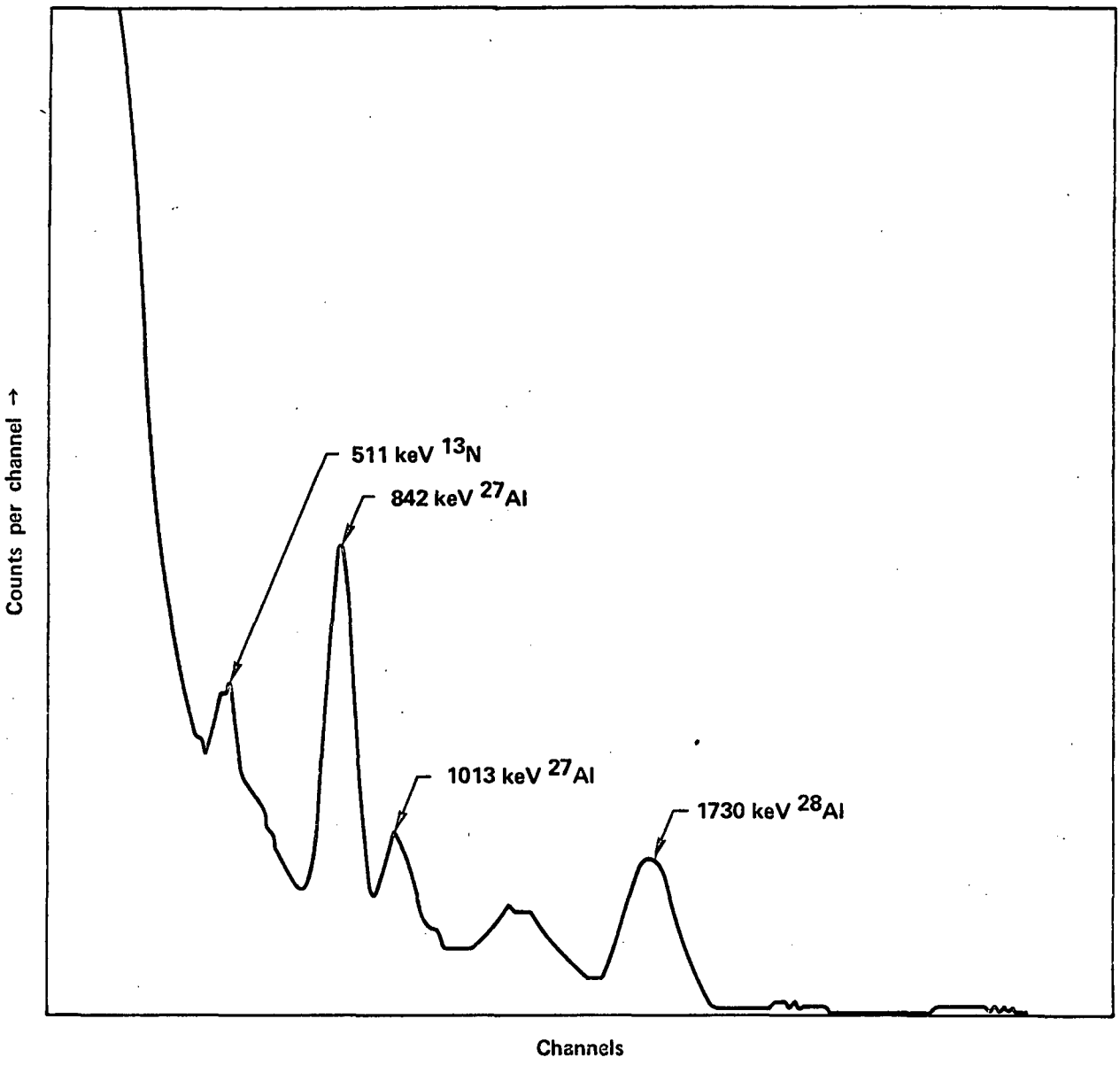


Fig 14 NaI Scintillation Detector Pulse Height Spectrum of an Aluminum Suitcase Filled with Clothing (from Ref 15)

"The system studied which uses sodium iodide scintillation gamma ray detectors is not feasible for detecting four sticks of dynamite in a typical piece of passenger luggage. It is not feasible to measure the luggage's nitrogen content, free from elemental interferences with the fast neutron technique. A threshold on the nitrogen level measured by any technique may not be set which allows both low false alarm rates and high detection probability for so small an amount of nitrogen"

At PicArsn (Ref 19), the fast neutron activation approach for detection of expls in suitcases was extended to the activation of both nitrogen and oxygen using two γ-ray detector stations in sequence. After 14 MeV neutron irradiation, the baggage is first monitored for 6.1 MeV γ-rays from the $^{16}O(n,p)^{16}N$ reaction (7.5 sec half-life), followed by measurement of the 10 min ^{13}N. Because expls are also rich in oxygen and have characteristic ratios of N/O, it was felt that this approach would increase the probability of detection with a corresponding decrease in the false alarm rate

From exploratory expts with suitcases containing 800g of RDX and a variety of common materials such as cotton, nylon, brass, Na bicarbonate, etc, a greater reliability for expls detection was observed using the dual N and O signals. For example, where the nitrogen signal is masked by the presence of Cu in brass, the oxygen signal can indicate the presence of an expl. Likewise, where the presence of Na bicarbonate masks the oxygen signal, the nitrogen activity can signal a suspect bomb. However, the PicArsn workers conclude that the additional reliability introduced by the dual-signal approach is insufficient to alter the overall pessimistic assessment, drawn by LLL, as to the feasibility of the fast neutron activation technique

The introduction of tight personal security procedures and visual or X-ray inspection of carry-on luggage at all domestic and international airports in 1972, resulted in almost complete elimination of "skyjacking" incidents in the USA. This situation has most likely interrupted or delayed the further development of automatic non-destructive inspection methods for expls in baggage at airline terminals

6) Explosives Safety in Neutron Activation Analysis

This section will deal briefly with some aspects of expls safety peculiar to neutron activation analysis expts. We are concerned here with a) the possible effect of the ionizing radiation dose on the energetic material which will cause it to be more sensitive or hazardous to normal handling as an expl, and b) the potential direct expl hazards involved in the physical and mechanical transportation of samples to and from the irradiation source and in a nuclear counting system

The effects of ionizing radiation on expls and related energetic materials have been well investigated over the years (see Radiation Effects on Explosives in Vol **9**) and are quite predictable. The properties of such materials are not measurably altered until subjected to doses in excess of a million rads. At these higher doses, the principal changes are due to chem decompn which, with very few exceptions, result in a decrease in sensitivity to mechanical stimulus and also in a dimunition of expl output. The radiation doses normally encountered in neutron activation procedures range from a few rads for 14 MeV fast neutron activation to several thousand rads for thermal neutron activations in a nuclear reactor. Thus, such doses are well under the limit at which measurable changes can occur

With regard to the hazard concern from physical and mechanical handling, the expl nature of the materials can pose a special problem. For example, during pneumatic transfer of samples in fast neutron activation, the polyethylene vials containing the expl approach speeds of 15m/sec and come to rest against a metal stop at both irradiation and count stations. However at PicArsn (Ref 13), in over 1000 irradiations and pneumatic transfers with up to 2.3g of shock-resistant secondary expls such as TNT, HMX, RDX and Nitrocellulose, no detonation occured. Similar experience has been reported at the US Naval Ordnance Station, Indian Head, Md (Ref 3) in over 100 irradiations with 40mg samples of RDX, HMX, anhydrous hydrazine and composite propInts

On the other hand, for low shock-resistant expls such as Pb Azide, Mercury Fulminate or

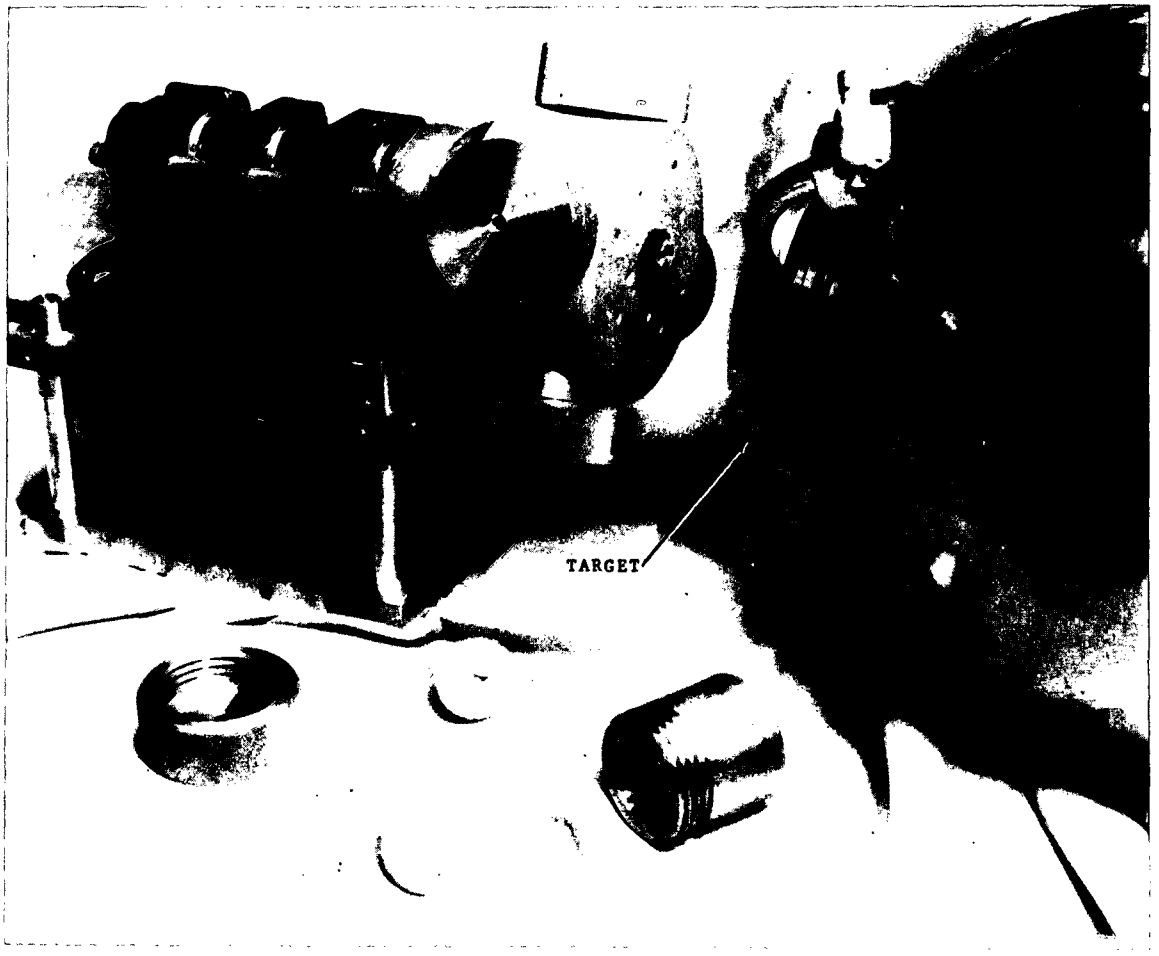


Fig 15 Special Self-shielded Irradiation Cells for Fast Neutron Activation of Initiating Explosives

initiating agents, pneumatic transfer of samples is *not* recommended. Here, only manual transfer of samples to the target and back to the count station should be performed under the most careful handling conditions. At PicArsn (Ref 22) special irradiation cells have been designed to contain initiating expls for fast neutron activation. Each cell is a hollow aluminum cylinder, 5cm in height by 4.2cm in diam with 7mm thick walls, and contains a threaded Al cap. The unit is vented in the cap and also on the bottom wall, and is designed to hold a small polyethylene vial cushioned by two polyurethane discs. These cells can withstand the detonation of up to 200mg of Pb Azide without causing fragmentation, but in practice are only used for amts of initiating expl up to 100mg. For activation expts, 4 cells are mounted on a Delrin thermoplastic wheel, 10cm in diam by 5.7cm thick, contg 4 sample wells. Fig 15 shows a photograph of the entire assembly, with the wheel containing the 4 cells mounted on a motor for single-axis rotation in front of the target of a 14 MeV Kaman nuclear sealed-tube neutron generator. Since this system is designed for manual transfer of samples only, it is limited to the analysis of elements that yield activated products with half-lives longer than about 60 sec

Written by **S. HELF**

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NUCLEAR COUNTING OF TAGGED EXPLOSIVES BY LIQUID SCINTILLATION

Because of their expl nature, the counting or radioassay of tagged expls can pose special problems with regard to safe manipulation. In particular, we are concerned here with expls such as TNT, RDX, HMX, NG, PETN, etc, tagged with low energy beta emitters such as carbon-14 and hydrogen-3 (tritium). Liquid scintillation (LS) counting has been developed over the past 20 years primarily for the radioassay of labeled biological samples in nuclear medical applications. At PicArsn this technique has also been applied successfully to the counting of radioactive expls (Refs 1, 2 & 4)

In the LS counting process, the radioactive sample is either dissolved or suspended in a special soln or gel system capable of producing visible light pulses upon interaction with the beta particles from the tracer atoms. These light pulses are then counted by conventional photomultiplier tube techniques. A LS system that has proven to be very popular for organic-soluble samples consists of the following: 4g of 2,5-diphenyloxazole (commonly called PPO) and 100mg of 1,4-di[2-(5-phenyloxazolyl)]-benzene (commonly called POPOP) in a liter of toluene. The scintillation-detection mechanism of this system is explained by Gardner and Ely (Ref 5) as follows: "

"1) Solvent (toluene) molecules are excited by incident radiation;
2) Solvent-molecule excitation energy is transferred to the PPO molecules, often called the *primary fluor* or *solute*;
3) The PPO molecules go to the ground state via the emission of photons with average wavelength of 3700Å;
4) The 3700Å wavelength photons interact and excite the POPOP molecules. The POPOP in this case is called the *secondary fluor* or the *wavelength shifter*; and
5) The excited POPOP molecules go to the ground state via the emission of photons with average wavelengths of 4200Å. These photons can be efficiently used to eject photoelectrons at the photocathode of the photomultiplier tube"

Expls tagged with ^{14}C or ^{3}H can be counted either in homogeneous soln with the scintillator system, or as a suspension of finely divided particles in a gel scintillator. These two methods are discussed separately below:

Homogeneous Solution Counting. This method is used for expls soluble in the toluene solvent. In practice, approx 50–200mg of sample, eg, TNT–^{14}C, is dissolved in 20ml of the toluene–PPO–POPOP soln in an optically clear glass vial of 22ml capacity. In the early stages of this development (Ref 2), problems arose in attempting to radioassay tagged nitrocompds dissolved in the scintillator system not containing the *secondary solute* or *wavelength shifter* POPOP. It was observed that nitrocompds served to markedly quench the scintillation process by restricting the light output and thus reduce counting efficiency. This is illustrated in Fig 1 in which eight different nitrocompds are compared with respect to relative counting efficiency as a function of concn in the toluene–PPO scintillator. In this expt, varying concns of each nitrocompd was added to the scintillator soln in which the toluene solvent was tagged with a fixed quantity of carbon-14. Counting efficiency is given as I/Io, on a semi-log scale, where I is the count rate for a particular concn of nitrocompd, and Io is the count rate of the pure scintillator (toluene–^{14}C–PPO). Each nitrocompd exhibits a characteristic attenuation of the counting rate of the pure scintillator soln. Moreover, the linearity of the data indicates a strong adherence to a Beer-Lambert exponential relationship

Helf & White (Ref 2) interpret the above behavior of the nitrocompds in inhibiting the scintillation process as one of simple light absorption rather than as a true *chemical quenching* (de-excitation process). To substantiate this, the UV and near-visible spectrum of each of the light compds in toluene–PPO soln was measured using the 50% extinction concn for each nitrocompd (as determined from Fig 1). All of the compds exhibit a definite absorption peak in the UV region. These spectroscopic data are listed in Table 1. To fully correlate these light absorption data with the curves in Fig 1, consideration must be given to the emission characteristics of the pure scintillator. PPO in toluene (4g/ℓ) has an emission range of 3400 to

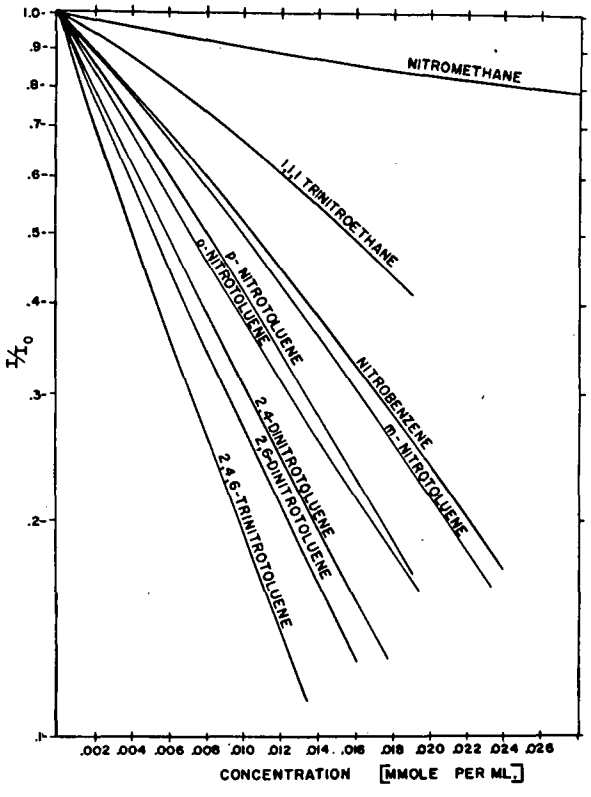


Fig 1 Quenching of the Scintillation Process by Organic Nitrocompounds in Toluene–^{14}C–PPO

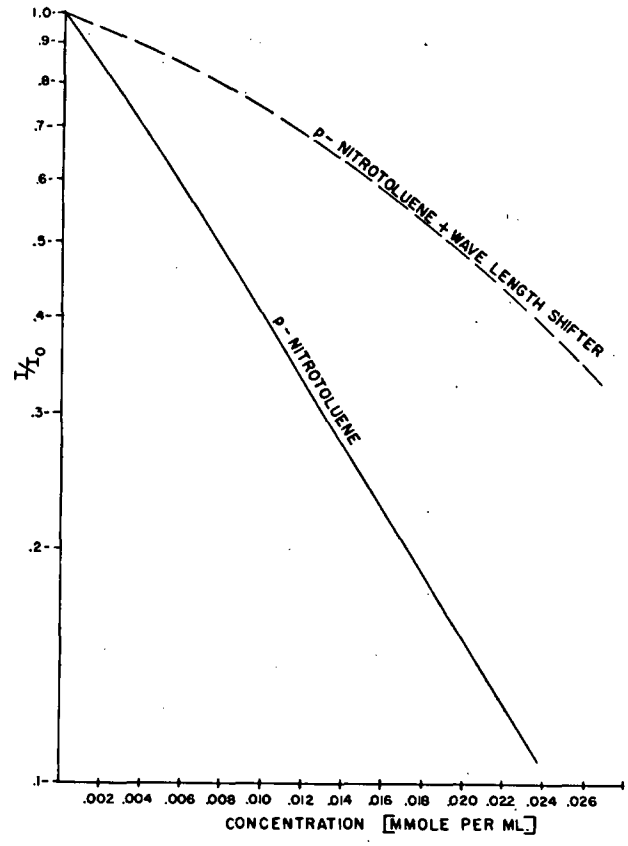


Fig 2 Quenching of Scintillation by p-Nitrotoluene in Toluene–^{14}C–PPO with and without POPOP

Table 1. Absorption Data for Nitro Compounds

Compound	Concn, Mmole per Ml[a]	Absorption Peak, Å	Absorption Range, Å	% Transmission at Peak
Trinitrotoluene	0.0040	3500	3380–4250	53
2,6-Dinitrotoluene	0.0052	3470	3380–4250	54
2,4-Dinitrotoluene	0.0060	3475	3380–4250	53
o-Nitrotoluene	0.0072	3510	3400–4250	60
p-Nitrotoluene	0.0078	3510	3390–4250	66
m-Nitrotoluene	0.0096	3500	3400–4200	68
Nitrobenzene	0.0120	3480	3420–4250	66
Nitromethane	0.0485	3150	2900–3850	98
1,1,1-Trinitroethane	0.0115	3625	3550–4100	97

[a]Solutions contained in silica cells, 1 mm thick

4300Å with a max at 3800Å. The absorption overlap of the nitrocompds is plainly evident. The position and slope of each curve in Fig 1 can be qualitatively correlated with the absorption range and % transmittance at the peak for each compd. Nitromethane, which absorbs more at shorter wave lengths and exhibits the least overlap of the toluene–PPO emission spectrum, accordingly has the least effect on the count rate of the pure scintillator

The addition of a *secondary solute* or *wavelength shifter* can serve to offset much if not all of the action of tagged nitrocompds in reducing counting efficiency. For expl nitrocompds, a shift of the emission spectrum considerably into the visible region where absorption effects are not so pronounced is clearly indicated. The *secondary solute* POPOP has been found to be most efficient for this purpose (Ref 2). This enhanced effect on the scintillation process is illustrated in Fig 2 for p-Nitrotoluene

Expl compds tagged with ^{14}C or ^{3}H can be counted by homogeneous soln liquid scintillation with efficiencies approaching 90% and 50%, respectively, for unquenched systems (100% efficiency denotes that all beta particles emitted from a sample are counted). For organic nitrocompds, counting efficiency will be somewhat reduced due to partial absorption of light pulses as discussed above, but much higher than the 1–10% obtainable with end-window Geiger detectors

Suspension Counting in Gel Scintillators. For tagged compds that are not soluble in toluene, one can resort to a technique whereby the solid sample, in finely divided form, is suspended in the liquid scintillator. By increasing the viscosity of the soln, the problem of particle settling can be eliminated. Al stearate was originally used to thicken toluene solns, and later Thixcin-R, a castor oil derivative, was introduced for the same purpose (Ref 1). The thickened, semi-transparent solns were referred to as *gel scintillators.* The two former thickening agents have since been supplanted by Cab-O-Sil (Ref 3), an aerated silica gel with a very high surface area of $200 m^2/g$. Cab-O-Sil gels, fluid enough to pour yet viscous enough to maintain stable suspensions, are prepd merely by shaking the sample together with the toluene–PPO–POPOP soln,

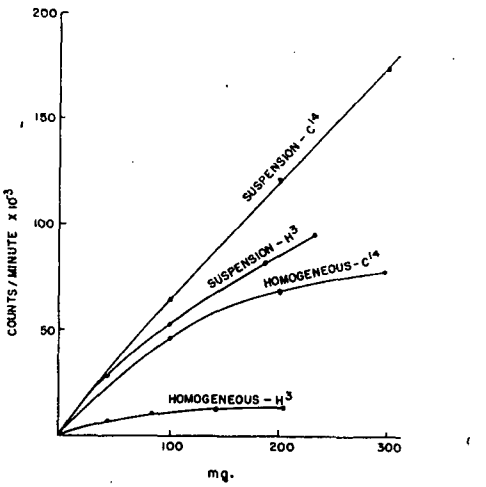


Fig 3 Comparison of Homogeneous Solution and Suspension Counting of Tagged HMX Samples

and 4% by wt Cab-O-Sil which can be added directly to the counting vial (Ref 8)

A direct comparison of homogeneous soln vs suspension counting is shown in Fig 3 for HMX samples tagged with Carbon-14 and with Tritium. Although completely insoluble in pure toluene, small amts of HMX can be dissolved in the toluene–PPO–POPOP scintillator containing dimethylsulfoxide in 25% by vol for homogeneous soln counting. The counting rates for increasing quantities of HMX–^{14}C and HMX–^{3}H are shown in 20ml vols of gel suspensions and homogeneous solns. The advantage in counting efficiency for the suspension systems in both cases is apparent. With the homogeneous solns, there is a marked decrease in counting efficiency with increasing concn because of quenching by the nitramino compd. The advantage of suspension over soln counting is even more obvious for the tritium-labeled expl. This is because the weaker light pulses produced by the action of the ^{3}H betas in the scintillator are even more strongly affected by the quenching action of HMX molecules in soln

For greater details on the techniques of LS counting in general, including the specialized nuclear instrumentation required and sample handling and preparation, see Refs 5, 6 & 7

Written by **S. HELF**

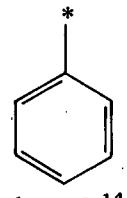
Refs: 1) C.G. White and S. Helf, Nucleonics **14**, No 10 (1956), 46 2) S. Helf and C.G. White, AnalChem **29** (1957), 13 3) D.G. Ott et al, Nucleonics **17**, No 9 (1959), 106 4) S. Helf et al, AnalChem **32** (1960), 238 5) R.P. Gardner & R.L. Ely, Jr, "Radioisotope Measurement Applications in Engineering", Reinhold Pub Corp, NY (1967), 91 6) E.D. Bransome, Jr, Ed, "The Current Status of Liquid Scintillation Counting", Grune & Stratton, NY (1970) 7) D.L. Horrocks & C.T. Peng, Eds, "Organic Scintillators and Liquid Scintillation Counting", Academic Press, NY (1971) 8) E. Rapkin, "Guide to Preparation of Samples for Liquid Scintillation Counting", New England Nuclear Corp, Boston, Mass (1975)

NUCLEAR TRACERS IN EXPLOSIVES CHEMISTRY

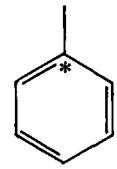
Radioactive tracer atoms have been used to study chemical reaction mechanisms in the production of TNT, RDX/HMX and NC. The results of these three independent investigations at PicArsn are summarized below:

Use of Carbon-14 to Study the Origin of Tetranitromethane (TeNMe) in TNT Manufacture. In the production of TNT from the reaction between toluene and mixed acids (nitric/sulfuric), TeNMe forms in amounts between 0.2–0.4% of the total wt of TNT. This TeNMe has been held responsible for several explns which have occurred in TNT plants, causing fatal injuries to personnel and severe damage to facilities. These explns were attributed to the presence of TeNMe in the acid fume lines and the acid storage tanks. Mixts of TeNMe and readily oxidizable materials are known to form very powerful and sensitive expl mixts. Since TeNMe is also isolated from the nitration of Nitrobenzene (NB), the TeNMe formed in the nitration of toluene may arise from the oxidation of the aromatic ring and/or methyl group. In an effort to gain more information on the origin of TeNMe from TNT production, radioactive carbon-14 (^{14}C) was used as a tracer to determine the extent to which each of the carbon atoms in the toluene skeleton of the various nitro-substituted isomers contributes to TeNMe carbon (Refs 10 & 12)

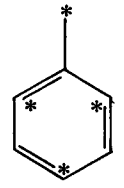
The specifically labeled toluenes in the study were:



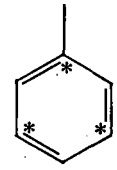
toluene-7-^{14}C



toluene-1-^{14}C



toluene-2,4,6,7-^{14}C

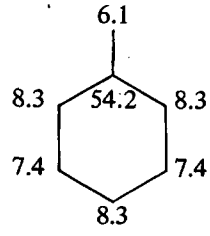


toluene-1,3,5-^{14}C

where the asterisk denotes the presence of the labeled carbon.

The contribution of the carbon atoms from the 1- and 7- positions to TeNMe carbon were obtained by determining the specific activity of the TeNMe isolated from the nitration of toluene-1-^{14}C and toluene-7-^{14}C, respectively. Similarly, by nitrating toluene-1,3,5-^{14}C, it was possible to determine the 3- and 5-contributions, since the contribution of the 1-position could be subtracted and the 3- and 5-positions were considered to be equivalent. Finally, the contributions of the 2-, 4- and 6-positions were determined from the nitration of toluene-2,4,6,7-^{14}C by subtracting the contribution of the 7-position. An approximate contribution for each of these positions (2-, 4- and 6-) was obtained by considering them to be equivalent

The percentage of TeNMe carbon arising from each position in the toluene carbon skeleton is summarized as follows:



The largest single contribution (54.2%) is from ring carbon-1 attached to the methyl group, and the bulk (94%) of the TeNMe formed is via oxidation of the aromatic ring

Additional ^{14}C-tracer studies were conducted to determine the specific isomer participation for TeNMe formation. In the dinitration mixt there are six isomers present: 2,4-, 2,6-, 2,3-, 2,5-, 3,4- and 3,5-Dinitrotoluene (DNT). It was observed that 83% of the TeNMe formed from carbon-1 came from the DNT isomers derived from m-Nitrotoluene. The relative participation of DNT isomers for TeNMe formation is summarized in Table 1

Table 1

Dinitrotoluene Isomer	Isomer in Dinitrotoluene mixt, %	Participation rel to 2,4- and 2,6-Dinitrotoluene
2,3-	1.16	58.5
2,5-	0.56	93.6
3,4-	2.20	34.1
3,5-	0.08	793.0
2,4- 2,6-	96.0	1.0

The values in the last column of Table 1 represent the factors by which the TeNMe concn would increase over that of the total TeNMe arising from the nitration of 2,4- and 2,6-DNT if each of these isomers constituted 96% of the DNT mixt. Thus, the unsymmetrical Dinitro isomers of toluene, which constitute only 4% of the mixt contribute most heavily to the formation of TeNMe via oxidation of the aromatic ring

From a chemical kinetic aspect, one can interpret these data such that the rate of nitration of the meta-DNT isomers is slower than the rate of nitration of the 2,4- and 2,6-DNT's. The values reported in the last column of Table 1 can thus be considered as a measure of the speed of nitration of the various isomers. That is, the larger the value of the participation in TeNMe formation, the slower the rate of nitration of the isomer to TNT. Therefore, according to these results, the nitration of 2,3-, 2,5-, and 3,4-DNT should be slower than that of 2,4- and 2,6-DNT; the nitration of 3,5-DNT should be even slower

These data can also be explained from considerations of the profound effect that the groups attached to the aromatic ring have on both orientation and ease of introduction of the entering group. In the trinitration step, the orientation of the third nitro group is determined by one of the following effects: (a) Reinforcement of the directive influence of the methyl and two nitro groups. For example, in the nitration of 2,4-DNT, the methyl group favors substitution at the 6-position. The nitro groups also favor substitution at this position. The same situation exists in the nitration of 2,6-DNT. When total reinforcement occurs, the rate of nitration is rapid. (b) Entering nitro group is directed to the same position by the methyl group and one nitro group. This type of directive influence is observed in the nitration of 2,3-, 2,5- and 3,4-DNT. Since there is only partial reinforcement, the nitration proceeds at a slower rate and therefore more oxidation of the ring takes place. (c) No reinforcement of directive influence. This is observed in the nitration of 3,5-DNT. The nitration of this compd should proceed at a much slower rate, and attempts to nitrate it have been unsuccessful. Thus it will be subject to much oxidation and will contribute heavily to TeNMe formation

The formation of TeNMe from the various DNT isomers was subsequently also studied at the Stanford Research Institute (Ref 17). The results agreed with those described above in that TeNMe was observed from all DNT isomers with the exception of the 2,4-DNT. No TeNMe was formed from the 2,4-isomers, whereas very small amounts were reported in the PicArsn study. However, the Stanford workers conjectured that the scale used in their study may have been too small to produce detectable quantities of TeNMe

Tracer Studies on the Nitrolysis of Hexamine to RDX and HMX. The formation of RDX and/or HMX molecules from the nitration or nitrolysis of Hexamethylenetetramine (Hexamine) is a complex process and has been postulated to take place *via* two separate paths. One involves the selective cleavage of the Hexamine molecule to the appropriate cyclic nitramine (RDX, HMX or both) depending on the specific

nitrolysis conditions. The other assumes the complete degradation of the Hexamine molecule to methylene and amino or methyleneamino type fragments, followed by recombination of these fragments to a particular cyclic nitramine, or combination of both, again depending on the reaction conditions

Detailed reviews of the chemistry of Hexamine and its nitrolysis to RDX, HMX and other related cyclic and linear polynitramines, including discussions of various postulated reaction mechanisms, are given by Smolin and Rapoport (Ref 9) and by Wright (Ref 15). Methods for the prepn of RDX are also described in Encycl **3**, C611 to C615

The following very brief discussion on synthesis of cyclic polynitramines is given merely to provide the historical background necessary to discuss the tracer studies:

The original practical method of RDX synthesis, as developed by Hale of PicArsn in 1925 (Ref 1), involves treatment of Hexamine with a large excess of abs nitric acid and results in 40% yield based on 2 moles of RDX from 1 mole of Hexamine. Ross and Schiessler (Ref 15), in 1940 at McGill University, succeeded in synthesizing the same compd from paraformaldehyde (p-CH_2O) and AN in Ac_2O in 35% yield based on p-CH_2O. (Subsequently, after WWII, this was found to be identical to the secret process of Eble, developed in Ger). The McGill workers postulated that, in their process, methylene nitramine (CH_2=N–NO_2) is formed as an intermediate, which then trimerizes to RDX. However, the existence of methylene nitramine has never been proven. Werner Bachmann (Ref 2) of the University of Michigan, during WWII, conceived of a "combination process" in which the Hale nitrolysis of Hexamine would occur first, and the remaining methylene would be converted to RDX by the Ross-Schiessler route. Using three feed streams: Ac_2O, Hexamine in acetic acid, and AN in nitric acid, the Bachmann process results in an 80% yield of RDX (two moles from one of Hexamine), including a small amount of HMX. It should be noted that HMX is formed as a by-product in all three of these processes along with a variety of linear polynitramines. Subsequently, workers at the Holston Ordnance Works (now the Holston Defense Corp) (Ref 3) and at PicArsn (Ref 4) modified the original Bachmann conditions to yield a product more rich in HMX over RDX. At PicArsn, it was also demonstrated that by including a small quantity of p-CH_2O with the initial reactants, the yield of HMX/RDX mixt was increased to over 90% containing 85% HMX

Although direct evidence in support of either the selective cleavage of Hexamine or the recondensation from small fragment mechanism is lacking, the former concept has been and still is preponderantly favored by the more classical researchers in this field. Smolin and Rapoport (Ref 9), in reviewing all of the work prior to 1959 on Hexamine nitrolysis with respect to isolation and identification of aceto compd derivatives, conclude that "the evidence then is overwhelming with respect to the aceto compds and all major and minor reaction products of Bachmann and Schiessler-Ross reactions that their synthesis proceeds by first the reformation of Hexamethylenetetramine followed by selective solvolytic (nitrolytic and acetolytic) cleavage rather than by synthesis of these products directly from fragments. The Schiessler-Ross reaction represents the second phase of the Bachmann reaction and constitutes a synthesis of Hexamethylenetetramine followed by a Hale type solvolysis."

George F. Wright (Ref 15) of the University of Toronto, is equally adamant in his support of the selective cleavage route and is very explicit in illustrating his proposed mechanism (Fig 2)

Wright assumes that Hexamine is stabilized in soln as the di-nitric acid salt. With strong nitric acid, as in the Hale process, nitrolysis at *b,b'* leads to Compound A. Further nitrolysis of A at *c* results in RDX and dimethanolnitramine, $O_2NN(CH_2OH)_2$. A can also nitrolyze *d* to give Compound B which upon loss of CH_2O can also result in RDX. It is noted, however, that neither A nor B has been isolated and that the existence of dimethanolnitramine is deduced by isolation of its diacetoxy analogue from the spent nitrolysis liquor. Under milder nitrolysis conditions, such as prevail in the Bachmann process, DPT is first formed from hexamine dinitrate via nitrolysis at *a,a'*. Upon further nitrolysis at *f,f'*, HMX is formed. Wright also explains the formation of linear polynitramines

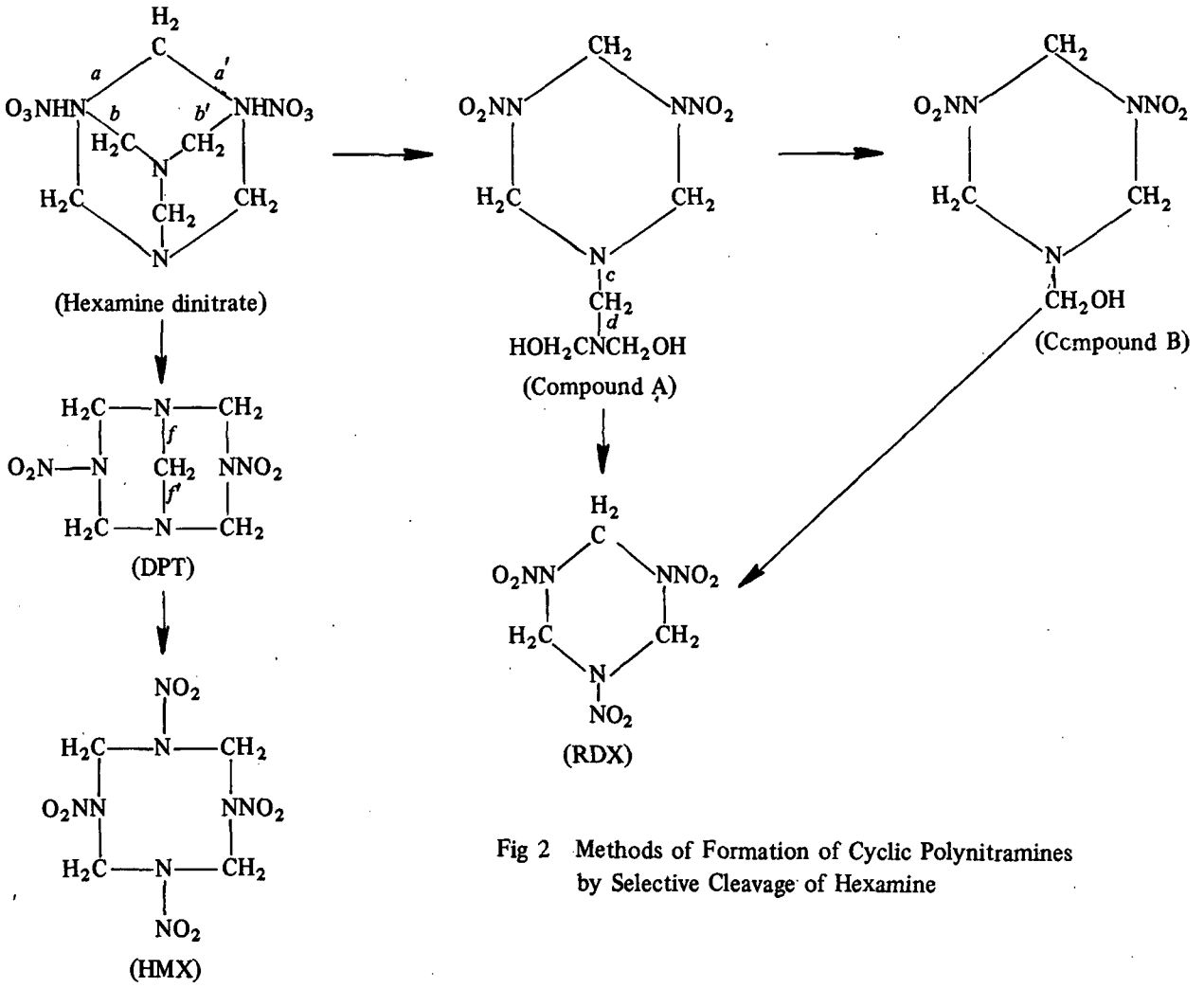


Fig 2 Methods of Formation of Cyclic Polynitramines by Selective Cleavage of Hexamine

by the selective cleavage of A, B and DPT via different modes. In these various processes, where CH_2 groups are split off, they appear as CH_2O, which reform to Hexamine and thus "go thru the circuit" again. Wright designates this entire sequence of reaction schemes as "nitrolysis-resynthesis". He makes it clear, however, that any resynthesis from fragments must go thru the reformation of Hexamine

At PicArsn, the nitrolysis of Hexamine was studied using radioactive carbon-14 (Refs 7, 11) and stable nitrogen-15 (Ref 14) as tracers. Reaction conditions employed were a modification of the Bachmann Process (Ref 2) favoring the formation of HMX over RDX. In particular, the role of small amounts of added paraformaldehyde (p-CH_2O) in influencing higher yields of HMX, was examined. Briefly, a typical prepn is: To a flask containing a slurry of paraformaldehyde, acet acid and a trace of Ac_2O, the following reagents are added simultaneously at controlled rates over a 15-minute period: (a) a soln of Hexamine in gl acet acid, (b) Ac_2O, (c) a soln of AN in nitric acid. The reaction temp is maintained at 44 ± 1° thruout this procedure. The mixt is aged for 15 minutes and a second portion of Ac_2O and AN–nitric acid is added again over a 15-minute period. This reaction mixt is aged for another 60 minutes. Hot w is then added and the slurry is refluxed for 30 minutes. The HMX/RDX product is obtained by chilling and filtering this mixt. This procedure is diagrammatically illustrated in Fig 3

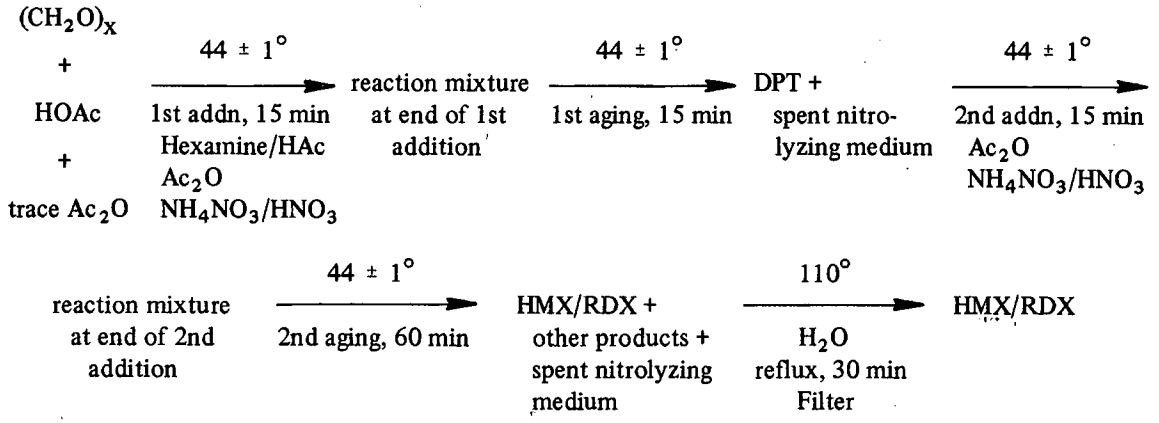


Fig 3 Flow Diagram for the Nitrolysis of Hexamine

From this process, the yield of HMX/RDX is approx 90% of theory (based on Hexamine molecule), and 85% of this mixt is HMX

The tracer expts conducted to study the mechanism of nitrolysis and product formation in the above process are briefly outlined in Table 2

Table 2

Tagged Species	Products Isolated & Assayed for Tagged Atom Content
Hexamine-^{14}C	HMX, RDX
Paraformaldehyde-^{14}C	HMX, RDX
Paraformaldehyde-^{14}C	DPT
$^{15}NH_4NO_3$	HMX, RDX

In the carbon-14 expts, HMX/RDX product was isolated qualitatively, separated into its components, and each component assayed for carbon-14 beta radioactivity using a liquid scintillation counting technique (Ref 11). DPT-^{14}C was isolated as an intermediate product from the reaction mixt and similarly radioassayed. For the nitrogen-15 tagged AN expts, HMX and RDX were assayed mass spectrometrically for $^{15}N/^{14}N$ ratios from which atom $\%^{15}N$ contents were calcd. In the course of these expts, each tagged species was added initially and also at subsequent stages of the reaction process. The important observations and results are summarized as: (1) During the first stage in the addition of reactants and aging, all of the original Hexamine and p-CH_2O is consumed and DPT is the major product isolated. The quantity of DPT isolated is approx doubled when p-CH_2O is included. In the formation of DPT, a complete equilibration of carbon atoms occurs between Hexamine and p-CH_2O. When the p-CH_2O is added to the reaction mixt at later intervals during this first reaction stage, there are corresponding decreases in the degree of carbon atom equilibration as well as in the amount of DPT isolated; (2) If the p-CH_2O is added to the reaction medium before the second addition of reagents, a complete equilibration of carbon atoms occurs between the p-CH_2O and DPT (and any other possible precursors of cyclic nitramines) in the formation of HMX/RDX. When the p-CH_2O is added at later intervals during the second aging period, there is a decrease in the degree of equilibration as well as in the yield HMX/RDX; (3) CH_2 equilibration between Hexamine, DPT and p-CH_2O is independent of ammonium ion concn; (4) The addition of more than the normal quantity of p-CH_2O results in complete equilibration of $-CH_2$ groups, although the yield of HMX/RDX does not increase; (5) CH_2 group exchange before chemical reaction between p-CH_2O, Hexamine or intermediate or final products does not occur; (6) Under these reaction conditions (modified Bachmann Process), AN does not condense independently with p-CH_2O to yield HMX and RDX; (7) Amino nitrogen, from Hexamine and AN, equilibrates in the formation of DPT; however this is due to exchange and not reaction; (8) In DPT, upon reacting further to yield HMX and RDX, only the nitrogen atoms in the $-(CH_2)_3N$ species exchange with amino atoms in AN; ie, the nitro substituted amino nitrogens fail to exchange; and

(9) In the absence of p-CH_2O, HMX and RDX are derived mainly from Hexamine nitrogen with about 5% of the RDX derived from AN. In the presence of p-CH_2O, 7% of the HMX and 40% of the RDX are formed from AN

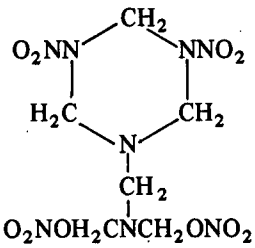
The interpretation drawn from the above results is that in the first reaction stage, Hexamine degrades non-selectively and completely to methylene containing fragments which then recondense to form DPT. Similarly, in the second stage, DPT also degrades non-selectively, with all $-CH_2$ groups chemically equivalent, to reform the insoluble cyclic nitroamines which remain stable in the spent nitrolysis medium. Therefore, the relative ratio of HMX to RDX is not controlled by the selective cleavage of a large molecule but is rather influenced by the particular conditions controlling the recombination of a common methylene-containing fragment such as $HOCH_2NHNO_2$ or $[-CH_2\overset{|}{N}-NO_2]$. The authors postulate that the addition of p-CH_2O increases the concn of methylene-containing fragments which exist in the precursors to HMX/RDX, and thus accounts for the small increase in yield of these products

The path of amino nitrogens in this process is more difficult to deduce from the results of the tracer expts because the rate of exchange of amino nitrogens among the various reactant species is faster than the rate of reaction. Nevertheless, it is clear that the C–N bonds in the unnitrated amino group, $-CH_2-NH-CH_2-$, are highly labile in the nitrolysis medium and are readily subject to rupture; on the other hand, once formed, the nitramino group, $-CH_2-N-NO_2$, is completely stable, and the corresponding C–N and N–N bonds are neither subject to exchange nor are they readily degraded in the spent nitrolysis medium

Although the results of these tracer studies with carbon-14 and nitrogen-15 were published in 1960 and 1965, respectively, there has been no stampede, on the part of polycyclonitramine chemists to get on board the "synthesis from fragments" bandwagon. On the contrary, in reviewing these tracer studies, Wright (Ref 15) actually concludes that these "results are not contradictory to the nitrolysis-resynthesis postulation" involving the reformation of Hexamine. An apparent weakness, however, in Wright's thesis, as illustrated in Fig 2, is the assumption that HMX can only be formed thru the precursor DPT. The PicArsn studies (Refs 7, 11) did substantiate the formation of DPT as the major intermediate under Bachmann reaction conditions. However, HMX has been identified or isolated as an impurity or minor product in almost every synthetic route leading to RDX, including conditions where DPT is not necessarily formed

In addition to the Ross-Schiessler process, utilizing p-CH_2O and AN, the synthesis of RDX/HMX mixts has also been reported starting with other small molecules (Ref 7), namely, methylamine nitrate; methylenediamine dinitrate; and nitramine (NH_2NO_2) in combination with CH_2O. In these reactions, the intermediate formation of Hexamine or a cyclic analog, is not necessarily established

Bell and Dunstan (Ref 16) have reported that the addition of methylenedinitramine to Hexamine nitrolysis mixts, aged at 0° for 5 and 120 minutes, gave RDX in yields of 120 and 106%, respectively, compared with 52 and 83% in the absence of the dinitramine. However, rather than supporting a synthesis from small molecules, the authors contend that these results substantiate the existence of a postulated bis(nitroxymethyl) aminomethyl precursor of RDX, namely:



$O_2NOH_2CNCH_2ONO_2$

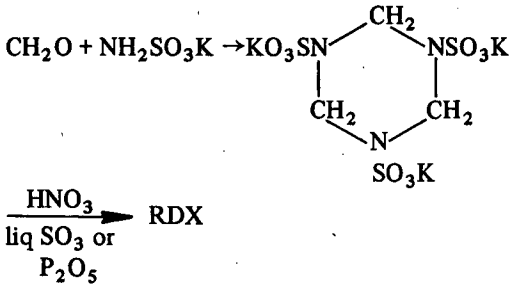
It should be noted that this intermediate is the dinitroxy derivative of Compound A, postulated as the precursor for RDX by Wright according to Fig 2

The synthesis of RDX via the Triazine Process (Ref 13) involves the condensation of formaldehyde with acetonitrile followed by nitration:

$$3CH_2O + 3CH_3CN \rightarrow [CH_2NCOCH_3]_3 \xrightarrow{3HNO_3} RDX + 3CH_3COOH$$

Although the yield of RDX is high, the economic advantage of the Thatcher Process over Hexamine nitrolysis is yet to be demonstrated (Ref 19)

RDX has also been prepd in high yields by the nitration of the condensation product of CH_2O and potassium sulfamate (Wolfram Process) (Ref 15):



$$CH_2O + NH_2SO_3K \rightarrow KO_3SN(CH_2)_2N(CH_2)_2NSO_3K$$

$$\xrightarrow[\text{liq } SO_3 \text{ or } P_2O_5]{HNO_3} \text{RDX}$$

This method is not economical because of the high cost of the starting materials

Solomon, of the Illinois Institute of Technology Research Institute (IITRI), has reported the synthesis of HMX from the condensation of straight chained nitramines, bis(hydroxymethyl) methylene dinitramine and methylene dinitramine. However, details of this work were not available as of this writing

Thyagarajan and Majumdar (Ref 18) have studied the condensations of urethanes with formaldehyde under various exptl conditions and accomplished the selective synthesis of either six-membered 1,3,5-triazines or eight-membered 1,3,5,7-tetrazocines. These are non-nitrated analogs of RDX and HMX respectively. Their results are summarized in Fig 4

Condensation of methyl urethane, $H_2NCOOCH_3$, with CH_2O gives rise to the methylene diurethane (III) and this compd, under different specific conditions of refluxing, results in the various specific linear (IV & V) and cyclic products (I & II) as shown. The observations of relevance here are that the various products, both linear and cyclic, are interconvertible under acid catalysis *including I into II and conversely.* The authors have thus shown that "the condensation of urethanes with formaldehyde under acid catalysis affords a variety of products, depending upon the reaction temp and length of reaction time. Products of such condensation are capable of reversal to their constituent components and resynthesis to simple or complex products". In the opinion of this writer, the analogy of the observations with these systems with those observed from the tracer expts with Hexamine nitrolysis is striking

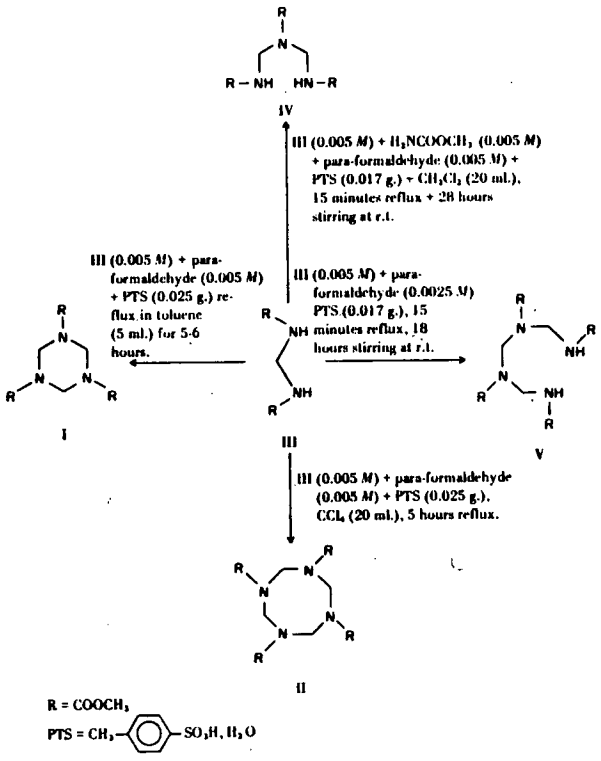


Fig 4 Condensation Products of Urethane with Formaldehyde

In conclusion, there appears to be some supporting evidence, other than these tracer studies, that the synthesis of HMX and RDX molecules can be accomplished thru a build-up from single methylene-containing species or other small molecules, and that this route can also take place via a total degradation and resynthesis from molecules such as Hexamine. However, the development of an economical process for the large scale production of these expl nitramines, in particular HMX, via a method precluding the use of Hexamine, is yet to be accomplished

Use of Sulfur-35 to Characterize the Sulfate Content in Nitrocellulose (NC). Military grades of NC are prepared by nitrating a suitable grade of cellulose, either cotton linters or wood pulp, with a mixt of nitric and sulfuric acids. After nitration, the great bulk of the spent acid is removed by centrifuging, and the NC is drowned in w. In the USA, a long stabilization treatment follows, consisting of (a) three preliminary

boils in acidulated w, (b) beating to a desired fineness, (c) four additional boils, and (d) several cold w washes. This prolonged treatment, which is considered necessary to obtain NC with a satisfactory degree of stability, has been developed empirically (See Vol **2**, C107). Numerous exptl studies have been made to explain the need for the extended stabilization treatment and, if possible, to shorten it. Analytical data have been obtained which show that the prestabilized, ie, freshly prepd and drowned NC contains appreciable quantities of sulfate (up to about 1%). Instability of NC has been generally attributed to the presence of this sulfate content, and the prolonged boiling and beating process is considered by many workers as necessary to remove this impurity. The literature contains many reports of investigations dealing with the nature of the sulfate content in NC and its effect on the stability of the product (Ref 5). However, the subject is replete with diverse and conflicting statements. The different theories of the stabilization of NC, particularly as related to the role of the sulfate impurity, can be summarized as follows:

Theory A. Unstabilized NC contains appreciable quantities of chemically combined sulfur in the form of sulfate esters plus occluded free sulfuric acid. The primary step in the stabilization is hydrolysis of the sulfuric esters which is promoted by boiling the NC in an acid medium. The esters, present as the half ester, $ROSO_2OH$, and to some extent as the full ester, $ROSO_2OR$, (where R = NC residue), are considered to be much more easily hydrolyzed than their metallic salts, $ROSO_2OM$, which are believed to form in the presence of alkaline or alkaline earth solns

Theory B. All NC before stabilization, contains a certain amount of residual nitrating acids consisting of both nitric and sulfuric acids, but mostly the latter. The occluded sulfuric acid is trapped in the fine structure of the NC fibers and renders the products less stable, especially at elevated temps. The amount of sulfate esters present, if any, is small in quantity and easily hydrolyzed by merely washing the fibers with cold w. Boiling the NC in a w or acid medium enhances the diffusion of sulfuric acid from the inner structure of the fibers and facilitates removal of the acid by subsequent washing

Theory C. Instability of NC is due to the presence of three types of impurity. These are: occluded free sulfuric acid, sulfuric hemiesters and full esters, and nitrated degradation products of cellulose. The hemiester content is less in more highly nitrated cellulose, whereas the free sulfuric acid content is greater. The acid boil stabilization procedure removes all three types of impurity

Theory D. The presence of small quantities of sulfate, either as combined or free acid which is readily removed, does not greatly affect the stability of the NC. The real cause of instability is the presence in more intimate association with the NC, of other compds which cannot be removed by exhaustive washings. These compds which are acidic in character and exist in small quantities, are formed during the nitration of the cellulose. They can be removed only by prolonged boiling in either w or alc. The presence of acid or salt solns does not increase the ease of stabilization during boiling

The nature and amount of sulfate content present in NC and the mechanism for its removal during the stabilization process was investigated at PicArsn using the radioactive tracer, sulfur-35 (Ref 5). Through the use of this radionuclide, a rapid and sensitive radiometric method for sulfate analysis in NC samples was developed by tagging the sulfuric acid in the nitrating mixed acid. The magnitude of the beta activity of the sulfur-35 in the sample is directly proportional to the total sulfate content present, either as free sulfuric acid or some chemically combined state. With this tracer technique a large number of sulfate determinations are easily performed at one time. Samples of NC with as little as 0.004% sulfate were accurately analyzed by this method (Ref 6)

Determination of the nature of the sulfate content was attempted by following the concn of this impurity in two ways: (1) during the course of laboratory simulated industrial stabilization procedures, and (2) from successive dissolutions of unstabilized NC samples in various solvents and subsequent repptn from non-solvents. This approach was based on the premise that free occluded sulfuric acid would be released from the fibers by the soln-pptn treatment, whereas chemically combined sulfate would remain unaffected. The full details of the various expts can be found in Ref 5; some typical results are shown in Table 3 for four samples of NC of different nitrogen content

Table 3

Comparison of Sulfate Removal in Samples of Nitrocellulose by Acid Boil and Precipitation Treatments

Percent Nitrogen	Percent Sulfate of Nitrocellulose Samples: Prior to Treatment	After Treatment by THF-Benzene Precipitations	After Treatment by 56-hr Acid Boil	After 56-hr Acid Boil plus treatment by THF-Benzene Precipitations
13.09	0.72	0.05	0.13	0.05
13.37	0.80	0.05	0.13	0.04
13.13	0.97	0.09	0.11	0.09
13.35	0.84	0.05	0.05	0.05

The important observation from the data in Table 3 is that NC samples subjected to acid boil followed by tetrahydrofuran (THF)-benzene treatment yielded essentially the same sulfate contents as samples subjected to THF-benzene treatment alone. From this the authors interpret "that sulfate contents from THF-benzene treatments actually represent absolute values of the difficult-to-remove sulfate which may very well be true sulfate ester". It is also tentatively concluded that approximately 90% of the original sulfate content in unstabilized NC is readily removable sulfuric acid with the remainder the "more difficult-to-remove" sulfate ester. Dilute acid boil treatment of NC for 56 hours does not eliminate all of the free sulfuric acid and leaves the "difficult-to-remove" sulfate practically unchanged

In a later investigation, radioactive sulfuric acid was also used to study the removal of occluded acid from freshly nitrated cellulose by cold saline leaching (Ref 8). It was observed that extraction with Na sulfate soln causes a greater release of acidity than extraction with distilled w. Of the total acidity released, the bulk is sulfuric acid and the remainder, nitric acid. The amount of acidity released by saline leaching is inversely related to the nitrogen content of the NC, that is, less acid is extracted when the NC has a higher nitrogen content. The same reference also describes the evaluation of a cold saline leach in combination with short aq boils to produce a stable NC from cotton linters. The 100° vacuum stability test showed that a combination of a 4-hour cold saline leach and a 10-hour w boil, before the standard beating and poaching operation, resulted in a pyrocellulose (12.6% N) comparable in stability to a sample boiled for 40 hours. However, the substitution of a saline leach for boiling time appeared to have no advantage for high grade (13.45% N) NC. The use of saline leaches for the stabilization of NC was judged to be of no particular advantage

Written by **S. HELF**

Refs: 1) G.C. Hale, JACS **47** (1925), 2754 2) W. Bachmann & J. Sheehan, JACS **71** (1949), 1942 3) R.B. Herring et al, "The Laboratory and Pilot Plant Preparation of HMX", Holston-OrdWorks Report No **20-T-14**, Holston, Texas (1952) 4) J.P. Picard et al, "An Improved Batch Process for the Preparation of HMX", PATR **2059** (1954) 5) T.C. Castorina, S. Helf, H.A. Aaronson & J.V.R. Kaufman, "Characterization of the Sulfate Content in Unstabilized Nitrocellulose", PATR **2107** (1955) 6) S. Helf et al, AnalChem **28** (1956), 1465 7) T.C. Castorina et al, "The Role of Paraformaldehyde in the Preparation of HMX by the Picatinny Process", PATR **2481** (1958) 8) R.N. Shelley & S. Helf, "Use of Saline Leaches to Stabilize Nitrocellulose", PATR **2550** (1958) 9) E.M. Smolin & L. Rapoport, "The Chemistry of Heterocyclic Compounds – s-Triazines and Derivatives", Chapt 10, Interscience, London (1959) 10) F.S. Holahan, T.C. Castorina, J.R. Autera & S. Helf, "The Use of Carbon-14 as a Tracer to Study the Origin of Tetranitromethane in TNT Manufacture", PATR **2695** (1960) 11) T.C. Castorina et al, JACS **82** (1960), 1617 12) F.S. Holahan et al, JACS **84** (1962), 756 13) D.W. Thatcher,

USP 3178430 (1965) 14) T.C. Castorina & J.R. Autera, IEC **4** (1965), 170 15) H. Feuer, Ed, "The Chemistry of the Nitro and Nitroso Groups", Part 1, Chapt 9 (G.F. Wright), Interscience, NY (1969) 16) J.A. Bell & I. Dunstan, JCS(c), **1969**, 1559 17) H.M. Peters et al, "Improved Synthesis for TNT Production", SRI Project **PYU-7360-011**, Final Report, Contract No DAAG 05-68-C-0723, Menlo Park, Calif (1972), 59 18) B.S. Thyagarajan & K.C. Majumdar, JHeterocyclicChem **11**, 937 (1974) 19) L.F. Albright & C. Hanson, Eds, "Industrial and Laboratory Nitrations", Chapt 23 (E.E. Gilbert et al), ACS Symposium Series 22, American Chemical Society, Washington, DC (1976)

Nudets. A US nuclear detonation warning system. A matrix of seismic sensors spread thruout the USA intended to estimate the point of impact and power of nuclear-detonated nuclear warheads
Ref: E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 147-R

Nuevo Anagón. A Spanish Ammonal contg AN 70, Al-Zn alloy 10 & charcoal 10%. See also Vol **1**, A292-L
Ref: A. Pérez Ara (1945), 247

Nuodex. See under Laminac 4116 in Vol **7**, L3-L

Nutation. The axis of a spin-stabilized projectile in flight is subject to spasmodic small conical vibrations, called nutation, which should not be confused with yaw (qv) or precession (qv). The instant a spinning projectile leaves a gun, the turbulence produced by the release of propInt gases causes nutations to occur. Their amplitude is usually small, and, in the case of concentric fast spinning projectiles, they disappear due to the action of equal and opposite centrifugal forces. If the projectile spin is insufficient, the amplitude of the nutations increases, soon causing the projectile to tumble in flight
Refs: 1) R. d'Adhémar, "Sur le Mouvement Pendulaire des Projectiles Stables", MAF **8**, 3rd fasc (1929); Ibid **9** 3rd fasc (1932); Ibid **12**, 2nd fasc (1933); Ibid **13**, 939–78 (1934) 2) R. d'Adhémar, "Théorie du Mouvement Gyroscopique des Projectiles", AnnSocSciBruxelles **55**, A (1935) 3) K. Popoff, "Sur le Mouvement Pendulaire des Projectiles", MAF **15**, 1133 (1936); "Sur les Intégrations des Equations Differentielles du Mouvement Pendulaire des Projectiles", MAF **16**, 735 (1937); "Sur le Mouvement Pendulaire du Projectile Autour de son Centre de Gravité. Mouvement de Nutation", MAF **17**, 33 (1938) 4) R. Sutterlin, "Sur le Mouvement de Nutation des Projectiles au Départ et sur son Amortissement", MAF **17**, 71–118 (1938) 5) T.Felstyn, MAF **19**, 378, 397 (1940) 6) J. Dupuis, "Influence de la Nutation Initiale sur les Portées et Durées de Trajet", MAF **24**, 555–75 (1950) 7) H.V. Wagner, Ordn **37**, 341 (1952) 8) OrdTechTerm (1962), 206-R

NX (Explosif) (Nitrate d'ammoniaque-Xylite). A Fr military expl consisting of AN 70 & Trinitroxylene 30%, used as a bursting charge in projectiles
Ref: Anon, "Handbook of Foreign Explosives", **FSTC 381-5042**, US Army Foreign Science and Technology Center (Oct 1965), 131 & 229

Nyalite. A low-freezing expl, contg Nitrostarch, prepd in 1905 at Repaune, Fr by the DuPont Co to compete with **Masurite** (qv) and **Flamless Securites** (See Vol **6**, F50-L). It was discontinued shortly after its introduction as improved permissible expls were developed
Refs: 1) VanGelder & Schlatter (1927), 586 2) Urbański **2** (1965), 419

Nylon, Aminoethyl. See under Aminoethylnylon (AEN) and Its Perchlorate (AENP) in Vol **1**, A205-L

Nysebastine. A Dynamite patented in 1876 by Fahneljelm contg NG 45–48, charcoal 15–35, Na or K nitrate (or chlorate) 5–25, & Na carbonate 5% max
Ref: Daniel (1902), 586

Nysol. An expl prepd by nitrating a soln of naphthalene in xylene, and used as an ingredient of low-freezing Dynamites
Ref: Bebie (1943), 112

0

O, Explosifs du type. Fr designation for Cheddites. See Vol **2**, C155-L ff

Oakley Quarry Powder. A blasting expl consisting of AN and Tetryl
Refs: 1) Marshall, Dict (1920), 69 2) Thorpe's Dict **4** (1940), 487

Oaklites. Brit expls of the "Carbonite" type (see Vol **2**, C61-R) contg NG 24.0–26.0, NC 0.5–1.5, K nitrate 32.5–35.5, woodmeal 33.5–36.5 & Mg carbonate 0.5%
Ref: Naoûm, NG (1928), 402

Oare Powders. Expls manufd in 1898 by the Cotton Powder Co, Ltd, of Faversham (Kent), Engl. They originally contained, as the main ingredients, Chile saltpeter (Na nitrate) and Dinitrobenzene, but later the latter ingredient was replaced by TNT
Ref: Daniel (1902), 587

Oarite. An expl patented by Trench in 1891 contg NG 20, NC 10, Dinitrobenzene 10, K and Ba nitrates 60%
Refs: 1) Daniel (1902), 587 2) Giua, Trattato **VI** (1) (1959), 386

Oat Hulls, Nitrated. Proposed as an ingredient of expls in combination with such oxidizers as AN, Na nitrate, etc. Nitrated balsam pulp or bagasse (see Vol **2**, B4-L) could also be used
Ref: W.deC. Crater, USP 2096089 (1937) & CA **32**, 357 (1938)

Obermüller's Test. One of the tests for detg the stability of NC based on heating the sample in a vacuum and measuring the evolved gas by means of a Hg monometer. Prior to Obermüller's invention (1904), the concept of measuring the gas press was used by Abel, Hesse and Mitasch, but their apps were not as convenient to use as that of Obermüller. The method was soon adopted in Germany and Spain, and was used for many years. It was later modified by Wilcox (Refs 3 & 4), Pleus (Ref 5) and Lenze (Ref 6)

It should be noted that nearly simultaneously with Obermüller, A. Dupré invented a very similar method (Ref 8, p 245), and that Taliani's method [GazzChimItal **51**, I, 184 (1921)] can be considered an improvement over that of Obermüller

Following is a brief description of the method. It is simpler than that of Bergmann and Junk (see Vol **2**, B102-R), which was invented earlier and used by the Ger Govt since 1898
Procedure. A weighed quantity (1 to 2g) of NC to be tested is placed in a 12ml test tube, with a small glass rod with a flattened end resting on the surface of the NC to prevent it from being ejected upward on the application of vacuum. By means of a ground-glass connection, the top of the test tube is connected to a retort-shaped tube, which in turn is connected to a manometer. After evacuation of the air, the test tube is placed in a bath previously adjusted to a standard temp (135° or 140°), which is maintained thruout the duration of the test. The NC begins to decomp immediately and yield gaseous products, and the rate of decompn is measured by the increase in press, this rate being greater for NC of poor stability

Working at a standard temp of 140° with a tube, with its connections, having a vol of 37ml, Obermüller found that 1g of stable NC did not cause a greater press increase than 100mm of Hg in one hour. Tests conducted by Wilcox with stabilized US mil NC's indicated that in most cases the press developed in 60 minutes was about 100mm of Hg (Ref 3, p 274)

The rate of decompn, calcd from data obtained using Obermüller's test, agrees fairly well with those calcd using Sapojnikoff's formula (Refs 2 & 3, p 2801)
Refs: 1) P. Obermüller, JSCI **24**, 347 (1905) 2) A. Sapojnikoff, JRussPhysChemSoc **38**, 1186 (1906) 3) O.W. Wilcox, JACS **30**, 271 (1908) 4) Ibid, SS **3**, 246 (1908) 5) B. Pleus, SS **5**, 121 (1910) 6) F. Lenze & B. Pleus, SS **14**, 315 (1919) 7) Reilly (1938), 87 8) H. Kast & L. Metz, "Chemische Untersuchung der Spreng-und Zündstoffe", F. Vieweg, Braunschweig (1944), 241–46

O'Brien Explosives. A series of patents were issued to J.F. O'Brien of Chicago, Ill, USA between 1913 and 1915 for new commercial expls. Typical formulations included K chlorate 30, Nitrostarch 10, Si dioxide 55, & crude petroleum with coal dust 5ps (Ref 1); K chlorate 87, naphthalene 6.5, asphalt 6.5, crude oil distillate 1.5 & Si dioxide 44ps (Ref 2); K chlorate with Na nitrate 60, liq TNT 15 & sawdust 25ps (Ref 3); and Amm perchlorate 20–65, Na nitrate 55, liq DNT 10–15, sawdust 14–23 & free C 1–3.5ps (Ref 4)

Refs: 1) J.F. O'Brien, USP 1070836 & USP 1070837 (1913) & CA **7**, 3416 (1913) 2) Ibid, USP 1071949 (1913) & CA **7**, 3542 (1913) 3) Ibid, USP 1073279 (1913) & CA **7**, 3665 (1913) 4) Ibid, USP 1132873 (1915); Colver (1938), 685

Obscuring Power of White Smokes. The total obscuring power, **TOP**, of a white smoke agent used for screening purposes, is obtained by multiplying the product of volume, in cubic ft or smoke produced per lb of material, and the reciprocal of the smoke layer, in ft, necessary to obscure the filament of a 40-watt Mazda lamp. The TOP for some white smoke agents, at low altitudes where atm constituents are plentiful, is given in Table 1

Table 1

TOTAL OBSCURING POWER OF WHITE SMOKES

Chemical	TOP, ft^2/lb
White Phosphorus	4600
$TiCl_4 + NH_3$	3030
SO_3	3000
FS*	2550
$HCl + NH_3$	2500
HC Mixture*	2100
$SiCl_4 + NH_3$	1960
FM*	1900
Oleum	1890
$SnCl_4$	1860
$PCl_3 + NH_3$	1600
$PCl_3 + NH_3$	1800
$HClSO_3 + NH_3$	1600
$SiCl_4$	1500
$HClSO_3$	1400
BM Mixture*	1400
BergerMixture	1250
FM + 1,2-Dichloroethane	1235
SO_2Cl_2	1200
$Cl_2 + NH_3$	750
$AsCl_3$	460
Type-S Mixture*	460
Crude Oil	200

*FS-chlorosulfonic acid & sulfur trioxide
HC Mixture-hexachloroethane, zinc, inorg perchlorate & amm chloride
FM-titanium tetrachloride
BM Mixture-zinc, carbon tetrachloride, sodium chloride, amm chloride & magnesium carbonate
Berger Mixture-zinc, carbon tetrachloride, zinc oxide & kieselguhr
Type-S Mixture-sulfur, inorg nitrate & charcoal

The so-called "standard smoke" is a smoke of such a density that a 25-candlepower light is just invisible when observed thru a layer 100 ft thick. A comparison of some white smoke agents at low altitude, where atm constituents are plentiful, in terms of the amount of smoke agent required to produce 1000 cubic ft of standard smoke, is given in Table 2

Table 2

AMOUNT OF SMOKE AGENTS REQUIRED TO PRODUCE 1,000 CUBIC FEET OF STANDARD SMOKE

Compound	Amount Required, oz
Phosphorus	0.060
FM + NH_3	0.090
SO_3	0.094
FS	0.110
HC Mixture	0.120
FM	0.150
Oleum	0.151
Crude Oil	2.000

All of the TOP and standard smoke measurements are made at low altitude, where atm constituents available for reaction with the primary smoke particles are plentiful. The importance of atm constituents is illustrated in Table 3 where the number of grams of smoke formed per gram of smoke agent used is tabulated

Table 3

AMOUNT OF SMOKE PRODUCED PER UNIT WEIGHT OF SMOKE AGENT AT 75% RELATIVE HUMIDITY

Agent	Amount
Fog Oil	1.0 (does not produce aqueous solution)
Zinc Chloride	2.5 (water vapor absorbed)
Ferric Chloride	3.1 (water vapor absorbed)
Aluminum Chloride	5.0 (water vapor absorbed)
Phosphorus	7.11

It is evident, for the agents compared, that white P yields the greatest weight of aq soln in equil with air at 75% RH per unit-weight of the smoke agent. The ratio for fog oil is unity (1.0) since the fog oil is not hygroscopic and only the agent is available to form the smoke particles. The values do not take into account ingredients which remain behind as residues or otherwise contribute little to the obscuring power. The absolute values will vary with the RH, but change very little with air temp at any one value of the RH. Also, the relative results are not changed. It is important to note that these measurements chiefly concern the obscuring or screening power of the smoke and no consideration is given to other factors which might be important for a signal smoke, tracking aid, or tracking and acquisition smoke

Refs: 1) R.P. Teele & H.K. Hammond, "Development of a Laboratory Test for Evaluation of the Effectiveness of Smoke Signals", NBS Rept **4742** (1956) 2) Anon, "Military Chemistry and Chemical Agents", **TM 3-215** (1963), 43–50 3) Anon, EngDesHdbk, "Military Pyrotechnics Series. Part I. Theory and Application", **AMCP 706-185** (1967), 7–32 4) Ellern (1968), 147–49

Observation Test for Smokeless Powders. See under Methyl Violet Tests in this Vol

Obturate. To stop or close an opening so as to prevent escape of gas. To seal, as with delay elements
Ref: OrdTechTerm (1962), 207-R

Obturated, or Percussion Type Primer. A type of primer which consists of a cup into which the primer charge is loaded, and an anvil which is pressed into the open end of the cup, its point extending slightly into the mixt. A paper disc is placed over the mixt before assembly to assist in sealing. A primer of this type is usually pressed into an ammo component and fired by hitting the bottom of the cup with a firing pin, which forces the mixt against the anvil. Since the cup is not pierced, obturation (sealing) is obtained after the primer is fired because the primer as a whole is pressed into its containing cavity. The primer cups are constructed of ductile metals, commonly brass, in order to avoid rupture by the firing pin
Refs: 1) Ohart (1946), 47–48 2) E.R. Lake, "Percussion Primers, Design Requirements", Report **MDC-A0514**, McDonnell Aircraft Co, St Louis, Mo (30 June 1970) 3) Anon, EngDesHdbk, "Explosives Series. Explosive Trains", **AMCP 706-179** (1974), 5-2

Obturation. A process that seals the breech of a gun and prevents the escape of propInt gases at the time of firing. In all modern firearms, light and medium artillery, it is effected by the momentary expansion of the brass or copper cartridge case

In separate-loading ammo, obturation is achieved by a special device, called an **Obturator** (qv)

The term obturation is also applied to the sealing of the chamber in which the delay element of an expl train is located. Obturated delay elements are so constructed as to retain all gases emitted by the initiator and the delay element until the relay or other base charge explds. Advantages of obturated delays include the inherent independence of these sealed units from effects of press or humidity of the ambient atm, and the absence of fumes that might have harmful effects on other components of the system. Obturation also helps in the design of short delays, because the resulting increase in press increases the burning rate
Refs: 1) Ohart (1946), 123 2) OrdTechTerm (1962), 207-R 3) Anon, EngDesHdbk, "Explosive Series, Explosive Trains", **AMCP 706-179** (1974), 6-1 & 6-10

Obturator. An assembly of steel spindle, mushroom head, obturator rings, and a gas-check or obturator pad of tough plastic material used as a seal to prevent the escape of proplnt gases thru the breechblock of guns using separate-loading ammo, and therefore not having the obturation provided by a cartridge case

A device incorporated in a projectile to make the tube of a weapon gas-tight, preventing escape of gas until the projectile has left the muzzle
Ref: OrdTechTerm (1962), 207-R

Obturator Pad. Pad of tough plastic material, forming part of an **Obturator** (qv)
Ref: OrdTechTerm (1962), 207-R

Obturator Rings. Accurately machined and fitted rings forming part of an **Obturator** (qv)
Ref: OrdTechTerm (1962), 207-R

Obturator Spindle. Part of the breechblock assembly of a gun which fires separate-loading ammo. It extends thru the breechblock and holds in position the various parts of the **Obturator** (qv), while permitting the breechblock independent rotation around these parts
Ref: OrdTechTerm (1962), 207-R

Obus (Fr). Artillery shell
Obus à balles (Fr). Shrapnel
Obus à coiffe (Fr). Shell with armor-piercing cap
Obus à culot tronconique (Fr). Boat-tailed shell
Obus à étoiles (Fr). Star shell
Obus à fragmentation (Fr). Fragmentation shell
Obus à gaz (Fr). Gas shell
Obus à ogive trempée (Fr). Shell with hardened cap
Obus à segments (Fr). Segment shell
Obus bivalent (Fr). HE shell with chemical filler
Obus brisant (Fr). HE time shell
Obus d'emploi particulier (Fr). Chemical shell
Obus D en fonte aciérée (Fr). Cast steel shell
Obus de réglage (Fr). Special shell for adjustment of fire
Obus de rupture (Fr). Armor-piercing shell
Obus d'exercice (Fr). Dummy projectile
Obus éclairant (Fr). Illuminating shell
Obus explosif (Fr). HE shell
Obus fumigène (Fr). Smoke shell
Obus fusant (Fr). Time shell
Obusier (Fr). Howitzer
Obusier de siège (Fr). Siege howitzer
Obusier sur bât (Fr). Pack howitzer
Obus incendiare (Fr). Incendiary shell
Obus non éclaté (Fr). Dud
Obus perforant (Fr). Armor-piercing shell
Obus plein (Fr). Shot, solid shell
Obus toxique (Fr). Gas projectile, gas shell
Obus traceur (Fr). Tracer shell
Ref: Anon, "French Military Dictionary", **TM30-502** (1944)

Occupational Diseases and Hazards in Explosives and Ammunition Plants. See under Industrial Hygiene in Vol **7**, I93-R

OC, Explosifs du type. Fr designation for Cheddites. See Vol **2**, C155-L ff

o-Chlorobenzylmalonitrile (CS). $ClC_6H_4CHC(CN)_2$, mw 188.5, white cryst powd, mp 93–95°, bp 310–315°, bulk d 10–20 lbs/cu ft, pepperlike odor. CS has a min purity of 96%; is insol in w and alc, sol in methylene chloride

CS is a tear agent used for training and riot

control (see Chemical Agents or Chemical Warfare Agents in Vol **2**, C165-Rff)
Median lethal dosage. 25000mg-min/m^3 for resting men
Median incapacitating dosage. 10 to 20mg-min/m^3
Rate of detoxification. Quite rapid, incapacitating dosages lose their effects in 5 to 10 minutes
Skin and eye toxicity. Highly irritating but not toxic
Rate of action. Very rapid
Physiological effects. CS produces immediate effects even in low concns. The median effective concn for respiratory effects is 12 to 20mg/m^3; concn for eye effects is 1 to 5mg/m^3. The onset of incapacitation is 20 to 60 seconds and the duration of effects is 5 to 10 minutes after the affected individual is removed to fresh air. During this time affected individuals are incapable of effective concerted action. The physiological effects include extreme burning of the eyes accompanied by copious flow of tears; coughing, difficulty in breathing, and chest tightness; involuntary closing of the eyes; stinging sensation of moist skin; running nose; and dizziness or swimming of the head. Heavy concns will cause nausea and vomiting in addition to the above effects
Protection required. Protection is provided by the protective mask and ordinary field clothing secured at the neck, wrist, and ankles. Personnel handling CS should wear rubber gloves for additional protection
Decontaminants. Area decontamination is not required as CS has a short duration of effectiveness. Personnel exposed to CS may shower as necessary; however, when CS dust or particles are on the skin, showering should be delayed for 6 hours to prevent stinging and reddening of the skin. Individuals affected by CS should move to fresh air, face the wind, and remain well spaced; and should not rub their eyes. To remove accidental gross contamination, personnel should remove clothing and immediately flush body with copious amts of water to remove most of the agent; apply 5% Na bisulfite soln to remove remainder (except in or around eyes); and then rinse body
Munitions suitable for use. The pure cryst form (identified by symbol CS) is used as filling for burning-type grenades and capsules. A mixt of 95% of the cryst agent and 5% of silica gel aerogel (identified by symbol CS1) is used as filling for bursting-type grenades and in all bulk irritant agent dispersers
Refs: 1) Anon, "Military Chemistry and Chemical Agents", **TM 3-215** (1963), 37–38 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 332

Ochsé's Cartridges. These cartridges, patented in Fr in 1893–94, were made of 2.5mm thick steel, 3cm in diameter and 18cm long, and could withstand a press up to 1200 atms. Prior to use, they were filled with Na hydroxide soln, and then tightly closed. An electric current of 0.85 to 1.0 amp and 8–10 volts was then passed thru the soln until it completely decompd into H_2 and O_2. After placing such "charged" cartridges into the bore-holes of mines, they were connected to a source of electrical current. The electric sparks, produced by the current, caused an expln inside the cartridge. The effect produced by each steel tube was equivalent in strength to a 150g cartridge of an AN expl, such as Westphalite (qv) or Dahmenite (see Vol **3**, D1-R)

Tests conducted at the end of the last century at Mont-Cenis, Fr, and Westphalia, Ger, indicated that the use of Ochsé's cartridges was uneconomical and dangerous
Ref: Daniel (1902), 588

Octamethylolcyclohexanediol, $HOHC[C(CH_2OH)_2]_4CHOH$, mw 356.36, can be prepd by reduction of the corresponding "diene". *Octamethylolcyclohexanedione,* $OC[C(CH_2OH)_2]_4CO$, mw 352.33, can be prepd by condensation of the corresponding cyclic ketone with aldehyde

Both of these compds yield expls on nitration. It is claimed that these expls have a high detonation velocity, can be poured at temps below 100°, and are stable when stored at 50°

The same investigators proposed the use of nitrates of other cyclic keto-alcohols, such as tetramethylolcyclohexanone, tetramethylolcyclopentanone, etc, as expls. All of these alcohols can be prepd by condensing cyclic ketones with formaldehyde in the presence of alkalies or al-

kaline earths
Refs: 1) W. Friederich & K. Flick, GerP 509118 (1929) & CA **25**, 819 (1931) 2) W. Friederich, BritP 345859 (1929) & CA **26**, 2058 (1932)

Octanitrocellulose. [also called Dinitrocellulose, $C_6H_8O_3(ONO_2)_2$, or Tetranitrocellulose, $C_{12}H_{16}O_6(ONO_2)_4$]; $C_{24}H_{32}O_{12}(ONO_2)_8$; mw 1008.56; N 11.11%; d 1.653g/cc; 178ml of NO evolved per 1 g sample; wh amorph mass

Sol in abs alc, gl acet acid, acet, eth/alc mixts, ethyl acet, NG, etc. Can be prepd by the nitration of cellulose with nitric acid in the presence of equal amts of sulfuric and phosphoric acids

Octa- and hexanitrocellulose are the principal ingredients of Collodion (see Vol **3**, C394-R), with the former being within the N range of Collodion Cotton (see Vol **2**, C103-R)
Refs: 1) E.C. Worden, "Technology of Cellulose Esters", Vol **1**, Part 3, 1650 & 1731, Eschenbach Printing Co, Easton, Pa (1921) 2) Bebie (1943), 112 3) A. Pérez Ara (1945), 367

Octanitroethylenediphenyldiamine. See Ditetryl or Bitetryl in Vol **5**, D1513-L

Octazatrienes or Octazones. Derivatives of HN:N.NH.N:N.NH.N:NH, some of which are expl. They were described by their discoverers, Wohl and Schiff (Ref 3), "as standing on the very edge of existence"

A typical derivative is **3,6-Diphenyl-1,8-bis-[4-bromphenyl]-octazatriene-(1,4,7)** or **N,N′-Bis-[4-brombenzoldiaza]-N,N′-diphenyltetrazone.** $C_6H_4Br.N:N.N(C_6H_5).N:N.N(C_6H_5).N:N.C_6H_4Br$, pale yel substance, mp 60°. Can be prepd by treating a cold ethereal soln of 3-phenyl-1-[4-bromphenyl]-tetrazene-(1) with a 1% soln of K permanganate (Ref 1). It is an expl
Refs: 1) Beil **16**, 756 2) F. Wohl & H. Schiff, Ber **33**, 2741 & 2749 (1900) 3) Hackh's (1972), 469-L

Octogen. Ger name for Cyclotetramethylenetetranitramine (HMX). See Vol **3**, C605-R to C610-R
Refs: 1) B.T. Fedoroff et al, "Dictionary of Explosives, Ammunition and Weapons, German Section". PATR **2510** (1958), 89-R 2) Urbański **3** (1967), 117

OCTOL (Octolite). Octols are secondary high expl mixts of **Octohydro 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)** (see Vol **3**, C605-R to C610-R) and **Trinitrotoluene (TNT)**, usually in the proportions of 3:1. During WWII a need developed for a stable, organic expl possessing a density & detonation rate exceeding that of **1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX).** (See Vol **3**, C611-L to C630-L). With F.C. Whitmore's first large-scale prepn in 1942 (Ref 1) of G.F. Wright's synthesis and naming of HMX (Ref 2), the next higher methylene nitramine homolog of RDX, this need was met. However, to desensitize and render HMX melt-castable requires mixing with a lower melting, more stable expl such as TNT. To maintain the advantages of high density in the cast expl requires that inhomogeneous mixts or slurries be made with TNT because the solubility of HMX or RDX in TNT is only about 5%. The pourability or apparent viscosity of molten TNT slurries of HMX was found to follow rules similar to those governing molten TNT slurries of RDX (also called Cyclotols; see Vol **3**, C479)

To achieve the desired cast density for Octol of 1.8g/cc it is necessary that the ratio of HMX:TNT be 3:1. However, at this ratio the apparent viscosity, or efflux, is strongly dependent on the polymorphic variety of HMX used and on its particle size distribution. In the initial pilot production of Octol (Ref 3) it was found that for the desired efflux of <15 sec, 60–70% of the solid HMX must consist of the beta-polymorph having particle diameters in the range of 500–800 microns. Such precise control of particle size was not possible at that time and early Octol casts were made at approximately 50 secs efflux. The economical production of Octol with a satisfactorily short efflux time continues to present a problem in loading shells with this expl (Refs 4, 11 & 29)

The expl performance of Octol was generally an improvement over that of Cyclotol. Based on the physical and chemical properties of HMX and RDX the following improvements were observed (Ref 4):

Type Performance	Improvement Predicted	Found
Shaped Charge Penetration	11%	18.5%
Plate Acceleration	11%	11%
Fragment Velocity	11%	7%

The higher specific gravity of 75/25 Octol can make the bursting charge of a shell containing it appreciably heavier than that of the same shell

loaded with Composition B (See Vol 3, C479), the standard at the conclusion of the Korean conflict. For example, the 105mm M1 shell would contain 0.4 pound more expl at a specific gravity of 1.80g/cc or higher. The detonation velocity of cast 75/25 Octol is about 8400m/sec; that of Composition B about 7800m/sec. This difference of 600m/sec in velocity coupled with the heavier bursting charge should yield not only more fragments per shell, but also fragments having a higher initial velocity. For fragmentation-type ammo this is the kind of improvement most desired. Firing tests showed that the substitution of 75/25 Octol for Composition B in the 105mm M1 shell produced a 15% greater number of fragments having an average 331 foot-seconds greater velocity over identical 180 degree coverage (Ref 6):

Table 1

Comparative Fragment Velocity Distribution ft/sec

Octol		Composition B
	Nose	
1517		1611
	Side	
4333		4043
	Base	
3421		3105

The improvement in penetration and damage produced by 105mm shaped charges of Octol over that of Composition B or TNT having the same charge geometry were further documented (Ref 10):

Table 2

Cumulative Crater Volumes Produced in Mild Steel Targets by 105mm Shaped Charges with Different Explosives

Depth of Penetration (cm)	Volume (cm^3)		
	TNT	Composition B	Octol
0	0	0	0
4	23.8	33.1	37.0
8	36.2	49.7	57.4
12	43.2	61.4	68.9
16	49.1	69.2	78.7
20	53.0	75.1	85.0
24	56.2	79.4	89.9
28	58.6	83.0	94.0
32	61.8	86.2	98.1
36	64.3	89.3	101.8
40	–	92.3	105.3
44	–	–	110.4

Using the exptly determined liner collapse velocities of Composition B, it was found that the foregoing values could be described by a theoretical hydrodynamic code based on detonation rates and expl densities with sufficient accuracy to justify a high degree of confidence in computed penetrations and damage for targets having Brinell hardness numbers between 100 and 300

The best shaped charge results are obtained with expl compns having the highest detonation pressure HE as illustrated (Ref 20):

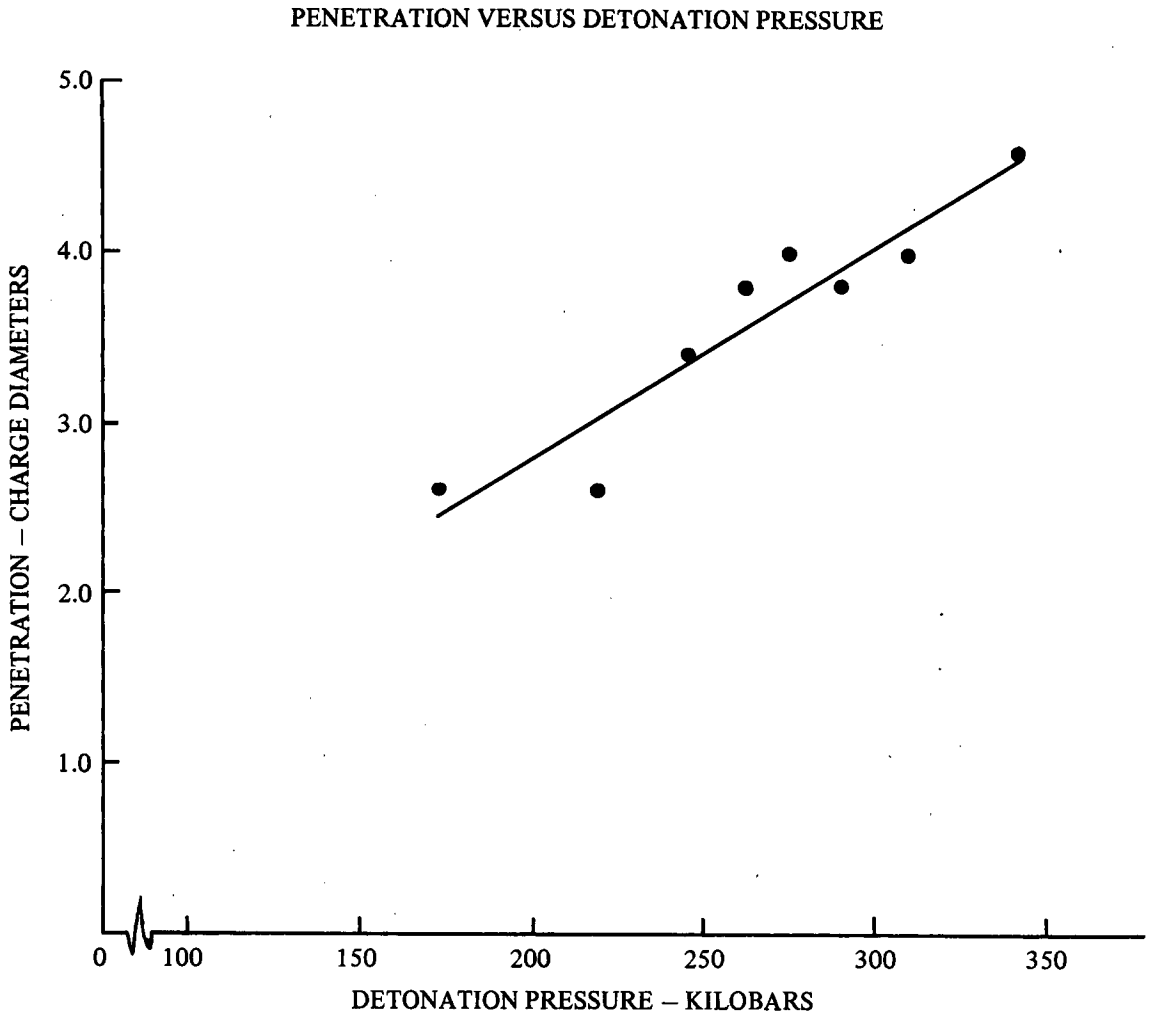


Fig 1 Penetration vs Detonation Pressure of Shaped Charges

Octol, at least at shorter standoffs, gives about 10% deeper penetrations than Composition B, but the latter is better at long standoffs since it seems to lessen perturbance of the shaped-charge jet

Rather surprisingly, early formulations of Octol were slightly more sensitive to impact than Cyclotol (Ref 4):

Table 3

	Impact Sensitivity (ERL Machine, 2.5kg wt)	
	RDX	HMX
Pure Explosive	20–24cm	26–32cm
Explosive/TNT (70/30)	53cm	47cm
Explosive/TNT (60/40)	69cm	52cm

In view of the lower impact sensitivity of HMX, the trend for Octol is most unexpected and was later (Refs 11, 33 & 34) shown to be caused by surface effects. The apparently greater sensitivity of Octol can be mitigated or reversed by control of the particle size distribution and by changes in the surface treatment of the HMX used in Octol compns

Octol shows a small increase in stability over that of Cyclotol at higher temps which may be sufficient to overcome the marginal stability of Cyclotol in specific cases

The 7–15% improvement in expl performance of Octol over that of Cyclotol is achieved at a 250–500% increase in cost (depending on purity), which has to be matched against the overall gain

in performance of specific weapons. For this reason Octol is most actively exploited as a replacement for Cyclotol only in warhead compns of costly weapons where shaped charge penetration or fragmentation is the major criterion of damage production. This includes the smaller guided missiles and some of the more costly air-to-air **(Falcon)**, air-to-surface **(Hellfire)**, and surface-to-air **(Chaparral)** rockets and missiles (Ref 39), where the warhead cost is only a minor fraction of weapon cost and a 7–15% improvement is well worth the cost increase

Expls similar to Octol, viz, HMX/TNT/Al/Wax, 47/31/22/3–5, have been prepd and tested for air-blast and underwater effectiveness. The performance improvements that resulted (1–2%) over Cyclotol analogs were not considered worth the additional cost (Ref 4), and other expls are generally exploited for such applications

In an age of precision use of expls to achieve precise effects, control of and stable spatial arrangement of the expl is required. Certain limitations and problems of this nature arise in the use of composite expls which are cast from inhomogeneous slurries. One problem is the aerodynamic heating which results when ordnance is carried exposed on high-speed aircraft. Missiles in flight experience similar but shorter term heating effects. Aerodynamic heating may be sufficient to produce melting and substantial expansion of the expl charge. The result may be a dud or a round that does not function as intended. Neither will the round function correctly after solidification unless the original spatial arrangement of the bursting charge components is regained. Associated with long-term, high temp cycling of composite expls is the exudation of portions of the expl charge as a result of thermal expansion. Exudation causes the development of cracks within the confined expl charge and an undesirable increase in sensitivity, especially to set-back pressure (Ref 7). A number of additives have been used to improve growth and crack resistance. Initially, the US Navy found that by dispersing $\leq$1% o-Nitrophenol in the expl melt before casting resulted in a reduction in exudation. Other crack and growth retarders such as Cyclohexanone, 2,4-Dinitroanisole, 2,4-DNT, and both o- and p-Nitrotoluene were all found to have less effect (Ref 12). Subsequently the French replaced TNT with 2,4,6-Trinitro-N-methylaniline or 2,4,6-Trinitro-N,N-dimethylaniline and obtained melt-castable expls that did not melt or exude at temps of up to 125°, but with a predictably lower detonation velocity than that of either Cyclotol or Octol (Ref 18). Analyses of exudates which migrate from technical grade TNT in cast expls revealed that a major constituent was DNT. A highly porous form of calcium silicate (Micro-Cel E) was next tried as an absorbent of the exudate-causing liq of the TNT matrix, but even at the 0.5% level it caused severe cracking of the cast. The purification of TNT to remove DNT and other exudation-causing impurities increased the brittleness of TNT-based cast expls. However, since DNT was known to be an effective plasticizer of NC in proplnt formulations, it was found that Octol + 0.45% plasticized high viscosity NC and Octol + 0.3% plasticized cellulose propionate (CP) had the optimum properties for crack resistance, exudation reduction, and least cast charge growth (Ref 19). The ineffectiveness of Micro-Cel for controlling exudation was conclusively demonstrated during temp-humidity cycling tests conducted on the Chaparral missile. The temp cycle used was from –4° to 103° for a 24-hour period, with missiles held at extremes for a 4-hour period and brought from one extreme to the other in eight hours. Exudate was observed on eleven of twelve missiles submitted to test (Ref 35)

Another variable peculiar to composite, cast expls that must be controlled to achieve precision penetration and predictable destructiveness is the variation in density and compn of the expl within the warhead. In melt-loading operations with Octol, problems occur which do not arise in melt-loading with TNT, Composition B, or Cyclotol. Specifically, there is a large amount of settling of HMX crystals while the charge is still molten. It has been shown that the average percent HMX in a warhead ranges between 70% and 77% whether loaded with 60/40, 65/35, or 70/30 Octol. Correspondingly, the HMX content of the riser produced is low, often reaching 40%. It was shown that by using 60/40 Octol instead of 70/30 for casting the M18 warhead for the 66mm M72 Light Anti-Tank Weapon **(LAW)** system, a better cast was obtained with optimum penetration (Ref 13). This improvement was attributed to the better fluidity of the 60/40 expl (Ref 16)

The superior shaped-charge performance of Octol, as indicated previously, is limited by perturbances of the detonation wave front that affects jets. The early emphasis on the precision of the metal parts associated with shaped charges

(Ref 5) was in the 1960's focused on the expl itself. At that time the penetration of confined shaped charges of 4.5 to 5.5 charge diameters was considered acceptable with an ideal value of 7 (Ref 20). Max penetration and damage or hole volume created in armor requires max energy content, which in turn demands high HMX concn, overcoming viscosity problems, reducing air entrapment, with the elimination of microporosity. It is desirable not to use melt-pour temps above 95° to decrease viscosity for a variety of reasons. For example, TNT shrinks from 11 to 12% on solidification, so that if the melt is too viscous during pouring, the entrapped air may not escape prior to solidification. These bubbles are further enlarged by the volume shrinkage of TNT, resulting in a porous cast of low density

Vacuum casting has been used in Germany by Boelkow B.m.m.H. to achieve more homogeneous casts and eliminate microporosity (Ref 14). Subsequently, Reichel showed that by programming the temp of the entire melting-filling cycle and centrifuging the poured charge at 25000 ft/sec^2 for 10 to 15 minutes, crack-free charges of highest density could be produced. These loading methods were evaluated with 1 kg unconfined shaped charges, 96mm in diameter, incorporating a 60 degree 2mm thick copper liner. Using the product of penetration depth and hole volume at the optimum standoff as a figure of merit (PV), the following comparisons were obtained (Ref 17):

	Max Penetration cm	Hole Volume cm^3	PV cm^4
Conventional Cast Cyclotol	68	190	13,000
Vibration Cast Cyclotol	76	240	18,000
Vibration Cast Octol	82	275	23,000

These expts were designed to defeat the NATO heavy tri-partite target, which requires not only a high basic penetration to overcome the three spaced layers of armor, but requires especially a perfectly aligned jet to defeat the plates at the long compound standoffs. Such precision shaped charges require not only carefully made metal parts but equally precise expl components. The superiority of these more elaborate casting techniques is reflected in the penetration of nearly 9 charge diameters shown in performance chart for Octol (Fig 2)

The feasibility of improving the melt-casting of Octol thru application of ultrasonic energy has been investigated as part of the US Army's general program to upgrade the performance of the **LAW**. It has been shown that ultrasonic agitation of molten slurries and gel-like materials generally leads to shear-thinning and permits flow even thru small orifices and into complex molds. In the case of Octol, ultrasonic techniques made possible the successful casting of Octol in which the weight percentage of the solid phase HMX is increased above the point at which normal gravity flow ceases. Using ultrasonic activation of either regular or precision **LAW** warhead bodies in an axially symmetric (longitudinal) mode at 15kHz, it was possible to obtain castings of Octol 80/20, which will not flow under standard melt-casting conditions, that appeared void-free by X-ray. Continued application of ultrasonic energy for 5—10 minutes after filling promoted settling of HMX particles out of the riser funnel into the warhead body, increasing the HMX content to 65% near the base of the cone with a compn gradient declining to about 80% at the fuze end. Similar results were obtained with 75/25 Octol (Ref 22). There is evidence that it is desirable in Octol-filled forward-firing, conical shaped charges, that the heavier HMX settle out of suspension around the base of the liner cone. However, sectioning and analysis shows that even prolonged mechanical agitation, as opposed to ultrasonic activation, does not yield a uniform longitudinal gradient of Octol density or HMX concn along the axis of **TOW, DRAGON** or **SHILLELAGH** warheads. These variations in compn are thought to be responsible for erratic penetrations observed with these missiles but cannot at present be verified non-destructively (Refs 30 & 38)

Thus it can be seen that continuous improvements in defensive armor require ever more sophisticated expl technology for its defeat, which in turn results in the escalation of military budgets for conventional warfare. The increased cost of HMX relative to other expls has caused continuing efforts to reduce manufg costs, to improve and more precisely evaluate its effectiveness. In a recent, very painstaking comparison of Cyclotol and Octol, the effects of changes in the compn, density, and diameter of the expl charge upon detonation velocity were determined. HMX was found more ef-

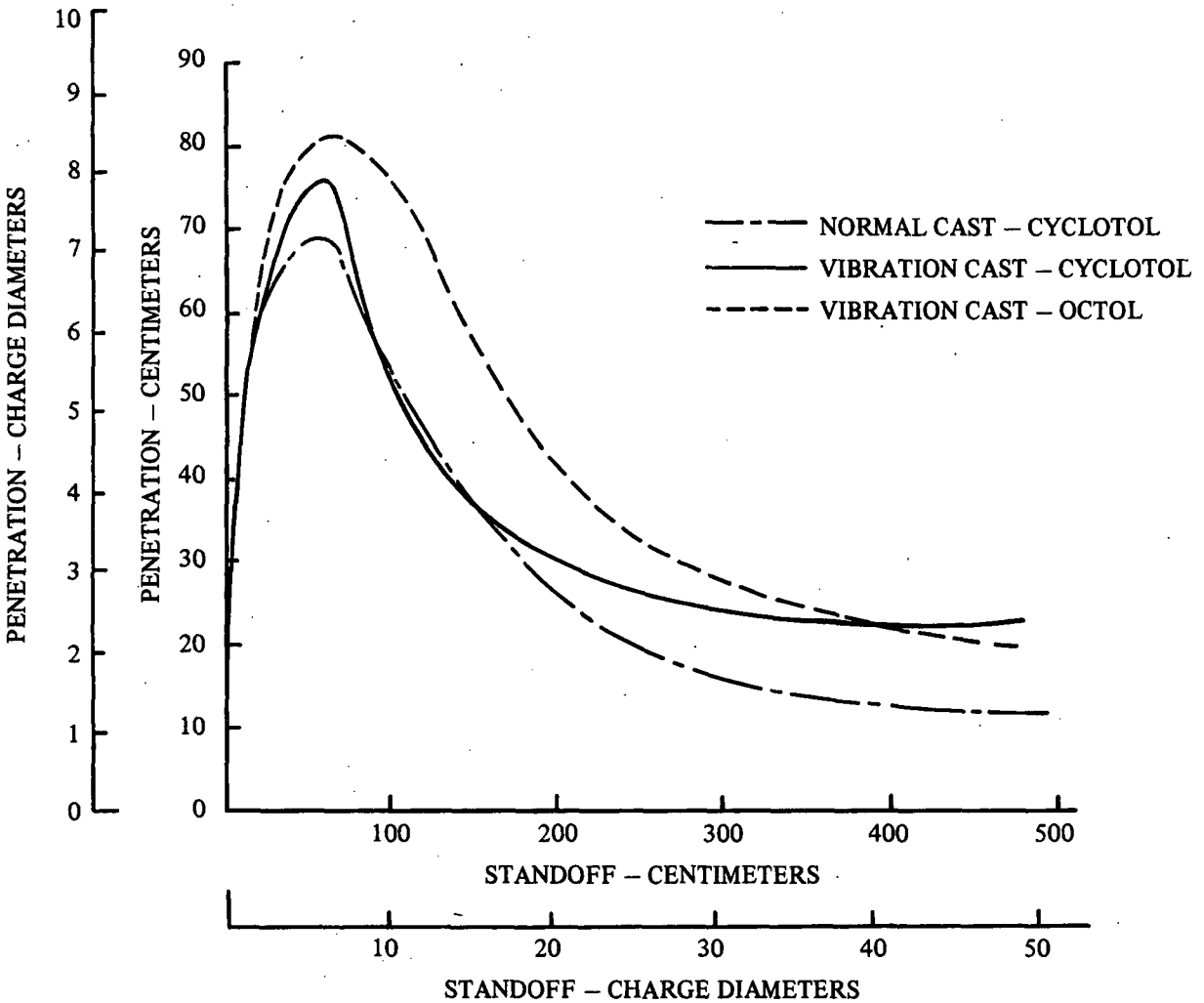


Fig 2 SHAPED CHARGE PERFORMANCE FOR SEVERAL CASTING METHODS
(96mm diameter, 60° Copper Cone, 2mm wall, unconfined)
(Stacked plates, St37 Steel)

fective than RDX in increasing the density of the charges and charges containing HMX detonated more rapidly; otherwise, the increase in detonation velocity was the same for Cyclotol and Octol. With 40–30% TNT and infinite diameter of charge the results were (Ref 21):

	RDX A	HMX B
Increase in Density/% increase A or B, mg/cm³/%	1.75	2.85
Increase in Detonation Velocity/Unit Density, msec/mg/cm³	3.40	3.50
Increase in Detonation Velocity/% increase A or B at Constant Density, msec/%	16.0	15.0
Detonation Velocity at 65% A or B and Max Density, msec	8070	8254

A linear relationship between Chapman-Jouguet pressure and density was confirmed for Cyclotol and Octol (Ref 28). Despite the near-equal performance of RDX and HMX at equal densities there appears to be no economical way of making the density of RDX equal to the cast density of HMX. Dinitrobenzene (DNB) has been evaluated as an economical or emergency substitute for TNT but charges prepared with DNB gave somewhat poorer performance than those with TNT. Results indicate that TNB could be used as an emergency replacement for TNT in large-diameter munitions (Ref 25). Active efforts are being made to reduce manufg costs by replacing batch processes with continuous granulation (Ref 23) and continuous melt-pour processes (Ref 26)

Table 4 details the physical, chemical and expl properties of Octol Type I and Type II

Table 4

Properties of Octol Type I and Octol Type II

	Type I	Type II	Refs
Composition			
HMX % $C_4H_8O_8N_8$	75	70	
TNT % $C_7H_5O_6N_3$	25	30	
Chemical and Physical Properties			
Density (Nominal Cast), g/cc	1.80 to 1.82	1.80 to 1.81	9, 27
Density (Theoretical Max), g/cc	1.832	1.819	9, 24, 27
Air Blast			
Weight of Charge 3022g			
Distance from charge, 10 ft			
Overpressure, psi	37.4	37.9	27
Impulse, psi – msec	18.1	21.2	27
Distance from Charge, 15 ft			
Overpressure, psi	13.1	14.6	27
Impulse, psi – msec	12.5	15.5	27
Distance from Charge, 20 ft			
Overpressure, psi	7.1	6.7	27
Impulse, psi – msec	9.1	11.2	27
Autoignition Temperature, °C	100	108	27
Explosion Temperature, °C	288	289	27
Seconds 0.1 (no cap used)	–	–	
Seconds 1	–	–	
Seconds 5 (flames erratically)	350	335	24
Detonation Rate (no confinement – cast)			
Density, g/cc	1.81	1.80	24
m/sec	8643	8377	24
0.5″ x 0.5″ x 6″, m/sec	8328	8241	27
1.0″ x 1.0″ x 6″, m/sec	8396	8305	27
1.5″ x 2.0″ x 6″, m/sec	8364	8310	27
	8480	–	32
VonNeumann Spike Pressure, kbar	452 ± 10		15
Chapman-Jouguet Pressure, kbar	314 ± 7		15
VonNeumann Spike Shock Velocity, m/sec	8550 ± 30		15
Chapman-Jouguet Velocity, m/sec	8550 ± 30		15
VonNeumann Spike Particle Velocity, m/sec	2930 ± 70		15
Chapman-Jouguet Particle Velocity, m/sec	2040 ± 50		15

(Continued)

Table 4 (continuation)
Properties of Octol Type I and Octol Type II

	Type I	Type II	Refs
Dielectric Properties			
Resistance, ohms	$2x10^{10}$		9
Resistivity, ohm-cm	$2.99x10^{10}$		9
Dielectric Constant			
@ 100c	3.121		9
@ 1kc	3.070		9
@ 10kc	3.042		9
@ 100kc	3.013		9
Dielectric Strength			
.040" thick, v/mil	150		9
.039" thick, v/mil	128.2		9
Fragment Velocity, ft/sec			
Initial	6159	6139	27
At 20 ft from sample	5790	5772	27
M26 Hand Grenade (ave first 6 ft)	5124	–	24
Pit Fragmentation			
105mm M1 HE Projectile	Number Fragments		
½– 2 grains	1611	1297	24
2– 5 grains	777	665	24
5– 10 grains	535	497	24
10– 25 grains	719	661	24
25– 50 grains	480	471	24
50– 75 grains	246	247	24
75– 150 grains	339	322	24
150– 750 grains	293	295	24
750–2500 grains	8	12	24
	5008	4467	
Friction Pendulum			
Steel Shoe	Unaffected	Unaffected	24, 27
Fiber Shoe	Unaffected	Unaffected	24, 27
Heat of Combustion			
cal/g	2676	2722	24
ΔH_{DET} $H_2O_{(L)}$ (calc), cal/g	1570	–	32
ΔH_{DET} $H_2O_{(G)}$ (calc), cal/g	1430	–	32
Heat of Explosion			
cal/g	1131	1074	32
Heat of Fusion			
kcal/mole	+2.57	–	32
76.9% HMX, 23.1% TNT			
cal/g	29.4	–	32
Specific Heat			
76.9% HMX, 23.1% TNT			
cal/g/°C –79°	0.200	–	24
cal/g/°C –80° to +80°	0.240	–	24
cal/g/°C 33° to 74°	0.245	–	24
cal/g/°C 90° to 150°	0.323	–	24

(Continued)

Table 4 (continuation)
Properties of Octol Type I and Octol Type II

	Type I					Type II	Refs
Impact Sensitivity							
Picatinny Arsenal Apparatus							
inches			17			18	24
Sample wt, mg			25			26	24
inches			15			19	27
Sample wt, mg			19			20	27
Mechanical Properties	**−62°**	**−40°**	**23°**	**52°**	**71°**		
Compressive Strength @ .05 in/min:							
Stress at rupture, psi	1182	1169	1509	1022	635	–	27
Compression at rupture, %	0.21	0.23	0.20	0.26	0.23	–	27
Mod of Elasticity, psi x 10^{-3}	720	492	1344	892	526	–	27
Work to prod rupture, ft-lb/in^3	0.11	0.14	0.14	0.16	0.15	–	27
Impact Strength							
Charpy, inch-pounds	1.80	1.88	1.81	1.76	1.81	–	27
Izod, inch-pounds	–	–	1.27	–	–	–	32
Shear Strength							
Stress at rupture, psi	599	529	769	640	498	–	27
Torsional Shear @ 36°/min							
Stress at rupture, psi			113			–	27
Mod of Elasticity, psi			101,000			–	32
Tensile Strength @ .05 in/min							
Stress at rupture, psi	88	81	146	113	120	–	27
Elongation at rupture, %	.019	.014	.010	.015	.018	–	27
Mod of Elasticity, psi x 10^{-3}	445	678	1565	1548	1102	–	27
Work to prod rupture, ft-lb/in^3	.0007	.0005	.0006	.0008	.001	–	27
Sensitivity to Initiation							
Minimum deton charge Lead Azide, g			0.3			0.3	24
Sensitivity to Setback Pressure psi @ 71°							
Probability of Reaction							
0.1%			95000			80000	27
50%			119000			119000	27
99.9%			149000			176000	27
0.0%			76000			92000	24
Linear Coefficient of Thermal Expansion % x 10^{-3}/°C							
−50° to −20°			1.73			2.59	27
−20° to +20°			3.38			2.75	27
20° to 50°			7.02			7.38	27
50° to 65°			7.13			8.05	27
Vacuum Stability ml gas/5g sample/40 hrs							
120°			0.39, 0.65			0.37, 0.76	24, 27
130°			1.13			0.97	27
140°			2.66			1.50	27
150°			11			5.10	27
160°			–			11	27

Uses. In addition to fragmentation and shaped charge applications that have already been mentioned, Octol and Octol-like mixts are employed as oil well formation fracturing agents (Ref 31), and in combination with suitable polyester or polyurethane resin binders to compound high efficiency, special-purpose expls (Refs 36 & 37) with detonation rates of 8400–8690m/sec, friction sensitivities of 24–36kg and compression strengths of 710kg/cm²

Analytical. The quantitative analysis of Octol, Type I and Type II is given in US Military Specification **MIL-O-45445A** (Ord) (30 Sept 1962) which also lists the following requirements (Ref 8):

Moisture, %	0.25 max
Insol particles, number of particles retained on No 60 US standard sieve	5 max
Acetone insol matter, %	0.10 max

Viscosity, seconds	Type I 15 max	Type II 12 max
HMX	75.0 ± 2.4	70.0 ± 2.0
TNT	25.0 ± 2.0	30.0 ± 2.0

The quantitative analysis procedure involves gravimetric detn of the HMX on a moisture-free basis after benzene extraction of, and differential detn of TNT. Moisture content is detd by conductometric titration of sample in an acetic-sulfuric acid suspension. Acetone insoluble matter is determined gravimetrically

Written by **D. J. VEAL**

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Tooling and Loading Procedures for Production of Laminated High Explosive Cylinders", **NWC-TP-4774** (1970) (Conf) Y) R.E. Vincent, "Development of the XM225 Warhead Section and XM224 Guided Missile Warhead for Dragon (Medium Antitank/Assault Weapon–MAW)", **DRD-36** (1971) (Conf) Z) J. Simon & R. Disperso, "The Evaluation of the Effect of Explosive Filler on Shaped Charge Performance and Lethality Effectiveness", **BRL-1552** (1971) (Conf) AA) C.D. Johnson, "Feasibility Demonstration of a Propellant Dispersion Concept for Aircraft-Dispensed Submunitions", **AFATL TR-72-12** (1972) (Conf) BB) R.R. Mineslinger, et al, "Synthesis of High-Energy Compounds and Development of Heat-Resistant, Castable Explosives", **AFATL TR-72-8** (1972) (Conf) CC) W.H. Snyder, C.R. Hoggatt & L.L. Brown, "Performance of Testing Services on High Explosive Devices and the Reduction of Accumulated Data", **DRI-4633-7210-F** (1972) (Conf) DD) W. Witt, U. Sabranski & H. Orth, GerP 2131282 (1972) & CA **79**, 99992 (1973) EE) R. Vincent & E.L. Clark, "Shaped Charge Liner Studies Using Various Materials", **DRD-444** (1973) (Conf) FF) R.C. Dean & B.E. Craddock, "Hard Structure Munition-Phase IIC", **GER-15945** (1973) (Conf) GG) C.R. Hoggatt, E.S. Grubin & W.H. Snyder, "Performance of Testing Services on High Explosive Devices and the Reduction of Accumulated Data", **DRI-4782-7309-F** (1973) (Conf) HH) D.R. Kennedy & A.W. Hall, "X-Charge Investigation", **FMC-338-001** (Jan 1974) (Conf) II) D.R. Kennedy & W.G. Messenger, "Aimable Cylindric Warhead Prototype Development", **AFATL TR-74-56** (1974) (Conf) JJ) D.H. Mallory, "Sequential Jet Shaped Charge", **NWC-TR-5534** (1974) (Conf) KK) W.A. Schmeling & W.H. Snyder, "The Static Performance of the XM248 Warhead for SAM-D", **DRI-5148(A)-7409** (1974) (Conf) LL) J. Brossard, "Determination of Detonation Properties in Explosive Mixtures", ActaAstronautica **1**, 1181–6 (1974) & CA **83**, 156 (1975) MM) D. Georgevich, O. Klamer & D.E. Seeger, "Alternate Fill Evaluation in Rocket, 66mm, HEAT, M72A2 (LAW)", PATR **4702** (1975) (Conf) NN) S.K. Vasudeva, "Military Explosives and Propellants", JSciIndRes **34**, 100–109 (1975) & CA **83**, 197 (1975)

Octyl. Brit designation for Bitetryl or Ditetryl, described as 1,2-Bis(2′,4′,6′-trinitronitranilino)-ethane in Vol **2**, B131-R and Vol **5**, D1513-L. Urbański (Ref) describes it as Hexanitrodiphenylethylenedinitramine
Addnl Ref: Urbański **3** (1967), 69–70

Odite. An older Brit coal-mine expl contg AN 88 & DNB 12%
Ref: Marshall, Dict (1920), 70

Oerlikon. The two Swiss arms firms of Oerlikon of Zurich and Hispano-Suiza at Geneva dominated the world markets in fast firing 20 and 30mm guns used for anti-aircraft fire, and mounted on armored vehicles for the attack of lightly protected targets. In 1972, Oerlikon obtained a controlling interest in Hispano-Suiza, and the products of the two firms have since been controlled from Zurich. As a result of this takeover, the guns of Hispano origin (see Vol **7**, H114-L) now being produced by Oerlikon have been redesignated
Refs: 1) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 333 2) R.T. Pretty & D.H.R. Archer, Eds, "Jane's Weapon Systems 1974–1975", Franklin Watts, NY (1974), 438–39 (20mm & 25mm guns) 3) F.W.A. Hobart, Ed, "Jane's Infantry Weapons 1975", Franklin Watts, NY (1975), 760, 762, 763, 767, 769, 771 & 772 (20, 25, 30 & 35mm guns & their ammo)

Off-Carriage Fire Control. A process of controlling fire on a target with the aid of a sighting device which is not mounted directly on the weapon
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 333

Offensive Grenade. A grenade having a light container, designed to kill or injure by blast and concussion, distinguished especially from a fragmentation grenade (see Vol **4**, D830 & D831). The offensive grenade is so called because the thrower, being out of range of the grenade's effects, can continue to advance as he throws and does not

have to take cover. In the US Armed Forces this type of grenade is now obsolete (see Vol **4**, D830-L)
Refs: 1) Ohart (1946), 355 & 359 2) OrdTechTerm (1962), 144-L

Offset Bombing. Any bombing procedure which employs a reference or aiming point other than the actual target. This type of bombing is employed when the target cannot be seen or is a poor reference point. When employed, the compensating factors are either set into the bombsight or computed by the bombardier
Ref: OrdTechTerm (1962), 208-R

Offset Distance (Nuclear). The distance the desired ground zero or actual ground zero is offset from the center of an area target or from a point target
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 333

Off-The-Shelf-Items. These items required by the military services which are generally used thruout the civilian economy and which are available thru normal commercial distribution channels
Ref: OrdTechTerm (1962), 208-R

OFS. Code name for 1-Methyl-5-chlorotetramethylene-1,3,5-trinitramine

OFX. Code name for 1-chloro-2,4,6-trinitro-2,4,6-triazaheptane

Ogive. The curved or tapered front of a projectile. As a geometrical body, a convex solid of revolution in which the generating area is bounded by an arc of a circle, the center of which lies on the side of the axis of revolution opposite to the arc. When applied to a projectile contour the radius of the arc is expressed in calibers, such as *"7-caliber ogive"*. With a bullet, bomb or other projectile having a fuze forming the nose, the ogive is included between a point where the projectile begins to curve or taper, and a point on the line where fuze and body meet. In other types of projectiles, the nose of the projectile is included as part of the ogive
Ref: OrdTechTerm (1962), 208-R

Ogive, False. A rounded or pointed hollow cap added to the nose of a projectile to improve streamlining. Also called *windshield or ballistic cap*
Ref: OrdTechTerm (1962), 208-R

Ogive, Rifle Grenade. A hollow metallic item designed for attachment to the forward end of a practice rifle grenade. It cushions the impact and permits reuse of the grenade
Ref: OrdTechTerm (1962), 208-R

Ohlsson, J. V. (1833–1923). Swedish expls specialist, who in collaboration with J.H. Norrbin in 1867, patented the first AN based expl, *Ammoniakkrut* (See Vol **1**, A306-R to A307-L)
Refs: 1) Anon, SS **4**, 181–2 (1909) 2) A. Larsen, "Johan Ohlsson–Obituary", Technich-Tids **53**, AlmannaAvd 45–6 (1923) & CA **17**, 1703 (1923)

Oil-Explosive Combinations. See under Slurry Explosives in Vol **6**, E469-R, and under Ammonium Nitrate Blasting Explosives in Vol **1**, A341ff

Oils, Nitrated. See under Fats, Fatty Oils, Tallows, Butters, Waxes and Fatty Acids in Vol **6**, F8-L to F9-L
Addnl Ref: F. Gehre, "Nitration of Vegetable and Animal Oils", FrP 398748 (1909) & Colver (1938), 723

Okell's Powders. Smokeless powds patented in 1899 in Fr and in 1900 in Belg (in collaboration with VanOlegar). The NC in these proplnts was prepd by nitration of wood (preferably stripped alder) with 11 parts of mixed acid consisting of 1 p nitric acid (d 1.50g/cc) and 3p of sulfuric acid (d 1.84g/cc). The NC was washed, first with w and then with a soda soln. After drying

at 40–50° to reduce the moisture content to 7–8%, the NC was gelatinized with a mixt contg 78p of eth, 15p of acet and 12p of alc per 100p of NC, and then mixed with other ingredients of smokeless powd. For example; *Cannon Powder:* NC 80 to 88, plus a mixt of 1p K or AN with 3p Ba nitrate, 20 to 12%; *Sporting Powder:* NC 94, K nitrate 5 & K dichromate 1%
Ref: Daniel (1902), 589–90

Oleates. A compd of an alkaloid or a metal with oleic acid. Al oleate has been used for coating the ingredients of expl mixts to prevent reaction under storage conditions. For example see Buechert's expl in Vol **2**, B320-R
Ref: Hackh's (1972), 472-L

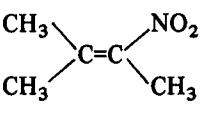
Olefins, Nitrated (Nitroolefins)

A series of nitrated *and unsaturated* hydrocarbons. The base molecule for nomenclature purposes is usually called the "ethylene series" because the first member is ethylene, C_2H_4; hence a molecular type $C_nH_{(2n-x)}N_xO_{2x}$ is derived. Other compds in the series are named after corresponding paraffins by adding to the stem "ene" or "ylene" such as 1-nitro propylene, $C_3H_5NO_2$. Olefins with two conjugated double bonds are called "dienes", such as butadiene. For more than two conjugated double bonds terms such as "triene", etc, are used (Ref 8)

Olefins can be prepd by numerous methods which are described in textbooks on organic chemistry such as Ref 7

According to Urbański (Ref 6), ". . . Besides adding concentrated HNO_3 to olefins, true nitration of olefins thru electrophilic substitution can take place to yield nitroolefins. . . In 1878 Haitinger (Ref 1) found that nitration of isobutylene with anhydrous nitric acid led to several products, among which was nitroisobutylene $(CH_3)C_2{=}CHNO_2$, in 10% yield

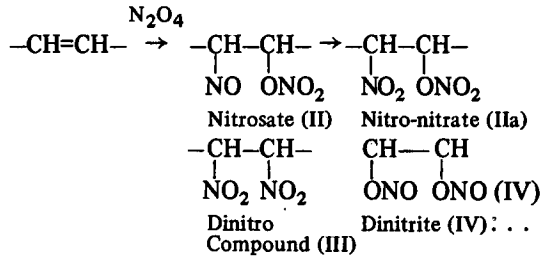
In 1935, Michael and Carlson (Ref 4) reported that with fuming nitric acid, trimethyethylene gave crystalline 3-nitro-2-methyl-2-butylene in 20% yield:



More recently Petrov and Bulygina (Ref 3) investigated in detail the conditions under which several olefins can be nitrated. They found that good yields could be obtained with concentrated nitric acid reacted with olefins at *ca* 60°C, and with less concd nitric acid at a slightly higher temp, ie, 80–90°C. Nitration was possible with 20% nitric acid, containing nitric dioxide when reacted at 70°C. Probably, . . . nitric dioxide is the nitrating agent, while the role of nitric acid is to regenerate the NO_2 radical . . .

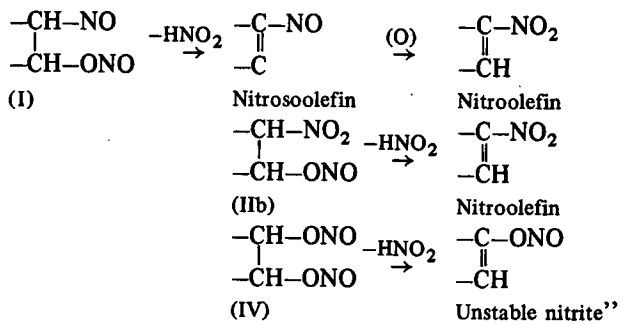
When olefin hydrocarbons react with nitrogen dioxide or nitrous and nitric anhydride, they are added to a double bond . . .

By addition of nitrogen dioxide, nitrosates (II) (nitroso-nitrates) or dinitro compds (III) or dinitrites (IV) are obtained. Nitrosates (II) can be oxidized to nitro-nitrates (IIa), viz:



The addition of N_2O_4 to compds with conjugated double bonds takes place in a way similar to the addition of halogens to these compds . . .

Schaarschmidt and Hoffmeier (Ref 2) found that on treating an unsaturated hydrocarbon with N_2O_4 a mixt of products of the I, II, III and IV types was obtained. Only the dinitro compds of type III were stable. Others underwent decomposition in the following way:



According to Hass et al (Ref 5), "All nitro alkenes polymerize with more or less rapidity. For this reason they should be used promptly after synthesis. The polymerization products are black, viscous materials readily soluble in

acetone and benzene."
Refs: 1) L. Haitinger, Ann **193**, 366 (1878) & Monatsh **2**, 286 (1881) 2) A. Schaarschmidt & H. Hoffmeier, Ber **58**, 1047 (1925) & CA **19**, 2634 (1925) 3) A.D. Petrov & M.A. Bulygina, DoklAkadN SSSR **77**, 103 (1931); not found in CA 4) A. Michael & G.H. Carlson, JACS **57**, 1268 (1935) & CA **29**, 5811 (1935) 5) H.B. Hass et al, JOC **15**, 8–14 (1950) & CA **44**, 4412 (1950) 6) Urbański **1** (1964), 81–107 7) A. Zlatkis et al, "A Concise Introduction to Organic Chemistry", McGraw-Hill, NY (1973) 8) ChemRubHdb (1975), C5 to C10

Presented below are selected nitroolefins which may be expl compds

Nitro Allyl Acetate. See under "Nitropolymers", in this Vol

3-Nitroacrylic Acid. See Vol **1**, A97-R & L

Dinitrobutenes. See Vol **2**, B376-L

Mononitrobutene. See Vol **2**, B375-R to B376-L

Trinitrobutene. See Vol **2**, B376-L & R

X,X-Dinitrocaprylene or X,X-Dinitrooctylene. See Vol **2**, C40-L

2,2-Dibromo-1-Nitro-Ethene (?) (β,β-Dibromo-α-Nitro-Ethylene). $CH(NO_2):CBr_2$, mw 230.85, N 6.07%, OB to CO_2 −17.33%; large, six-sided rhombic prisms; mp 112°. V sol in warm ethanol and insol in w. Prepn is by bubbling gaseous bromine into an aq soln of Na styphnate $[C_6H(NO_2)_3(OH)(ONa)]$. Separation from the co-product, bromopicrate, is achieved by washing the ppt with warm ethanol

The compd decomps at 120–25°
Ref: Beil **1**, 195

Nitroethylacrylate. See Vol **6**, E202-L

Ethylene Nitro. See Vol **6**, E282-L & R

1-Chlor-1-Nitro-Ethylene and Polymer. See in this Vol under "Nitropolymers"

Eulite. See Vol **6**, E342-R to E343-L

2,5-Dinitrofuran. See Vol **6**, F241-L

5-Nitro Furfural-N-Nitriminoguanidine. See Vol **6**, F243-L

5-Nitro-3-Ethyl-Hexene.
$CH_3.C(NO_2):CH.CH(C_2H_5)_2$, mw 157.24, N 8.91%, OB to CO_2 −218.77%, greenish yel liq, bp 84° at 1mm, d 0.9551g/cc at 25°, RI 1.4602 at 25°. Prepn is by heating 5-Nitro-3-ethyl-hexanol with a soln of Na carbonate in methanol for eight hrs

The compd decomps very rapidly when distd below atm press
Ref: Beil **1**, {845}

3,4-Dinitro-3-Hexene. See Vol **7**, H92-R to H93-L

1,1,1,6,6,6-Hexanitro-3-Hexene. See Vol **7**, H93-L

Oleum. Fuming sulfuric acid; a soln of sulfur trioxide in sulfuric acid used as a sulfating and sulfonating agent. See under Acidity in Acids in Vol **1**, A88-R to A90-R; Acids Used in Manufacture and Analysis of Explosives in Vol **1**, A93-L to A93-R; and under Nitration in this Vol

For analytical procedures, see under Glass Bulbs for Weighing Acids in Vol **6**, G78-R to G79-R

Olin Powder. Same as Ball Powder

Oliver, Gen Paul A. (1830–1912). American soldier and inventor in the expls field. He founded the Oliver Powder Co (see below), in which work was done by machinery invented by him. His earliest invention dates back to 1868, and relates to machinery for the manuf of gunpowder. Six addnl patents were granted him between 1868 and 1889. The main feature of these inventions was that gunpowder should be handled in small batches and with an excess of moisture, thereby reducing risk to a minimum, and making violent explns impossible. The ingredients were first mixed in a vertical rotating tub with rotating stirrers, and then fed to a roller press consisting of smooth and teethed rollers, in which they were ground together, pressed and corned. From the roller press, the powder went to a continuous belt dryer equipped with a woven wire belt

Oliver's method is still used, in a modified form, at some BkPdr plants
Ref: VanGelder & Schlatter (1927), 215–16

Oliver Powder Company. An American company manufg commercial expls, founded shortly after the American Civil War by General P.A. Oliver, near Wilkes Barre, Pa. The original plant was destroyed by fire, and another was constructed at a new location, also near Wilkes Barre. The company was sold to the duPont Co in 1903
Ref: Van Gelder & Schlatter (1927), 215–16

Oliver's Flameless Dynamite. A safety mining expl, manufd in the last century by the Oliver Powder Company. Another Dynamite manufd by the same company was called Meteor Dynamite
Refs: 1) Daniel (1902), 590 2) VanGelder & Schlatter (1927), 586

Oliver's Powder. A BkPdr, patented in Engl in 1869, in which peat replaced the charcoal, and K chlorate, desensitized by either wax, lard or rosin replaced the K nitrate. Also see refs under Chlorate Explosives in Vol **2**, C205-R
Ref: Daniel (1902), 590

Onager. An ancient weapon consisting of a slinglike catapult which threw stones from a bag or wooden bucket. It was so called after a mythylogical monster, Onager, which was said to throw stones at its pursuers with its feet
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 334

On-Carriage Fire Control. A process of controlling fire on a target with the aid of a sighting device mounted directly on the weapon
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 334

Oncin. A twelfth-century weapon having a hooked iron head resembling a one-sided pick
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 334

Onit. The name, now obsolete, used by AB Bofors, Nobelkrut; Bofors, Sweden, prior to WWII, to designate Hexogen (Cyclonite or RDX) as the basic material used in *Bonits* (see Vol **2**, B242-R)
Ref: C.M. vonArbin of Bofors Co, private communication with B.T. Fedoroff (March 6, 1963)

Ontos. Designated as the M-50, this US Marine Corps system is a full-track self-propelled direct-fire and antitank weapon. It is armed with six 106mm recoilless rifles, one .30cal machine gun, and four .50cal spotting rifles. It has a top speed of 40mph and a crew of three
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 334

Opacifiers in Solid Propellants. Carbon black and other pigments having high energy absorption coeffs in the visible spectral range (nigrosine black dye, Prussian blue, methylene blue, etc) have been used as additives (0.1 to 0.5% content) in translucent double-base proplnts to provide opacity, and thus prevent malfunction due to ignition below the surface at the site of minor imperfections

According to Crawford (Ref 1) and Hickman (Ref 2), grains of double-base proplnt exhibit unstable burning characteristics caused by the formation of minute holes (called *worm holes*) or cracks in their interior during burning. The intense radiant energy developed on burning can cause the ignition of dust or gases accumulated in these imperfections, and results in simultaneous burning in many areas. The incorporation of opacifiers seems to obviate the formation of these imperfections, and does not allow the radiant energy of burning to penetrate within the proplnt grains
Refs: 1) B.L. Crawford, USP 2440327 (1948) & CA **42**, 5230 (1948) 2) D.S. Bruce & E.L. Klein, USP 2499295 (1950) & CA **44**, 4680 (1950) 3) C.N. Hickman, USP 2574479 (1951) & CA **46**, 1259 (1952) 4) OrdTechTerm (1962), 210-L 5) Anon, EngDesHdbk, "Explosives Series, Solid Propellants, Part One", **AMCP 706-175** (1964), 50-R

Open Ammunition Space. Ground area prepared or improvised for storage of ammo in open areas to supplement magazine space
Ref: OrdTechTerm (1962), 210-L

Open Bomb. In intelligence usage, an undisguised or unconcealed sabotage expl device, distinguished especially from an *infernal machine*
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 334

Opening Charge. A charge of expl necessary to burst ordnance contg gas, incendiary or smoke-producing compds. The expl used for this purpose could not be too vigorous, in order not to scatter the contents excessively. Hand grenades were sometimes "opened" by means of a detonator charged with MF. The Brit during WWI developed an opening charge which was termed *Ophorite* (see below)
Ref: Marshall **3** (1932), 176–77

Ophorite. A Brit perchlorate expl used during WWI as an *opening charge* (see above) in incendiary and gas shells and smoke bombs. Its compn was K perchlorate 60, Mg powd 40%. This mixt developed extreme heat on ignition, but very little gas, and thus did not scatter the shell or bomb contents excessively, which was desirable
Ref: Marshall **3** (1932), 113–14 & 197

Oppau Disaster. An expln which occurred in Oppau, Ger, on Sept 21, 1921, killing 509 people, injuring 1917, and causing enormous property damage. The catastrophe was caused by the use of HE to break up a hard mass of fertilizer consisting of a mixt of AN and Amm sulfate. This method had always been practiced at Oppau because it was believed at that time that AN could not be detond unless a combustible material was also present, and, in fact, about 20000 charges of HE had been previously used in a similar manner without incident

The Oppau disaster led to an extensive examination of the expl properties of AN and it was decided that it can be expld, although with difficulty, when the material is under strong confinement and is heated or initiated with sufficiently strong force

Notwithstanding these results, the treatment of AN was continued as though it were a combustible material rather than a HE, and numerous explns and fires occurred in succeeding years, the greatest to-date being the "Texas City Disaster" (qv) in 1947. See also Vol **1**, A312-L to A313-L, A333-R & A357-L to A363-R
Refs: 1) Anon, JSCI **40**, 381–82T (1921) & CA **16**, 164 (1922) 2) C. Comentz, ChemMetEngrg **25**, 818–20 (1921) & CA **16**, 165 (1922) 3) J. Kendall, ChemMetEngrg **25**, 949 (1921) & CA **16**, 343 (1922) 4) H. Kast, ChemZtg **48**, 133–5 & 158–60 (1924); IEC **16**, 635 (1924) & CA **18**, 2079 (1924) [Final report on the investigation of the Oppau explosion] 5) H. Kast, SS **21**, Appendix 43pp (1926) 6) R. Assheton, "History of Explosions", Institute of Makers of Explosives, Wilmington, Delaware (1930), 298–300 7) Marshall **3** (1932), 116 8) Meyer (1943), 394–5

Optical Chronograph. Same as Rotating Drum Chronograph, described briefly under Chronographs in Vol **3**, C304-Rff

Optical Methods for Study of Detonation. See under Cameras, High-Speed Photographic in Vol **2**, C13-L to C19-R, and under Detonation (and Explosion), Experimental Procedures in Vol **4**, D299ff

Optical Methods in Ballistics. See under Cameras, High-Speed Photographic in Vol **2**, C13-L to C19-R

Optimum Density. See under Limiting Density in Vol **3**, D66-R

Optimum Gun. See under Drozdov, N.F., in Vol **5**, D1555-L & R

Optolene. A liq rocket fuel (d 0.9g/cc) consisting of about 50% *Visol* (vinylisobutylether), 10–20% aniline, with the remainder being *Optol* (a coal tar product contg phenol). It was used in the *Wasserfall* missile in conjunction with concd nitric acid (contg about 10% sulfuric acid), which served as an oxygen carrier. The ratio was 0.24ps of Optolene per 1p of acid. The theoretical sp impulse for this mixt was 214 lb/lb/sec, with only 183 actually being obtained. This value was nearly equal to that obtained using Visol/nitric acid
Refs: 1) R. Gollin, CIOS **Rept 28-56** (1945), 19 2) PATR **2510** (1958), Ger 123-R

Orange Powders. Various BlkPdrs manufd in the last century by Laflin and Rand Powder Co at Orange, NJ, USA. Also see under Laflin and Rand Powder Co in Vol **7**, L2-R
Ref: Daniel (1902), 400

Orbital Bomb. A satellite contg a nuclear warhead which circles the earth in a low orbit and which can be commanded to descend on a particular target. No such weapons are now known to be operational, and their deployment would be prohibited under the terms of the Outer Space Treaty of 1966. However, this treaty does not prohibit anything making less than a full circle around the earth, hence the **FOBS** *(Fractional Orbital Bombardment System).* The FOBS method of nuclear delivery takes advantage of the orbital attack configuration while staying within the terms of the treaty. While a normal **ICBM** follows a very high parabolic path to target, highly "visible" to defending radars, a weapon in low orbit (≈100 miles) can make a sharp descent to earth, thus cutting radar warning time very substantially, to about three minutes. A FOBS path therefore consists of a blast-off movement into low orbit, a partial circle to the target earth zone, and a rapid descent. This would seriously prejudice **ABM** ballistic missile defense systems as now conceived. There is, however, a loss of accuracy and payload which make FOBs weapons unsuitable for a *counterforce* role against *hardened* missile silos
Ref: E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 97-L & 148-L

ORDNANCE

Definition. A term that includes, in US usage, nearly all combat weapons of the land, sea and air forces. British military usage generally restricts it to guns of artillery caliber. In its broadest meaning the term includes small arms, ammunition, artillery, mortars, recoilless rifles, field guns, howitzers, bombs, mines, grenades, torpedoes, rockets, rocket launchers, guided missiles, self propelled mounts, tanks, motor combat vehicles and pyrotechnics. In this sense, it is nearly equivalent to *munitions* or *materiel.* Weapons mounted on ships, aircraft or tanks are usually referred to as *armament* rather than as *ordnance*

Ordnance Department

History. The US Army organization that formerly, for over 100 years, had responsibility for the design, manufacture and procurement from private industry of weapons, ammunition and vehicles, for the training of personnel in their use, and for their storage, issue and maintenance. The Ordnance Department also served both the Navy and Air Force as directed by higher authority

The lapel insignia worn by ordnance officers

was a flaming bomb. It is said to be the oldest of US Army insignia, having been adopted in 1832

In the early years of its history the US Army functioned without a distinct ordnance branch. At first, in 1775, ordnance was the responsibility of a Military Stores Committee; then, from 1776 to 1812, of an officer titled the "Commissary of Artillery Stores" and a secret committee under a "Board of War and Ordnance"

The formation of the Ordnance Department resulted from four events following cessation of hostilities in 1784. In 1785, the Secretary of War was charged with taking into his care all military stores, equipment, and supplies of the US Army. Second, a "Surveyor of Ordnance" was authorized in 1789. Third, Congress provided for the erection and repair of magazines and arsenals, and for the establishment of national armories. Fourth, in 1795, a "Purveyor of Public Supplies" was appointed to conduct the procurement of all military and naval stores necessary for the service of the USA. Finally, the establishment of the Ordnance Department as a separate corps was effected by Congressional Act of 14 May 1812

As a post-war economy measure, Ordnance was combined with Artillery in 1821. This proved to be a failure, attested to by high ranking Generals and the War Department, so that the Ordnance Department was again organized as a separate corps by Act of 5 April 1832. An Act of 4 June 1920, amending the National Defense Act, placed the Ordnance Department under the Assistant Secretary of War charged with the business and supervision of procurement of all military stores needed in time of war, and reauthorized permanent commissions in the Department after a period of 20 years of "detailing" officers from other arms or services. In 1942, the Ordnance Department was placed under the Commanding General, Services of Supply (Ref 1)

On 28 June 1950, Public Law 581, known as the Army Reorganization Act, replaced the National Defense Act of 1920, changing the name of the Ordnance Department to Ordnance Corps, and merged Field and Coast Artillery (Ref 2)

On 1 August 1962, a major army reorganization was implemented, with the creation of two new Commands, Army Materiel and Combat Development. The Ordnance Corps was eliminated, and its functions and responsibilities were distributed among the following subordinate Commands of the Army Materiel Command (AMC): 1) Missile Command: essentially Army Ordnance Missile Command
2) Munitions Command: essentially a combination of the Ordnance Special Weapons – Ammunition Command and Chemical Corps
3) Weapons and Mobility Command: a combination of the Ordnance Tank – Automotive Command, the Ordnance Weapons Command, and the Transportation Corps
4) Communications and Electronics Command: the Signal Corps plus Ordnance fire-control radar
5) General Equipment Command: essentially engineer equipment and general supplies and equipment outside the responsibilities of the Defense Supply Agency
6) Test and Evaluation Command: responsible for environmental test centers, proving grounds, and the former Continental Army Command service test centers
7) Supply and Maintenance Command: responsible for the terminal Commands, overseas supply agencies, depots, storage and maintenance facilities

An office of Research and Development was established on the staff of AMC having control over such Laboratories as: Diamond Ordnance Fuze, Ballistics Research, Environmental Research, Materials Research, and Human Engineering (Ref 3)

Based on reports and recommendations of the Army Materiel Acquisition Review Committee (AMARC) on 1 April 1974, a major reorganization of AMC was instituted for completion within four years (Ref 4). The concept of separate development and logistic centers was replaced with Research and Development (R&D) Commands or Materiel Readiness Commands, under the US Army Materiel Development and Readiness Command (DARCOM). This reorganization represents a clear separation of R&D functions from logistic activities (Ref 5)

Mission. Armories at Springfield, Mass (estb 1777) and Harpers Ferry, West Virginia (estb

1794), together with the ten Arsenals listed below, were established to implement the Ordnance Department:

Arsenals	Year Established
Rome, Rome, NY	1813
Allegheny, Pittsburgh, Pa	1814
Watervleit, West Troy, NY	1814
Bellona, Richmond, Va	1816
Frankford, Philadelphia, Pa	1816
Pikesville, Pikesville, Mo	1816
Washington, Washington, DC	1816
Watertown, Watertown, Mass	1816
Augusta, Augusta, Ga	1817
Baton Rouge, Baton Rouge, La	1819

The mission originally assigned to the Ordnance Department was to design, develop, procure, store, maintain, and supply to the Army such equipment and supplies as are assigned to the Ordnance Department for procurement, in such quantities and at such times as are required to meet the requirements of Army supply programs and other directives of higher authority. It was also charged with training and furnishing specialized ordnance troops to service Commands and units of the field services

By 1945 there were six manufacturing Arsenals:

Arsenals	Year Established
Springfield Armory, Springfield, Mass	1777
Watervliet, West Troy, NY	1814
Frankford, Philadelphia, Pa	1816
Watertown, Watertown, Mass	1816
Rock Island, Rock Island, Ill	1863
Picatinny, Dover, NJ	1880

Each Arsenal had a standard mission: Under the general direction of the Chief of the Industrial Service, and with reference to the assigned material, each Arsenal designs and develops new and improved items, and in an emergency manufactures and supplies certain standard items; maintains and develops the knowledge of production; provides for the application of new manufacturing techniques; maintains pilot production lines in step with the industrial arts and operates them continuously for immediate use in supplying early demands of war; and acts thereafter as control and advisory center for the major production assumed by industry at large; provides engineering supervision and inspection standards relative to all production of assigned materiel; carries on the necessary activities related to the above

Organization. The monolithic structure of the Ordnance Department culminated in 1945 with the following organization and responsibilities:

1) **Office of Chief of Ordnance**
   a) Special Advisory Staff: Leaders of Industry, Finance, and other spheres to assist in formulating policies and procedures for efficient accomplishment of ordnance mission
   b) General office: Performs executive and administrative duties which are common to all activities
   c) Military Plans and Training Service: Training of Ordnance military personnel and planning for the betterment of ordnance service in the Army
   d) Research and Development Service: Plans and executes progressive plans for research and experimental development of new and improved ordnance materiel, and new, improved substitute materials for ordnance use
   e) Industrial Service: Procures, inspects, and accepts all ordnance materiel and spare parts, performing all related engineering work
   f) Field Service: Stores, issues, inspects, repairs, modifies, and maintains ordnance materiel and ammunition in assigned ordnance installations
2) **Field Installations**
   a) Specialized Centers and Suboffices: To provide centralized control over decentralized operations and industries such as Cannon Suboffice at Watervliet, Small Arms Ammunition at Frankford, and Inspection Gage and Fire Control Suboffices at Rock Island
   b) Manufacturing Arsenals (6): To act primarily as centers for technical expertise and development, rather than as manufacturing plants
   c) Procurement Districts (13): To carry designs and specifications thru procurement to manufacture in civilian industry. Performs final inspection of completed item
   d) Proving Grounds: Conduct field work of

designing, developing, testing and inspection of ordnance assigned them

e) Government Owned Manufacturing Plants (69): Produce ammunition (56), artillery (2) and small arms materiel (11)

f) Depots: Store ordnance items for issue (Ref 1)

The current organizational concept is directed at establishing individual development centers to emphasize the acquisition process. For ordnance items these centers will consist of:

a) Armament Development Center: responsible for small and large caliber weapon systems, chemical systems, and ballistics research

b) Harry Diamond Development Center: responsible for all non-communication related electronic research and development disciplines, such as fuzes, sensors, lasers, electro-optics, and improved electronics technology and electrical components

c) Missile Development Center: responsible for development and initial acquisition of Army missile systems

See also under "Army Ordnance Corps (US)" in Vol **1**, A485-R, and "Arsenal" in Vol **1**, A489-R

Written by **D. J. VEAL**

Refs: 1) W.C. Farmer, "Ordnance Field Guide", Vol **1**, Military Service Publishing Co, Harrisburg, Pa (1945) 2) Anon, Ordn **35**, 121 (1950) 3) Anon, Ordn **46**, 665 (1962) 4) J.R. Deane, Jr, Army, 68–72 (Oct 1975) 5) Anon, Army Research & Development Magazine, 4 (Jan–Feb 1976)

Organ Gun. A piece of ordnance with numerous gun barrels arranged side by side and capable of being fired simultaneously. In the fourteenth to the seventeenth century as many as 160 barrels were sometimes so arranged. Also see under Orgues

Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 335

Organic Peroxides and Hydroperoxides. See under Hydroperoxides, Organic in Vol **7**, H224-R to H227-R

Organic Promoters. To an expl mixt contg TNT, PA, Nitronaphthalene, and an oxidizer such as AN or Ba nitrate, is added one or more aliphatic or aromatic compds in which the *molecular length,* calcd from values of atomic radii and bond angles given in the Ref, is within 0.1A° of being equal to 3.89, 4.19, 4.84 or 5.13A°. Suitable organic promoters are ethyl acetate, methyl propionate, propanol, butanol; propionic, lactic and butyric acids; butyric aldehyde, benzyl alcohol, salicylic acid, 1,2-dichloroethylene, or glycine

Ref: US Powder Co, BritP 497145 (1938); CanadP 380077 (1939) & CA **33**, 4040 (1939)

Organic Vapors Explosion Hazard, Reduction of. See under Explosion Hazards of Organic Vapors, Reduction of, in Vol **6**, E373-L; Detonation (and Explosion), Hazards (Dangers) of, in Vol **4**, D366-L to D367-R; and D245-L

Orgues (Organs). Firearms consisting of a bumber of barrels firing simultaneously, invented in Fr in the sixteenth century by Pedro Navarro, an engineer in Louis XII's court. He designed some 200 orgues, his later masterpieces being 2 feet long and firing some 50 shots at once

It should be noted that previous to Navarro, in the fifteenth century, Leonardo daVinci invented multi-barrel guns which can be considered as distant ancestors of the recent anti-aircraft "pompons"

Ref: J.E. Newman, "The Tools of War", Doubleday Doran, NY (1943), 51

Oriastites. Expls similar to *Meganites* (see in this Vol), but contg no nitrated corozo (ivory nut). One of the varieties was: NG 60, nitrated wood (nitrolignite) 20, and Na nitrate 20%

Ref: Daniel (1902), 434 & 591

Oriental (Powder). Mixt of BlkPdr, K chlorate and ligneous materials such as tanbark, sawdust, etc. Also see Vol **2**, C205-R

Ref: Daniel (1902), 591

Origin–Identification of TNT. A study was conducted at PicArsn to demonstrate the feasibility of associating trace organic impurities in TNT to its origin of manuf. TNT samples from the process lines at three US Army Ammunition Plants were analyzed for their mono-, di- and trinitrotoluene isomer purity contents by gas chromatography. The isomer impurity profiles of TNT samples, representing a series of lots manufd over a two-month period were found to remain constant for a given plant. In addition, significant differences were shown to exist in the kind, number and concn of isomers among the representative samples from the three plants. Based on these results, the trace organic impurity profile of TNT is shown to be related to its origin

Ref: C. Ribaudo & J. Haberman, "Origin–Identification of Explosives Via Their Composite Impurity Profiles. I. The Relation of the Origin of Military Grade TNT to its Mono-, Di-, and Trinitrotoluene Isomer Impurities", PATR **4768** (1975)

Ormites. Mining expls contg nitrates as the chief ingredients, authorized for use in Engl in 1898

Ref: Daniel (1902), 591

Orsman's Explosives. Several expls were patented in Engl by W.J. Orsman between 1896 and 1900. One was called *Amvis* (see Vol **1**, A393-R); others were: a) A mining expl obtained when one p of finely pulped cellulose or the slightly nitrated product was blended with one p of hot chlorodinitrobenzene and 20p of powdered AN (BritP of 1896–7); b) A mining expl prepd by mixing one p of lampblack with one p of DNB and 24p of powdered AN (BritP of 1899–90)

Ref: Daniel (1902), 592

Ortho-Nitroaromatic Compounds; Hazards in Handling. The refs discuss the expl properties of o-nitrobenzoyl chloride and o-nitrophenacetyl chloride, both of which are likely to expld when heated to over 100°. It is suggested that these compds be prepd and utilized in soln without isolation of the acid chloride

Refs: 1) N.C. Cook & F.C. Whitmore, C&EN **23**, 2394 (1945) & CA **40**, 1034 (1946)
2) May & Baker, Ltd, Chem&Ind **1946**, 89 & CA **40**, 2985 (1946)

Orthophosphates. Expls characterized by the evolution of N on heating may be effectively stabilized by the addition of approx 1% of a neutral mixt of alkali metal dihydrogen orthophosphate (ie, NaH_2PO_4) and dialkali metal hydrogen orthophosphate (ie, Na_2HPO_4)

Ref: E. Whitworth & J.C. Hornel, USP 2470733 (1949) & CA **43**, 5594 (1949)

Oscillograph. A cathode-ray oscilloscope in which a photographic or other permanent record is produced by the electron beam of a cathode-ray tube. A cathode-ray oscilloscope is a test instrument that uses a cathode-ray tube to make visible on a fluorescent screen the instantaneous values and waveforms of electrical quantities that are rapidly varying as a function of time

In the ordnance field, oscillographs are used in chronographs and chronometers to determine the muzzle velocity of ammo and proplnts, as well as the velocity of detonation of expls. See under Chronographs in Vol **3**, C304-R to C319-L

Ref: D.N. Lapedes, Ed, "McGraw-Hill Dictionary of Scientific and Technical Terms", McGraw-Hill, NY (1974), 234-R

03 (0-Three) Explosive. See under Explosifs 03 or Promethees in Vol **6**, E363-L

Otter (or Paravane). A protective underwater device which, when towed with a wire rope from a fitting on the bow of a ship, rides out from the ship's side and cuts the cables of anchored mines. The mines then rise to the surface, where they can be seen and destroyed

Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 340

OTTO. A liq monopropInt used in a hot gas generator to give increased speed, range and depth to the US Navy's Mk48 torpedo
Refs: 1) Anon, "Chemistry Research Quarterly Progress Report (U), April–June 1965", US Naval ProplntPlant **TMR-231**, Indian Head, Md (1965) 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 336

Ottoson's Military Dynamite. See under PATR **1760** in Vol **5**, D1611-R

Out-of-Line Safety. A term descriptive of a method by which detonator safety or bore safety is attained. In the safe condition, one or more components of the fuze or booster expl train are in a non-aligned condition with respect to the other components, so that normal functioning cannot occur
Ref: OrdTechTerm (1962), 216-R

Output Characteristics. The characteristics of an expl component which determine the form and magnitude of the energy released. See under Output Tests in Vol **4**, D1084ff

Outrigger. Used mainly in antiaircraft artillery. An outrigger might be called a form of trail in that it aids in stabilizing the weapon. The outriggers are hinged, allowing them to be folded either horizontally or vertically for traveling, and extended in a horizontal plane when the mount is emplaced. Four outriggers are usually attached to each mobile gun mount
Ref: OrdTechTerm (1962), 216-R

Outrigger Torpedoes. Expl charges attached to a long pole and carried in small boats toward enemy vessels. When the vessels are reached, the torpedoes are placed against their hulls and fired, either by percussion or by electrical caps. This primitive and suicidal method of "torpedoing" ships was attempted by the Russians during the war of 1877–78, and several Turkish ships were sunk, together with the attacking forces
Ref: J.R. Newman, "The Tools of War", Doubleday, Doran & Co, NY (1943), 226

Overhit (Oversaturate). To hit a target with more destructive force than necessary to accomplish the desired amount of damage
Ref: OrdTechTerm (1962), 216-R

Overpressure. The pressure resulting from the blast wave of an expln. It is referred to as *positive* when it exceeds atm pressure and *negative* during the passage of the wave when resulting pressures are less than atm pressure. *Peak overpressure* is the highest overpressure resulting from the blast wave
Refs: 1) OrdTechTerm (1962), 216-R & 221-L 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 337

Overspin (Overstabilization). In a spin stabilized projectile, when the rate of spin is too great for the particular design of projectile, it becomes overstable and its nose does not turn downward as it passes the summit of the trajectory and follows the descending branch. In such cases the projectile is said to have 'overspin' or 'overstabilization'
Ref: OrdTechTerm (1962), 217-L

Oxalate Blasting Powders. Mining safety expls invented in Engl by Greaves and Hann in 1897–98 and manufd by the Oxalate Blasting Powder Co at Gatebeck (Westmoreland), which later became the Nitrates Explosives Co, Ltd. These expls were a modification of BlkPdr in which sulfur was partially or entirely replaced by one or more of the following: oxalic acid, oxalates of Amm, K or Na (simple or double), borax, boric acid, etc, each of which could contain w of hydration. The purpose of these substitutions was to obtain expls with a cool flame, so that they could be safely used in gaseous mines
Refs: 1) Daniel (1902), 592–3 2) Cond-ChemDict (1942 Ed only), 290

Oxalate Carbonite and Oxalate Gelignite. Expls containing oxalates as "cooling agents", manufd in Engl by the Nobel Explosives Co, Ltd beginning in 1899. See under Cooling Agents or Coolers in Vol **3**, C511
Ref: Daniel (1902), 593

LIST OF OXALATE COMPOUNDS

Barium Oxalate. BaC_2O_4, mw 225.36, colorl crysts; mp, decomps 400° to CO+$BaCO_3$, loses CO above 346°; d 2.568g/cc, v sl sol in w (0.0093g/cc at 18°, 0.0228g/cc at 100°), sol in acids & Amm chloride, insol in alc. Prepn given in Ref 1. Q_f in kcal/mole at 18°, BaC_2O_4 (c), –327.6; at 25°, $BaC_2O_4.½H_2O$ (c), –363.7; at 18°, $BaC_2O_4.H_2O$ (ppt), –397.37; at 25°, $BaC_2O_4.2H_2O$, –470.1; at 25°, $BaC_2O_4.3½H_2O$, –575.73 (Refs 5, 6 & 7)

Ba oxalate is *poisonous*, an eye, nose, throat and skin irritant, and produces dermatitis. It is a fire and expln hazard, dangerous when heated to decompn, and emits toxic fumes (Refs 5 & 9)

It has been used as a retardant in pyrots, imparting some green color to burning compns (Refs 5 & 8), and as an ingredient of gunflash simulators (Refs 2 & 3)

The requirements of the US Armed Forces are contained in Mil Spec **JAN-B-660**, "Barium Oxalate (For Use In Ammunition)", (5 Aug 1948): Color – white; moisture – 0.3% max; material insol in 10% HCl soln – 0.5% max; material sol in water – 0.3% max; water sol alkalinity – 0.1% max; water sol acidity – the water extract shall not be acid to methyl orange; barium oxalate – 92% min; calcium salts – 0.5% max; grit – none; granulation, thru No 100 US Standard Sieve – 90% min; apparent density – 0.50g/ml max
Refs: 1) Gmelin, Syst Nr 30; 8th Ed (1932), 144–149; supplement (1960), 303–305 2) O.G. Dunkle, "Study Toward Reducing the Smoke Effects From Flash Eliminating Agents", PATR **705** (1936) 3) D. Hart, "Development of Compositions and Materials for Simulator, Gunflash, No 3, Mk 1", PATR **1520** (1945) 4) L. Médard, MAF **28**, 467 (1954) 5) Anon, EngDesHndbk, "Military Pyrotechnics Series, Part Three, Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 45–6 6) Merck (1968), 121-R 7) CondChemDict (1971), 93-R 8) R. Lancaster, T. Simizu, E.A. Butler & R.G. Hall, "Fireworks, Principles and Practice", Chemical Publishing Co, NY (1972), 31 9) Sax (1975), 435-R & 988-L

Calcium Oxalate (Monohydrate). $CaC_2O_4.H_2O$, mw 146.12, colorl monoclinic crysts; mp, loses H_2O at 200°, d 2.2g/cc; insol in w, acet ac & alc, sol in acids. Prepn from Ca formate in Ref 1, and Ca cyanamide in Ref 2. Q_f at 298°K, –399.1kcal/mole; free energy of formation at 298°K, –360.6kcal/mole; entropy at 298°K, 37.28kcal/mole; heat capacity, 36.40 cal/degree/mole (solid) (Refs 5, 6, 7 & 8)

Ca oxalate is corrosive and produces local irritation. It has a caustic effect on mouth, esophagus and stomach, and can cause severe damage to kidneys (Refs 6 & 9). It can be dangerous when heated to decompn because of toxic fumes (Ref 6)

Ca oxalate has been used as a retardant in pyrots, imparting a pink color to burning compns (Ref 3), and as an ingredient of gunflash simulators (Ref 4)

The requirements of the US Armed Forces are detailed in Mil Spec **JAN-C-628**, "Calcium Oxalate (For Use in Ammunition)", (30 June 1948): Color – white; moisture – 0.5% max; material insol in 10% HCl soln – 0.5% max; material sol in water – 0.4%; barium salts – 0.5% max; calcium – 26.6% min; oxalate – 58.4% min; grit – none; granulation – thru No 100 US Standard sieve – 99% min; apparent density – 0.60g/ml max
Refs: 1) H. Bredt, USP 1622991 (1927) 2) I. Barsky & J. Buchanan, JACS **53**, 1270 (1931) 3) G.J. Schladt, "Modification of M-8 Flare Composition to Increase Candlepower", PATR **676** (1935) 4) D. Hart, "Development of Compositions and Materials for Simulator, Gunflash, No 3, Mk 1", PATR **1520** (1945) 5) E.S. Freeman & B. Carroll, JPhysChem **63**, 394 (1958) 6) Anon, EngDesHndbk, "Military Pyrotechnics Series, Part Three, Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187**

(Oct 1963), 45–6 7) Merck (1968), 194-L 8) CondChemDict (1971), 158-L 9) Sax (1975), 512-L & 988-L

Lead Oxalate. PbC_2O_4, mw 295.23; wh, heavy powd; mp, decomps 300°; d 5.28g/cc. Insol in w, sl sol in acet ac, sol in dil nitric ac & fixed alkali hydroxides. *Poisonous!*

Warren (Ref 1) evaluated Pb oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

Drop Test. (BurMines app; 2kg wt)	100+ inches
Expln Temp Test, 5 sec.	> 500°
Sand Test (200g bomb)	
Initiation by fuse, g sand crushed	0
Initiation by 0.3g MF, g sand crushed	0

There is no US Mil Spec for Pb oxalate

Refs: 1) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR **1389** (1944) 2) Merck (1968), 613-R

Mercurous Oxalate. $Hg_2C_2O_4$, mw 489.22, wh cryst powd. Prepd by Souchay & Lenfsen (Ref 2) by treating sol mercurous salts, such as the nitrate, with oxalic acid. Insol in cold w, alc & eth; decompd by hot w; insol in dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on impact (Ref 2); does not expld or deflagrate on heating or rubbing in a procelain mortar (Ref 3)

There is no US Mil Spec for Mercurous oxalate

Refs: 1) Beil **2**, 516 & [489] 2) A. Souchay & E. Lenfsen, Ann **103**, 308 (1857) 3) A. Langhans, SS **15**, 89–90 (1920)

Mercuric Oxalate. HgC_2O_4, mw 288.61, wh cryst powd; mp, decomps. Prepd by Souchay & Lenfsen (Ref 2) by adding an aq soln of mercuric nitrate to an aq soln of oxalic acid. Insol in cold w, difficulty sol in hot w and dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on heating or impact (Ref 2); deflagrates on rubbing in a porcelain mortar (Ref 3)

Warren (Ref 4) evaluated mercuric oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

Drop Test (BurMines app; 2kg wt)	95 inches
Expln Temp Test, 5 sec	170°
Sand Test (200g bomb)	
Initiation by fuse, g sand crushed	0
Initiation by 0.3g MF, g sand crushed	6.5

There is no US Mil Spec for Mercuric oxalate

Refs: 1) Beil **2**, 516 & [489] 2) A. Souchay & E. Lenfsen, Ann **102**, 42–44 (1857) 3) A. Langhans, SS **15**, 89–90 (1920) 4) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR **1389** (1944)

Note: R. Philip reported that Hg oxalates are always present as impurities in commercial MF, and that the determination of Hg is not sufficient to give the true fulminate content [R. Philip, SS **7**, 110, 156, 180, 198 & 221 (1912)]

Potassium Oxalate. $K_2C_2O_4.H_2O$, mw 184.23; colorl, odorless crysts; mp, loses H_2O at about 160°, when ignited is converted into carbonate without appreciable charring; d 2.13g/cc, sol in 3p of w. Can be prepd by heating a mixt of K formate or carbonate with oxalic acid and a small amt of K hydroxide, with subsequent extraction of w. Highly toxic by inhalation and ingestion

K oxalate was used as a cooling agent in mining expls such as Oxalate Blasting Powder (see in this Vol) and Gelatine-Prosperit (see in Vol **6**, G52)

There is no US Mil Spec for K oxalate

Refs: 1) Beil **2**, 513, (224) & [485] 2) Daniel (1902), 592 3) Naoûm, NG (1928), 418 4) Merck (1968), 856-L 5) CondChemDict (1971), 723-R

Silver Oxalate. $Ag_2C_2O_4$, mw 303.78, wh cryst powd; mp, decomps violently between 130° & 190° (see below); d 5.03g/cc. Sol in 24000p of w, moderately concd nitric acid, and ammonia. Can be prepd by mixing cold solns of oxalic acid and Ag nitrate (Refs 1, 2 & 6)

Berthelot (Ref 4) states that Ag oxalate explds very energetically when subjected to a shock or when heated to 130°. Wöhler found that the salt expld at 140° when heated in a current of hydrogen (Ref 2). Hoitsema (Ref 5), however, gives an expln temp of 190°

Taylor & Buxton (Ref 6) report that Ag oxalate is insensitive to impact. It expld with a weak puff when dropped on a hot metal surface at 260°, and at 232° on slow heating. It was not ignited by the spit of a fuze when compressed in a detonator capsule, and was not detonated by 0.25g of MF

Warren (Ref 7) evaluated Ag oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

Drop Test (BurMines app; 2kg wt)	90 inches
Expln Temp Test, 5 sec	210°
Sand Test (200g bomb)	
Initiation by fuse, g sand crushed	0
Initiation by 0.3g MF, g sand crushed	0

There is no US Mil Spec for Ag oxalate

Refs: 1) Beil **2**, 514, (224) & [486] 2) F. Wöhler, Ann **30**, 4 (1839) 3) A. Souchay & E. Lenfsen, Ann **103**, 311 (1857) 4) M. Berthelot, "Explosives and Their Power", Hake & Macnab, Paris (1892), 366 & 475 5) F. Hoitsema, ZPhysChem **21**, 142 (1896) 6) C.A. Taylor & E.P. Buxton, ArmyOrdn **7**, 69 (1926) 7) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR **1389** (1944) 8) Merck (1968), 948-R

Sodium Oxalate. $Na_2C_2O_4$, mw 134.01; white, odorless, cryst powd; mp, 250–270° with decompn; d 2.34g/cc. Sol in w (3.7g/100g at 20°, 6.33g/100g at 100°), insol in alc. Can be prepd by neutralizing an aq soln of oxalic acid with Na carbonate (Refs 1, 10, 11 & 13)

Na oxalate is a *strong poison!* It is corrosive and produces local irritation. Taken orally, it has a caustic effect on the mouth, esophagus and stomach, and can cause severe damage to the kidneys (Refs 10 & 11). It is dangerous when heated to decompn, emitting toxic fumes (Ref 10)

Na oxalate has been used as a cooling agent in mining expls, such as *Oxalate Blasting Powders* (see in this Vol) and Tremonite (qv), as well as in some Fr permissible expls contg NG (Ref 3, p 420). It has been evaluated as a flash reducing agent in proplnts (Ref 4), and is used in pyrots to impart a yellow color and reduce burning rate (Refs 5, 6, 7, 8, 9, 10, 12 & 14)

The requirements of the US Armed Forces are described in Mil Spec **JAN-S-210**, "Sodium Oxalate (Technical Grade)", (15 May 1945): This specification covers one grade of sodium oxalate, furnished in the following classes as specified in the contract or order: class a, class b, class c, and shall conform to the following requirements: Moisture – 0.50% max; oxalate purity – 99.0% min; insoluble matter – 0.50% max; sodium acid oxalate – 1.50% max; granulation – shall conform to the following requirements using US Standard sieves

Thru US Std Sieve (min)	Class a %	Class b %	Class c %
420 micron (No 40)	99	–	–
250 micron (No 60)	–	99.9	–
149 micron (No 100)	90	–	99.9

Refs: 1) Beil **2**, 513, (223) & [484] 2) Daniel (1902), 592 3) Naoûm, NG (1928), 419 & 420 4) D.R. Cameron, "Study of Flash Reducing Agents for FNH Powder", PATR **295** (1932) 5) G.J. Schladt, "Development of Pyrotechnic Composition For Amber Colored Signal", PATR **596** (1935) 6) Ibid, "Modification of M-8 Flare Composition to Increase Candlepower", PATR **676** (1935) 7) J.B. Nichols, "Modification of M-8 Flare Composition to Increase Candlepower", PATR **841** (1937) 8) A. Strasser, "Study of Use of 85% Grade of Sodium Oxalate in Pyrotechnic Compositions", PATR **1161** (1942) 9) H.J. Eppig, "Development of a T-15 Airport Flare Composition", PATR **1512** (1945) 10) Anon, Eng-DesHndbk, "Military Pyrotechnics Series, Part Three, Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 274–5 11) Merck (1968), 963-L 12) Ellern (1968), 125, 136 13) CondChemDict (1971), 806-R 14) R. Lancaster, T. Shimizu, R.E.A. Butler & R.G. Hall, "Fireworks, Principles and Practice", Chemical Publishing Co, NY (1972), 48

Strontium Oxalate, Anhydrous and Monohydrate. SrC_2O_4 and $SrC_2H_4.H_2O$; mw 183.65 & 193.67; colorl crysts. For mononydrate, required for soln of 1 p: 2000p of w. 1900p of 3.5% acet ac, 1115p of 23% acet ac, less sol in 35% acet ac; readily sol in dil hydrochloric or nitric acids. Heat of formation, kcal/mole at 18°, anhydr; at const press, −327.7; at const vol, −326.5. Free energy of formation, kcal/mole at 18°, monohydrate: (c) −360.8. The monohydrate begins to lose H_2O at 43°, with all gone by 177°. On further heating the wt remains const up to 400°. It dissociates into Sr carbonate and dangerous CO over the range 400–520° (Refs 3 & 5)

Sr oxalate can be prepd by treating hot aq oxalate or oxalic acid soln with a hot aq soln of a Sr salt (Ref 1)

Sr oxalate is highly toxic, corrosive and produces local irritation. When taken orally it may have a caustic effect on the mouth, esophagus and stomach (Ref 5)

Both SrC_2O_4 and $SrC_2O_4.H_2O$ are used as burning rate retardants and to impart a scarlet color to burning pyrot compns (Refs 2, 4, 6 &7)

The requirements of the US Armed Forces are detailed in Mil Spec **MIL-S-12210A**, "Strontium Oxalate", (11 Sept 1952): Strontium oxalate shall be of the following grades as specified:
Grade A – anhydrous strontium oxalate
Grade B – hydrated strontium oxalate, and shall conform to the physical and chemical properties listed in Table 1

Table 1
Chemical and Physical Properties

Property	Grade A	Grade B
Color	White	White
Moisture, percent, max	0.25	10.0
Strontium oxalate, percent, min	94.0	84.0
Iron, percent, max	0.01	–
Ammonium compounds, percent	None	–
Granulation		
Thru No 60 sieve, percent, min	–	99.0
Thru No 140 sieve, percent, min	99.0	–

Strontium oxalate shall be free of barium compounds, and shall contain not more than a slight amount of calcium compds. Conformance with these requirements shall be determined by means of a flame test

Refs: 1) Beil **2**, 515 & [488] 2) J.B. Nichols, "Development of a Substitute for the Potassium Chlorate Red Compositions Used in Pyrotechnics", PATR **604** (1935) 3) S. Peltier & C. Duval, AnalChemActa **1**, 358 (1947) 4) L. Médard, MAF **28**, 467 (1954) 5) Anon, EngrDesHndbk, "Military Pyrotechnics Series, Part Three, Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963) 6) Ellern (1968), 136ff 7) R. Lancaster, T. Shimizu, R.E.A. Butler & R.G. Hall, "Fireworks, Principles and Practice", Chemical Publishing Co, NY (1972), 49

Oxaldihydroxamic Acid (Oxalsäuredihydroxylamid, Oxaldihydroxamsäure, Dihydroxyloxamid, or Aethandihydroxamsäure in Ger). $C_2H_4O_4N_2$, mw 120.02, N 23.33%, OB to CO_2 −26.66%. Three isomers have been reported:

a) *Oxaldihydroxamsäure of H. Lossen:* HO.NH.CO.CO.NH.OH, prisms, mp 165° followed by expln. It was prepd by H. Lossen in 1869 (Ref 2) by the action of hydroxyloxamine on the ethyl ester of oxalic acid. Other methods of prepn are given in Ref 1. Sl sol in cold w, insol in acetic ac. Forms salts (Amm, Ba, Ca, Fe, K, Ag, Na & hydroxylamine), most of which expld between 130° and 180°

b) *Oxaldihydroxamsäure of W. Lossen & P. Behrend:* HO.NH.CO.C(OH):N.OH, unknown in the free state, but several of its salts were prepd and proved to be expl (Ref 3). $Ba(C_2H_3O_4N_2)_2$; mp, explds violently; was prepd by the interaction of ethyl oxalate, Ba hydroxide soln and hydroxylaminohydrochloride. Ca, Cu and Ag salts were also prepd; they all expld at about 50°

c) *Oxaldihydroxamsäure of N. Paolini:* HO.N:C(OH).C(OH):N.OH, white hygr prisms from eth & alc, mp 82–83°, decomps 90°, explds when heated rapidly. It was prepd by the action of benzene sulfohydroxamic acid on glyoxal. V sol in w, sl sol in eth & alc, sol in ether plus alc (Ref 4). It forms salts, some of which are expl. Hofmann & Ehrhardt (Ref 5) prepd its Cu-K salt ($K_3CuC_4H_3O_8N_4$) and stated that it expld at 180°. However, this salt, as well as other oxaldihydroxamic acids prepd by Hofmann & Ehrhardt, were

later claimed to be impure (Ref 6)
Refs: 1) Beil **1**, 555, (240) & [512] 2) H. Lossen, Ann **150**, 314–22 (1869) 3) W. Lossen & P. Behrend, Ber **27**, 1105 (1894) 4) N. Paolini, GazzChimItal **37**, II, 89 (1907) & JCS **92**, Abs 1, 832 (1907) 5) K.A. Hofmann & V. Ehrhardt, Ber **46**, 1463 (1913) 6) G. Ponzio & R. Sismondi, GazzChimItal **56**, 709 (1926)

Oxalic Acid. $(COOH)_2.2H_2O$, mw 126.07; monoclinic tablets, prisms, granules; mp 101–102°, giving off H_2O of crystn and starting to sublime; d 1.653g/cc at 18.5/4°. One g dissolves in about 7ml w, 2ml boiling w, 2.5ml alc, 1.8ml boiling alc, 100ml eth, 5.5ml glycerol; insol in benz, chlf, petr eth (Refs 2 &3)

Oxalic acid was formerly manufd by fusion of cellulose matter, eg sawdust, with Na hydroxide or by oxidation with nitric acid. It is now made by passing CO into concd Na hydroxide or by heating Na formate in the presence of Na hydroxide or Na carbonate (Refs 1 & 2)

Oxalic acid is caustic and corrosive to the skin and mucous membranes. Ingestion may cause severe gastroenteritis with vomiting, diarrhea and melana. Renal damage can occur as result of formation of excessive Ca oxalate. Severe poisoning can end fatally. Tolerance, 1 mg per m^3 of air (Refs 2, 3 & 4)

The US Armed Forces requirements for oxalic acid are covered by Federal Spec **0-0-690a**, "Oxalic Acid, Dihydrate, Technical", (July 1, 1968). It details three classes: class 1–large crystals, class 2–small crystals, and class 3–powder. It requires a min assay of 99.0% by wt as $H_2C_2O_4.2H_2O$, a max ash content of 0.20% by wt, and the following particle size characteristics using US Standard sieves:

For uses of oxalic acid, see under oxalic acid, anhydrous, below
Refs: 1) Beil **2**, 505, (219), [475] & {1534} 2) Merck (1968), 771–2 3) CondChemDict (1971), 649-R 4) Sax (1975), 988-L

Oxalic Acid, Anhydrous (Ethanedioic Acid, Aethandisäure or Kleesäure in Ger). $HO_2C.CO_2H$, mw 90.04, orthorhombic crysts from glac acet ac; mp, 189.5° dec, subl best at 157°; d 1.9g/cc. Sol in w (10p at 20°, 120p at 100°); sol in alc (24p at 15°); sl sol in eth (1.3p at 15°) (Refs 1 & 6)

Used as a cooling agent in some mining expls (Ref 2), such as Oxalate Blasting Powder (see in this Vol), and as a flash reducing agent in proplnts. V. Vender proposed heating oxalic acid with glycerin in order to obtain an expl compd, **Dinitroformin** (see Vol **6**, F173-R), suitable as an antifreeze in Dynamites (Ref 3). Oxalic acid can also be used for the prepn of glycerol monoformin, $CH_2OH.CHOH.CH_2OH + (COOH)_2 \rightarrow CH_2(O.CHO).CHOH.CH_2OH + CO_2 + H_2O$, which on nitration gives an expl dinitrate (Ref 4 & Vol **6**, F173-R). The Société Anonyme d'Explosifs et de Produits Chimiques in 1907 proposed the use of oxalic acid for the prepn of oxanilide, from which the expl **Hexanitrooxanilide** is obtained (Ref 5)
Refs: 1) Beil **2**, 502–39, (217–22), [471–83] & {1534} 2) Daniel (1902), 592 3) Naoúm, NG (1928), 197 & 374 4) Davis (1943), 222 5) Colver (1938), 387 & 711 6) Merck (1968), 772-L

Oxalic Acid Dihydrazide (Oxalylhydrazide, Oxalhydrazide, Oxalsäure-dihydrazid in Ger). $H_2N.NH.CO.CO.NH.NH_2$, mw 118.02, N 47.46%, OB to CO_2 –67.78%, needles from w;

Table 1
Particle Size Characteristics

Characteristic	Percent by weight Class 1	Class 2	Class 3
Passing thru a 2.00mm (No 10) sieve	–	100(min)	–
Retained on a 1.41mm (No 14) sieve	85(min)	–	–
Retained on a 500-micron (No 35) sieve	–	75(min)	None
Passing thru a 74-micron (No 200) sieve	–	–	20(min)

mp, starts to decomp at 235° (Ref 2), melts with decompn 244–45° (Ref 6), explds at 548° (Ref 5); sol in w, nearly insol in abs alc, eth, chlf and benz

It was first prepd by Curtius et al (Ref 2) by treating 1 mol of oxalic acid ethyl ester with 2 mols of hydrazine hydrate in alc. Other prepns are described by Bülow (Ref 3) and Borsche (Ref 6)

Oxalylhydrazide is an expl (Ref 5), and forms salts, some of which are expl, ie: Cu-K salt, $K_2Cu(C_2H_4O_2N_4)_2$, pale yel needles, sol in w and dil alkalies, explds at 270° (Ref 4)

Refs: 1) Beil **2**, 559, (243) & [514] 2) T. Curtius, G. Schöfer & N. Schwan, JPraktChem **51**, 194 (1895) 3) C. Bülow, Ber **37**, 2201 (1904) 4) K.A. Hofmann & V. Ehrhardt, Ber **46**, 1461 (1913) 5) R.L. Datta & N.R. Chatterjee, JCS **115**, 1010 (1919) 6) W. Borsche et al, Ann **475**, 122 (1929)

Oxalic Acid, Salts of. Bertholet (Ref 2) in 1883 noticed that some salts of oxalic acid, eg mercuric or silver, have the properties of primary expls. According to Urbański (Ref 14), although they have no practical application as initiators, it is interesting from a theoretical point of view, due chiefly to the fact that the general equation for the decompn of oxalates is: $A_{solid} \rightarrow B_{solid} + C_{gas}$. Thus it is similar to the decompn of azides

There have been several papers on Ag oxalate– $Ag_2C_2O_4$. Macdonald and Hinshelwood (Ref 7) confirmed the Berthelot equation, according to which the only products of decompn of Ag oxalate are metallic Ag and CO_2. Benton and Cunningham (Ref 9) found that the rate of thermal decompn of Ag oxalate may be increased by previously exposing it to ultraviolet radiation. During the thermal decompn of Ag oxalate, fragments of metallic Ag are formed. This has been confirmed by conductivity measurements (Ref 10) or by X-ray examination (Ref 11). Tompkins (Ref 12) investigated the thermal decompn of Ag oxalate at 110–130°. Its decompn, in his opinion, is similar to that of Ba azide

Mercuric oxalate (HgC_2O_4) appears to undergo decompn by a somewhat different mechanism with the formation of Hg and mercurous oxalate as intermediate products before full decompn occurs (Ref 13)

Other more exotic Hg derivatives of oxalic acid include the following:

Ethane Hexamercarbide (Di-anhydro-hexakis-[hydroximercuri]-äthan or Aethanmercarbid in Ger). $HO.Hg(OHg_2).C.C(Hg_2O)Hg.OH$, mw 1293.56, lemon yel powd; mp, 220° decomp, explds violently at 230°; sol in w, shows basic character. It can be prepd by refluxing yellow mercuric oxide in alc with K hydroxide for 36 hrs (Ref 3); other methods are described in Refs 6 & 8. Ref 5 states that rubbing the dry material between sheets of paper is sufficient to cause an expln. Its perchlorate explds on heating or friction with the evolution of green light (Ref 4, p 1336), as does its picrate (Ref 3, p 1907)

Tris-[Hydroxymercuri]-Acetic Acid. $(HO.Hg)_3.C.COOH$, mw 709.79, pale yel powd, puffs off on heating. Can be prepd by passing CO_2 thru tris-[Chlormercuri]-acetic acid $[ClHg)_3.C.COOH]$ dissolved in cold dil KOH

Its derivative, **Anhydro-tris-[hydroxymercuri]-acetic acid,** $HO.Hg(OHg_2).C.COOH$, mw 671.79, was prepd by Hofmann (Ref 4, pp 1330–32) in two forms, alkali-sol and alkali-insol. The nitrate of the first form puffs off on heating, while the nitrate of the second form sparks on heating, but does not expld

Refs: 1) Beil **2**, 561 & [514] 2) M. Bertholet, "Sur la Force des Matières Explosif", Paris (1883) 3) K.A. Hofmann, Ber **31**, 1904–7 (1898) 4) Ibid, Ber **33**, 1330–37 (1900) 5) K.A. Hofmann & H. Feigel, Ber **38**, 3654 (1905) 6) K.A. Hofmann & K. Leschevski, Ber **56**, 127–8 (1923) 7) J.Y. MacDonald & C.H. Hinshelwood, JCS **127**, 2764 (1925) 8) F.C. Whitmore, E.R. Hanson & F.L. Carnahan, JACS **51**, 899 (1929) 9) A.F. Benton & G.L. Cunningham, JACS **57**, 2227 (1935) 10) J.Y. MacDonald & R. Sandison, TrFaradSoc **34**, 589 (1938) 11) R.L. Griffith, JChemPhys **11**, 499 (1943) 12) F.C. Tompkins, TrFaradSoc **44**, 206 (1948) 13) E.G. Prout & F.C. Tompkins, TrFaradSoc **43**, 148 (1947) 14) Urbański **3**, 224 (1967)

Oxalyl-ethyl ester Azide (Azido-oxalic acid Ethyl-ester, Azido-oxalsäure-äthylester or Oxalsäure-

äthylester-azid in Ger). $N_3.CO.CO_2.C_2H_5$, mw 143.10, N 29.37%, OB to CO_2 –81.06%, colorl oily liq; bp, explds violently on heating; insol in w, sol in eth, decompd by hot alc. Can be prepd from the hydrazide of oxalylethylester and Na nitrite in well cooled aq soln

Refs: 1) Beil **2**, (244) 2) T. Curtius & K. Hochshwender, JPraktChem **91**, 434 (1915) & JCS **108** (I), 787 (1915)

Oxamic Acid Azide (Azido Oxamate, Oxamidoazide, Oxamidsäureazid or Oxalsäure-amid-azid in Ger). $H_2N.CO.CO.N_3$, mw 114.02, N 49.11%, OB to CO_2 –42.09%, crystals from acet+petr eth; mp, explds violently ca 115° or on rubbing. Can be prepd by treating the hydrazide of oxamic acid with Na nitrite in w

Refs: 1) Beil **2**, (244) 2) T. Curtius, JPraktChem [2] **91**, 426 (1915) 3) Urbański **3** (1967), 192

Oxamide (Oxalamide, Oxalic acid diamide, Ethanediamide, Ethanedioic acid diamide). $H_2N.CO.CO.NH_2$, mw 88.07, N 31.81%, OB to CO_2 –72.67%; white, odorl powd, triclinic needles; mp 417–19° decomp, d 1.667g/cc, sparingly sol in hot w, alc, insol in eth (Refs 1, 5 & 6). Q_C^V 202.64kcal/mole, Q_f^V 121.39kcal/mole (Ref 3). Can be prepd from formamide by glow-discharge electrolysis (Ref 4)

Oxamide has been used as a stabilizer for NC prepns (Ref 6), as a coolant in proplnt formulations because the amt of smoke contributed by it was small (Ref 2), and as a component of **Oxamide Explosive Composition** (see below)

The requirements of the US Armed Forces are detailed in Mil Spec **MIL-O-60863**, "Oxamide" (15 December 1967) as follows: moisture content – 0.1% max; purity – 99.0% min; acidity (as oxalic acid) - 0.05% max; pH – 6.5±1.5; residue on ignition – -.05% max; particle size, grade A – 4±2 microns; granulation, grade B – thru US Standard Sieve No 30, 100% min; thru US Standard Sieve No 325, 80% min

US Mil Spec **MIL-O-60371**, "Oxamide Explosive Composition" (29 June 1966), contains requirements for the following compns:

Composition B	83.3±2.0%
TNT	6.7±0.5%
Oxamide	10.0±0.5%
RDX	50.0±2.0%
TNT	40.0±1.0%
Oxamide	10.0±0.5%
Wax, Desensitizing	1.0±0.5%

In addition to analytical requirements for the above constituents, the Spec contains a moisture requirement of 0.25% max, an insol particles requirement, and a viscosity requirement

Refs: 1) Beil **2**, 545 2) C.S. Davis, "Development of Ideal Propellants", PATR **1745** (1949) 3) L. Médard & M. Thomas, MP **39**, 348–9 & 355 (1957) 4) J. Brown et al, JOrgChem **27**, 3698 (1962) 5) Merck (1968), 772-L 6) CondChemDict (1971), 649-R

OXANILIDE AND DERIVATIVES

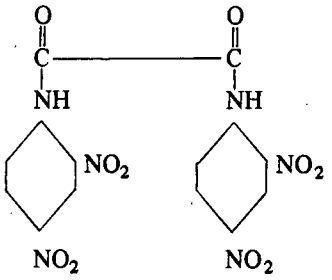
Oxanilide (N,N'-Diphenyloxamide, Oxalsäuredianilid in Ger). $C_6H_5.NH.CO.CO.NH.C_6H_5$, mw 240.25, N 11.65%, OB to CO_2 –213.11%, white plates from benz, mp 247–54°, bp >320°, insol in cold & hot w & eth, sl sol in hot alc, fairly sol in benz. It can be prepd by heating aniline with oxalic acid (Ref 2)

Oxanilide has been used as an antiflash agent in proplnts, and as a coolant and burning rate reducer in fuze powders (Ref 3). According to Davis (Ref 4), it functions well as an antiflash agent if it is distributed thruout a proplnt charge, but not if it is loaded into a gun in separate bags, like the Ger *Vorlage* or the Fr *Sachets Antilueurs*

On nitration, oxanilide yields expl tetra- and hexanitrates (see below)

Refs: 1) Beil **12**, 284, (207) & [165] 2) A.D. Macallum, JSCI **42**, 469T (1923) 3) S. Livingston, "Develop Non-Slagging Fuze Powder for the T-14 Fuze", PATR **843** (1937) 4) Davis (1943), 326

2,4,2′,4′-Tetranitro-oxanilide (TNO).



$C_{14}H_8N_6O_{10}$, mw 420, N 20.0%, OB to CO_2 −84%, OB to CO −31%, yellow needles from NB, mp 313° decompn (Ref 6)

Preparation.

Oxanilide: Two parts of oxalic acid are mixed with one part of aniline in a round bottom flask. The mixt is stirred and heated until the reaction is complete as evidenced by the cessation of effervescence. The mass is cooled to room temp, poured into several volumes of water (21–24°), filtered on a Büchner funnel and washed free of oxalic acid with water and then washed free of aniline with acet. The oxanilide is air dried to remove the acet and then dried at 100–110°

Tetranitro-oxanilide (TNO): A 5ℓ round bottom flask is equipped with a stirrer of a type which will produce a downward "swirl". The flask is surrounded with a water jacket for hot and cold water. Fifteen hundred grams (1.5 kilograms) of 98% plant grade nitric acid is placed into the flask. Five hundred (500) grams of oxanilide is slowly added to the acid under rapid agitation while the temp is maintained below 40°. After the addition of the oxanilide is completed (2½–3 hrs), the agitation is continued 10–15 minutes. The temp is then raised to 80° over a period of one hour and maintained at 80–85° for 3 hours. The acid slurry is then cooled to room temp and drowned by pouring over cracked ice. The product is filtered on a Büchner and washed with water until it is almost acid free. The filter cake is placed in a beaker and sufficient water added to form a "slurry". Live steam is run into the "slurry" under agitation for 10 minutes. The slurry is filtered and the residue washed. The latter treatment of the "slurry" is repeated until the wash water is found to be neutral to litmus paper. The TNO is washed with alc, then acet, air dried and finally dried at 100–10°. Yield 90 to 97.5% of theoretical (Ref 6)

Origin. A.G. Perkins in 1892 obtained TNO directly by heating a soln of finely powdered oxanilide in nitric acid. He also obtained the same compd by the action of a cooled mixt of nitric and sulfuric acids on oxanilide and pptg the product by pouring the soln into w (Ref 2)

Impact Sensitivity. PicArsn app, 11mg sample: 30 inches

Friction Pendulum Test. Steel shoe: unaffected; Fiber shoe: unaffected

Explosion Temperature. 5 second (no cap used): 392°

100° Heat Test. Loss 1st 48 hrs: 0.07%; loss 2nd 48 hrs: 0.00%; explosion in 100 hrs: none

Hygroscopicity. % wt gain at 30°, 90% RH: trace

Vacuum Stability Test. cc/40 hrs at 90°: none; 100°: none; 120°: 0.11

Sand Bomb Test (200g). 16.3g sand

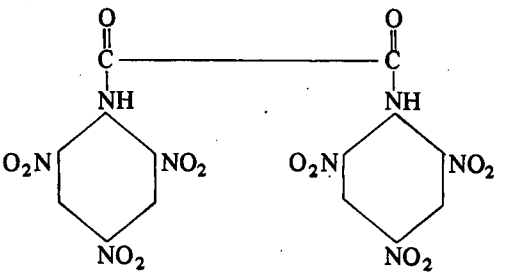
Sensitivity to Initiation. Minimum detonating charge, g; LA: 0.20; Tetryl: 0.25

Solubility. g/100cc solvent in: water at 100° <0.10; NB at 150°, <15. Sol in acet ac, nitric acid, caustic potash; v sol in dimethyl formamide; insol in ethyl alc, benz, butyl acetate, CCl_4 & ethyl ether (Ref 6)

Uses. Component of BlkPdr type formulations, delay and pyrot compns (Refs 3, 4 & 5)

Refs: 1) Beil **12**, 755 & (363) 2) A.G. Perkins, JCS **61**, 460 (1892) 3) B. Dubrow & J. Kristal, "Substitution of Tetranitro Oxanilide and Hexanitro Oxanilide for Tetranitrocarbazole", PicArsn Pyrotechnic Research Laboratory Rept **54-TF1-88** (20 Dec 1954) 4) S. Livingston, "Development of Improved Ignition Type Powders", PATR **2267** (1956) 5) A.M. Scott, "Pyrotechnic Delays in the United Kingdom", RARDE Rept **FXD/70/026** (1963) 6) Anon, EngrDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 331–34

2,4,6,2′,4′,6′-Hexanitro-oxanilide (HNO).



Preparation. To prepare Hexanitro-oxanilide, first prepare Tetranitro-oxanilide as described above under the entry "2,4,2′,4′-Tetranitro-oxanilide (TNO)"

A 1.5ℓ round bottom flask is equipped with a stirrer of the type which causes a downward swirl. The flask is jacketed for hot and cold w. 187g of nitric acid of specific gravity 1.49g/cc (commercial grade) is placed into the flask and 100g of sulfuric acid is added to the nitric acid under agitation. The mixed acid is cooled to 10°. 29.2g of Tetranitro-oxanilide is slowly added to the mixed acid under rapid agitation maintaining the temp at 8–10°. After the addition of the TNO is completed (approximately 25 minutes) the temp is raised to 85° over a period of 2 hours and held at 85–90° for one hour. The Hexanitro-oxanilide (HNO) "slurry" is filtered on a Büchner funnel and purified as explained under "Tetranitro-oxanilide" (Ref 10)

Origin. A.G. Perkin in 1892 obtained Hexanitro-oxanilide directly by heating to boiling a soln of Tetranitro-oxanilide (TNO) in a mixt of sulfuric and nitric acids. He also prepd the same compd from oxanilide by the action of a boiling mixt of fuming nitric and sulfuric acids (Ref 2)

Impact Sensitivity. PicArsn app, 12mg sample: 15 inches

Friction Pendulum Test. Steel shoe: unaffected; Fiber shoe: unaffected

Explosion Temperature. 5 second (no cap used): 384°

100° Heat Test. Loss 1st 48 hrs: 0.07%; loss 2nd 48 hrs: 0.05%; explosion in 100 hrs: none

Hygroscopicity. % wt gain at 25°, 90% RH: 0.19

Vacuum Stability Test. cc/40 hrs at 100°: 0.40

Sand Bomb Test (200g). 52.1g sand

Sensitivity to Initiation. Minimum detonating charge, g; LA: 0.30; Tetryl: 0.25

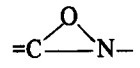
Exudation on Dry Storage. None

Solubility. g/100cc solvent in: water at 100°, 0.10; NB at 20°, <3; at 210°, 5. V sol in dimethylformamide, sol in nitric acid, insol in ethyl alc, acet, benz, butyl acet, CCl_4, ethyl ether & acet ac (Ref 10)

Uses. Ingredient of igniter and pyrot compns (Refs 6, 7, 8 & 9). Recommended in the older literature as an expl having approx the same power as TNT, and in mixts with AN, chlorates or perchlorates (Refs 3, 4 & 5)

Refs: 1) Beil **12**, 767 2) A.G. Perkin, JCS **61**, 462 (1892) 3) Société Anonyme d'Explosifs (Paris), FrP 391106 (1907) & CA **4**, 2733 (1910) 4) Colver (1938), 387 & 711 5) Davis (1943), 188 6) S. Livingston, "Preparation of Tetranitro Carbazole", PicArsn Chemical Research Laboratory Rept **136330** (11 April 1951) 7) L. Gowen & R. Dwiggens, "Case Gun Ignition Studies", **NAVORD 2321** (1952) 8) B. Dubrow & J. Kristal, "Substitution of Tetranitro Oxanilide and Hexanitro Oxanilide for Tetranitro Carbazole", PicArsn Pyrotechnic Research Laboratory Rept **54-TF1-88** (20 Dec 1954) 9) S. Livingston, "Development of Improved Ignition Type Powders", PATR **2267** (1956) 10) Anon, Eng-DesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 170–72

Oxaziranes. A class of organic compds containing the ring structure



S.T. Putnam & R.H. Earle, Jr, of the Hercules Powder Co reported that an attempt to prepare bis-(2-*tert*-butyloxazirane) caused an expln resulting in severe hand injuries to a researcher (Ref 2). The compd, after being prepd according to the method of W.D. Emmons (Ref 1), was transferred to a 2 oz wide-mouth bottle with a metal spatula. This was then covered with a polyethylene film and a screw cap, and stored overnight at 35°F. On the following day the material was being transferred to a round-bottom flask, again using a metal spatula, when the expln took place

The cause of the expln was not detd, but Putnam and Earle feel that it was probably caused by the presence of a small amt of some highly unstable contaminant. In making the c mpd they obtained a 29.4% yield, compared v th 51% reported by Emmons

Refs: 1) W.D. Emmons, JACS **79**, 5739–54 (1957) 2) Anon, C&EN **36**, 46 (9 June 1958)

OXAZOLIDONE AND DERIVATIVES

Oxazolidone-(2) (Anhydro-[β-oxyethyl]-carbamic acid). $H_2C.NH.CO.O.CH_2$, mw 87.08, N 16.09%, crysts from alc, mp 88–91°, bp ca 200° at 21mm. Sol in w and alc, sl sol in benz. Can be prepd by passing phosgene into a chlf soln of β-aminoethanol in the presence of Na bicarbonate

On nitration it forms expl nitro and nitroso derivatives (see below)

Refs: 1) Beil **27**, 135 & (259) 2) A.P. Franchimont & A. Lublin, Rec **21**, 47 (1902) & JCS **82**, Abs 1, 427 (1902)

3-Nitrooxazolidone-(2). $H_2\overline{C.N(NO_2).CO.O.CH_2}$, mw 132.08, N 21.21%, OB to CO_2 −48.5%, needles from benz, mp 111°. Insol in w, sol in benz. It was prepd by Franchimont & Lublin (Ref 2) by boiling a mixt of oxazolidone & concd nitric acid

Nitrooxazolidone was prepd and examined in Canada during WWII and was found to be very expl. Its impact sensitivity is 0.48 TNT (less sensitive), and it could not be detonated with a No 8 blasting cap (Ref 3)

Refs: 1) Beil **27**, 136 2) A.P. Franchimont & A. Lublin, Rec **21**, 49 (1902) & JCS **82**, Abs 1, 427 (1902) 3) Blatt, OSRD **2014** (1944)

3-Nitrosooxazolidone-(2). $H_2\overline{C.N(NO).CO.O.CH_2}$, mw 116.08, N 24.14%, OB to CO_2 −68.92%, needles from ethyl acet+petr eth, mp 53°. Can be prepd by treating oxazolidone with K nitrite in dil HCl at 0°, or by bubbling NO_2 thru an ethereal soln of oxazolidone (Ref 2). Sol in w, v sol in alc, ethyl acet & benz, sl sol in petr eth

Nitrosooxazolidone decomps on heating, often explosively, and ignites on contact with concd K hydroxide

Refs: 1) Beil **27**, 136 2) S. Gabriel, Ber **38**, 2410 (1905)

OXIDES, INORGANIC

Binary compds, formed from oxygen by combination of as many as eight oxygen atoms with another element, with the exception of carbon and hydrogen, are called inorganic oxides. These compds are cryst below their fp and can usually be reduced to the nonoxygen element with either hydrogen or carbon by heating above RT. The inorganic oxides according to Partington (Ref 15) are classified into different groups, among which are:

a) Acidic oxides, such as P_2O_5 and SiO_2, which react with bases to form salts containing the non-metallic element of the acidic oxide in the anion

b) Basic oxides, such as Na_2O, CaO, FeO and PbO, which react with acids to form salts in which the element of the oxide is in the cation. It is to be noted that Na_2O unites violently with w to form NaOH as does CaO to form $Ca(OH)_2$, while Fe and PbO react very slowly. If a metal forms more than one oxide, the lower oxide may be more basic, for example FeO and Fe_2O_3, where $Fe(OH)_2$ is the stronger base

c) Amphoteric oxides, such as ZnO and Al_2O_3, act as weakly basic oxides in the presence of strong acids, and weakly acidic oxides in the presence of strong bases

d) Higher oxides include dioxides which are further classified into (1) peroxides or superoxides when they contain the −O−O− group, such as Na_2O_2 and BaO_2, which give H_2O_2 when reacted with acids, (see under Peroxides in this Vol) and (2) dioxides or polyoxides when the oxygen atoms are linked separately by double bonds, such as O=Mn=O and O=Pb=O

e) Mixed oxides which are compds of two oxides so that the element has different valences, such as Pb_3O_4=2PbO, PbO_2 and Fe_3O_4=FeO, Fe_2O_3

Inorganic oxides are usually prepd by intimate contact between the element and oxygen or air. The reaction may be rapid and exothermic, as when finely divided pyrophoric materials ignite spontaneously in air or oxygen. Examples of these materials are iron, lead and phosphorus. Or, the reaction may be slow as when iron oxidizes when exposed to ordinary moist air, or when aluminum oxidizes at the surface upon exposure to air. Much of the time oxidation requires an elevated temp of well over 1000° and may be accompanied by the evolution of large quantities of heat and light, as in the oxidation of aluminum powder used in ordnance applica-

tions such as expls (see Vol 1, A146-L to A152-R), rocket proplnts (see Vol 1, A152-R), and pyrots (see Vol 1, A152-R to A154-L (including Magnesium))

Other methods of prepn include the heating of nitrates, as for Na_2O; of carbonates, as for CaO; or of hydroxides, as for MgO. Of course, many inorganic oxides occur in nature as ores. Examples of these are Fe_2O_3, Fe_3O_4 and SnO_2. For individual methods of prepn, see under the selected inorganic oxides described below

Several toxic effects of inorganic oxides become evident when oxides are inhaled in a finely powdered form. A high concn of powdered oxides can lead to asphyxiation on short exposure or lung cancer at somewhat lower concns if the exposure occurs over a prolonged period. Blood poisoning can occur if an inorganic oxide such as As_2O_3 is allowed to penetrate an open wound. Of course, oxides such as Na_2O and CaO have a markedly corrosive action on all body tissue (Ref 38). The specific toxicities of selected inorganic oxides are presented below

Inorganic oxides have many ordnance applications in batteries, ceramics, expls, nuclear energy and propn systs, proplnts, and pyrots. A brief dissertation on each of these applications is now presented

Much work has been accomplished using oxides to provide electrochemical energy sources in the form of *batteries*. The use of manganese dioxide in dry cell electrolyte to prevent polarization by hydrogen is well known. More recent uses of oxides in storeable electrical energy sources is shown in the study undertaken by Streigle (Ref 37) concerning a silver oxide–zinc battery for USA Ord. The Spec required a wt of 12 lbs, a voltage of 24V, a current of 0.15Ampere (5Ampere pulse), and a 50 hr operating life. It was decided that a KOH electrolyte (31% in soln) temp control could be readily obtd by isotopic heating using a radioisotope heater. Again, oxides were used in a study to find the best radioisotope for the purpose. Those considered were: glass (SiO_2), CeO_2, Cm_2O_3, Tm_2O_3, PuO_2. The radiation hazard and the costs involved eliminated all candidates but a 20% concn of Pu-238 or plutonium oxide

The ordnance applications of inorganic oxides as *ceramics* are of considerable interest. One such application is that of armor which has the advantages of having a lower density than steel, being easier to form than steel, and in one application, being optically transparent. Indeed, the development of a process for the production of useful sizes of optically transparent ceramic armor made from MgO was the objective of a program conducted by Niesse and Vasilos (Ref 42). Evolved was a process for making 8 x 8 inch magnesia sheets using vacuum hot pressing, annealing the hot pressed discs, polishing and coating the magnesia surfaces and bonding the magnesia sheets together. The yield of optically transparent magnesia discs averaged 35%. The majority of rejects were caused by gases in the initial pressing powder leaving clustered microvoids which resulted in hazy areas. In another program to fabricate ceramic armor by Rhodes and Delai (Ref 47), dense boron suboxide was processed by hot pressing. The correct adjustment of mfg parameters produced perfect billets 4 inches in diam by 0.375 inches thick. Other work on ceramic armor has been conducted using fused silica (Ref 22). This work resulted in a silica plate possessing 50% greater HEAT stopping power than a fused silica reference standard. A study made by Ryshkewitch (Ref 34) on berylium oxide ceramics shows four applications of ord interest, ie, nuclear reactors, electronics, turbines and rocket nozzles. Nuclear reactor applications will be described below. The electronic application concerns the use of BeO as a heat sink. In this very important function the thermal resistance of a BeO insulator (or rise in temp/watt of elect power applied) is negligible. Hence, the power input with sintered beryllia transistor insulation can be increased 100% and more above mica or anodized aluminum insulators previously used. For the rocket nozzle application, models of nozzles prepd by the National Beryllia Corp, each having an inner W surface of W-BeO gradient body consisting of concentric layers of W-BeO compn contg an increasing percentage of BeO with increasing radius of the nozzle cross-section, were tested by firing with a proplnt at 3200°, which developed more than 110 atm press without any evidence of erosion or of thermal shock damage

Fused silica impregnated with either silicon or epoxy resin can also be used for this application. These silica compn nozzles are able to

withstand the conditions of over 400 psi and over 2100° flame temp which are imposed in the oxyhydrogen test rocket motor during its firing

Again, according to Ref 34, BeO offers a possible solution to the problem of developing turbine components which will withstand the thermal stresses arising from supersonic speeds of mach 2 to mach 3 encountered in aircraft flight. The feasibility of this approach is based on the superior shock resistivity of beryllia (BeO), and the possibility of producing gradient BeO/metal turbine blades and other components which will retain their integrity under the imposed flight conditions. The above Ref, as well as the work of Ormsby and Brown (Ref 44), describes the use of lithia-alumina-silicate (LiO_2.(1 to 4) Al_2O_3.(2 to 8) SiO_2) or fused beryllia for use as radomes in aircraft or missile applications. Several exptl sintered beryllia radomes have been prepd by the National Beryllia Corp, using the slip-cast method. This technique fabricated radomes with a d of 2.88 g/cc and dielectric coefficients of 6.57 at 8.5 x 10^9 hertz and 5.87 at 3.3 x 10^{10} hertz. The General Dynamics Corp (Ref 33) has also done considerable work on slipcasting radomes of fused silica for SAM missiles. In another use of inorganic oxides by Greskovich and Woods (Ref 43), yttrium oxides have been used as a laser host material having both high peak and high avg power characteristics. A unique ceramic application is the work of Talty (Ref 55) who has studied yttria (yttrium oxides) stabilized zirconia (zirconium oxides) as a material used in regenerative storage heaters for high temp blow-down wind tunnels. Tinsley (Ref 48) has also used heaters comprised of the oxides of zirconium, aluminum, and yttrium to operate a full-scale, intermittent airflow, high enthalpy, high press test facility for aircraft and missile models in the mach 2 to 8 flight regime at 1850 psi and 445°F

In *explosives*, calcium oxide has been used for many years according to Daniel (Ref 1) in devices such as the *Igniter of Jarolimek*. This is a device used in blasting operations, and consists of a double cartridge containing compressed CaO in one end and a flammable mixt (usually a mixt of 50% $KClO_3$ and 50% mercuric fulminate) in the other end. The flammable end is attached to a MF blasting cap which was inserted in the main Dynamite charge (or other blasting expl). In order to produce an expln, a small quantity of w is brought into contact with the compressed CaO and heat is evolved which ignites the $KClO_3$–$Hg(OCN)_2$ mixt. The MF cap is detonated, thus exploding the main charge (Ref 1, p 16). Another expl use for CaO was proposed in 1853 for breaking coal seams. It was called *Sir George Elliott's "Quicklime Explosive"*. The technique consisted of compressing freshly prepd quicklime into dry bore-holes. When w is added, an expansion is produced as the result of the reaction $CaO + H_2O = Ca(OH)_2$, as well as from the pressure developed by the superheated steam produced from the w by the heat of reaction. The expansion ruptures the bore-hole and breaks apart the surrounding layers of coal (Ref 1, p 133). There are also the *Cartridges of Smith and Moore* which contained a perforated iron tube (connected with a source of w) placed inside a paper cartridge of compressed $Ca(OH)_2$ (Ref 1, p 133). Another device, the *Cartridges of Arnoutd* (Belgium), depended upon the heat produced by the action of w on CaO to produce instantaneous evapn of liq sulfur dioxide or nitrous oxide (Ref 1, p 134). Still another device, the *Cartridge of Steinau* (1887), used a perforated paper cartridge filled with CaO, in the center of which was a glass bottle containing w and a second smaller bottle of sulfuric acid. The cartridge was inserted in a bore-hole of the same diameter, and w was introduced. The heat developed by the CaO broke the w bottle and then the sulfuric acid bottle. The pressure produced by the superheated steam evolved then broke open the surrounding coal seams (Ref 1, p 738). Blais and Picard (Ref 22) have defined Specs and processes for the mfg of CaO to be used to manuf white calcium cyanamide which is the intermediary compd used to prep Guanidine Nitrate (see Vol **6**, G150-R to 151-R). Oxides such as ClO_2, XeO_3 and XeO_4 can be considered expls and are described as such below. Varrato (Ref 7) found that Ammonium Nitrate (AN) containing 0.5% zinc oxide was satisfactory for use in Amatol, as it did not cake or change in granulation after 7 months storage. According to Clear (Ref 12) there are several deleterious effects occasioned by the presence of iron or

copper oxides on TNT under conditions of increased pressure. It was found that these oxides cause decreases in ignition temp and an increase in the rate of decompn of TNT, with mixts of TNT and iron oxide igniting at temps as low as 90°. Both SiO_2 and red ferric oxide are used to increase the sensitivity of gelatinous detonators in an invention of Schlüter and Meyer (Ref 24). The improvement in sensitivity is due to the addn of 4.0 to 25% of SiO_2 with a grain size of <0.2mm and a d of 2.4g/cc to the formulation collodion cotton 0.8–2.0, TNT 0–6.0, AN 40–60, wood powder 0–5.0, and red Fe oxide 0.2%. A safer procedure for the use of Al, Mg, or Zn powders in expls and pyrots is provided by an invention of Ek and Eldth (Ref 26) in which these powders are inactivated by oxidation with subsequent impregnation using a high mol wt fatty acid. Another use of oxides in expls is that of silicon dioxide in the form of powdered glass and later powdered quartz, has been used in the *Gravel Mine* series of expl devices to provide adequate initiating sensitivity (Refs 29, 31, 32, 40 & 41). These miniature mines were designed to be initiated with as little as 30 lbs of force after being sown by aircraft, artillery or vehicles. The usual compn was quartz 50.0, silica 1.5, RDX 29.8, and LA 18.7%

In the field of *nuclear energy and propulsion systems* inorganic oxides have been used as fuel elements and as radiation moderators, reflectors and shields. Belle and Jones (Ref 19) have compiled data on uranium oxide in which topics such as the properties, preparation, activation, effect of other metal oxide addns, sintering, power cycling of fuel rods, etc, of UO_2 are discussed. Fast breeder fuel cycling based on a core fuel mixt of UO_2 and PuO_2 is discussed in Ref 20. The use of various oxides in nuclear energy are also described in Refs 23, 25 and 27. The role of beryllium oxide in nuclear reactor and propulsion systems is comprehensively discussed by Rothman in Ref 30 and by Ryshkewitch in Ref 34

In *propellants* (see Propellants, Solid in this Vol), some of the work reported by Dunkle (Ref 6) examined the addn of flash reducing agents versus smoke evolved in proplnt compns for the cal .50 rifle. The oxides examined included aluminum oxide, stannic oxide, silicon dioxide, ferric oxide and, after proplnt ignition, nickel and tellurium oxides from the metal additives in the proplnts. It was found that the greater the relative abs humidity, the greater the quantity or optical density of smoke produced by a proplnt, and that elimination of flash is dependent upon the mp of the inorganic residue, ie, residues with mp's of about 1400° such as aluminum and stannic oxides, are flashless and (specifically for these compds) smokeless, while low mp inorganic residues are good flash-suppressors. Clear (Ref 14) has reported that aluminum oxide has no adverse action on the storage stability of 2.36" rocket proplnt, but in intimate mixts of the proplnt with the oxide some reaction occurs at 120°; however, proplnts using alumina are feasible. Oxides have been used in proplnts for gas generating purposes, such as Hutchinson's invention (Ref 16), which uses self-sustained, exothermic, nondetonating, gas-evolving decompn reactions to actuate pressure-operated mechanical devices, for blasting operations, proplsn of rockets, etc. These reactions are obtd by igniting local areas of Nitroguanidine and/or Guanidine Nitrate compns contg 0.25–1.0 asbestos fiber and 0.2–10.0 wt% of H_2MoO_4, CeO_2 or U_2O_5. According to Johnson et al (Ref 51) such gas generating systems can employ pyrot-type metal oxides together with solid proplnts to generate electrophilic gases. Such gases consist of H_2MoO_4, $HReO_4$ and HBO_2. The oxides included in the proplnts are molybdenum oxides, boron oxides, rhenium oxides and tungsten oxides. Oxides such as iron oxide are being used in proplnts as a combustion catalyst. A report on the efforts to correlate composite proplnt burn rate, AP particle size distribution and ferric oxide specific surface and levels, has been proposed by Burnside (Ref 56). Two proplnt compns were used: viz, (1) hydroxy-terminated polybutadiene based proplnts (HTPB) consisting of HTPB binder 11.6, polyamine/epoxide binding agent 0.4, AP 77.6–76.0, aluminum (15 micron) 10.0, and ferric oxide 0.4–2.0%; and (2) carboxy-terminated polybutadiene based proplnts (CTPB) consisting of CTPB binder 14.0, AP 80.0–80.9, aluminum (5 micron) 5.0, and ferric oxide 0.1–1.0%. The experimentation was conducted using these proplnts contg ferric oxide of 3 to 2.64M^2/g surface area in lab scale motor firings. Results indicate that Fe_2O_3 specific surface is more significant at

high, 7–11 micron size AP levels than at low, 7–11 micron size AP levels. It was also concluded that catalysis probably takes place in the primary diffusion flame located at the AP binder interface. Inorganic oxides have been used as anti-fouling or anti-barrelwear additives for years. One of the early inventions, that of Hennig (Ref 2), used 1–5% tin or lead oxides (or carbonates) as additives to NC proplnts to prevent gun fouling. A number of other patents which are described in this Vol under **Propellants, Solid** also recommend the use of inorganic oxides, among other additives to proplnts, to reduce gun barrel wear or erosion. The oxides used include: MgO, TiO_2, Sr_2O_3, ZnO, BaO, Sb_2O_3, Ta_2O_5, WO_3, U_2O_5 and HfO_2. Also, according to Phenē (Ref 50) a similar effect is obtd by the addn of 1% MoO_3 to 7.62mm cast proplnt. Aside from barrel erosion considerations, fluorocarbon composite proplnt burning rates, pressure exponents, and temp coefficients of burning rates can be adjusted by the addn of magnesium, copper and manganese oxides. Also, a technique which is used to suppress unstable burning in polyurethane, nitropolyurethane, polyesteracrylate and rubber-base composite proplnts is the addn of finely divided oxides of Al, Zr, Si, Th, Ti, or La (Ref: see under Propellants, Solid in this Vol)

In *Pyrotechnics* military ord has found the greatest use for inorganic oxides. They are either incorporated initially in the compn or formed during the combustion phase of the pyrot, emitting both heat and light in the process. According to Schladt (Ref 3), oxides of metals such as iron, lead and silicon are reduced by aluminum and magnesium upon ignition to evolve intense light. A typical compn includes iron oxide 41.0, barium nitrate 33.5, and magnesium 25.5%. Another use of oxides reported by Schladt (Refs 4 & 5) is in the development of a compn for white smoke puff ground troop signals (rifle signal). This smoke compn (called SP-1) included red phosphorus 50.0, willow charcoal 40.0 and zinc oxide 10.0%. It was found satisfactory and recommended for use. Zinc oxide has also been used as a smoke charge when loaded into 3" antiaircraft shell (Ref 8). Similarly, yellow smoke compns have been created using As_2O_3 and powdered glass (SiO_2) (Ref 2a). According to Eppig (Ref 9) a T-15 airport flare compn containing titanium dioxide was developed which generates 400,000 candlepower. Again, Eppig (Ref 10) reports the use of titanium dioxide as the chief oxidant in a smokeless illuminant compn for the T24 flare. Of course the role of the inorganic oxide in pyrots has been investigated to determine its effect on heat of reaction, temp, enthalpy, etc. One such investigation has been conducted by Lipscomb (Ref 52a) into the effects of prepn temp, selected impurities, and mechanical activation of ferric oxide on the pyrot properties of the reaction $Fe_2O_3 + 3Ti = 3TiO + 2Fe$. Another such investigation by Lipscomb (Ref 54) concerns lead monoxide in its reaction with silicon while both are doped with varying amounts of lithium and chromium. It was found that these impurities effected the enthalpy of the reaction Pb + Si = SiO + Pb drastically, changing activation energies and reaction kinetics. Still another investigation by Kirshenbaum et al (Ref 49) examined the flare performance of the gaseous system $H_2 + OF_2 + BF_3$ resulting in $BO_2 + HF + BO$. It was concluded that the performance of gaseous systems are quite comparable to solid flare systems and that visible emission is in the main from excited BO_2. Of the many pyrots which have been patented, more than several use inorganic oxides. An igniter compn for tracer projectiles devised by Clay and Sahlin (Ref 17) is of interest. This compn replaced magnesium with Ca silicide as the fuel resulting in a dim or invisible trace to a minimum distance of 25 yds and a bright and properly colored trace at greater distances. A typical igniter compn consisted of SrO_2 78.0, BaO_2 4.0, PbO_2 4.0, Ca silicide 7.0 and Ca resinate 7.0%. In two other inventions of Heiskell (Ref 18), dark-burning, non flash pyrot igniter mixts were devised consisting in one compn of CuO 50.0, Mn 49.0 and graphite or stearic acid to act as a binder and lubricant 1.0%; and in another compn of BaO_2 80.0 and CrS 20.0%. Other possible O_2– bearing compds described included BaO_2, Sb_2O_5, and PbO_2. In still another invention, that of DeMent (Ref 28), various colored smokes are generated using inorganic oxides. For example a grey smoke consists of As_2O_3 1, $NaClO_3$ 4, dextrin 3, and trichloracetic acid 1.8 parts. More than 370 formulations are described, many using germanium dioxide, boron

trioxide, and/or titanium dioxide. The inventor suggests uses in military signaling, movement screening, and toxic or radioactive aerosol dissemination. A patent by MacDonald (Ref 36) describes a pyrot compn contg ferric oxide and finely divided SrO_2. This incendiary compn is obtd by initially melting 240 parts of aluminum with 715 parts of Fe_3O_4 plus 30 parts of SiO_2 at 840-1005° for 10-15 mins. The RT compn produces intense heat when ignited in air. In a patent by Dede et al (Ref 39) lower metal oxides are used to obtn ignition mixts of decreased combustion temp. Thus, Cu_2O 63.6 and $KClO_3$ 36.4% are homogenized and granulated to 50 microns, then mixed with 0.5 part of a 2% tylose soln, rehomogenized and regranulated to 100–500 microns, and dried at 60° to 1% w content. In another patent, that of Perkins et al (Ref 46), a non corrosive igniter was developed with a display functioning reliability increase of from a base of 50–60% to 75–80%. The compn includes PbO_2 oxidizer 65–70, Zr fuel (20–100 microns) and stabilized red P 2–6%, and, because of its greater display functioning reliability, it is used with corrosive tracer compns in smaller than usual tracer cavities within the projs so that premature ignition and resultant barrel corrosion is prevented. In the invention of Helms and Rozner (Ref 52), inorganic oxides are used in a pyrot compn to provide a jet of molten material thru a torch nozzle while under the press generated by N, or an inert gas, or gasification of a substance such as polytetrafluoroethylene, which is included in the hot reaction mixt. The compns used in the invention generate large amts of heat at a controlled rate in the readily useable form of a hot gas driven molten jet. In one version of the invention the pyrot compn consists of a finely divided mixt of Ni 5–50, a metal oxide such as Fe_2O_3, Fe_3O_4, and/or Cr_2O_3 20–76, plus Al (or a mixt of Al with Mg, Zr, Bi, Be or B in 1 to 1 ratio) 15–50%, all contained in the gas source, ready to be sprayed out upon ignition. One of the latest inventions employing inorganic oxides is that of Lipscomb and Smith (Ref 53). In this invention the heat of combustion (Q_c) of Fe_2O_3 or ZnO is increased approx 50% (see table below) by soln of a metallic salt such as $Fe_2(SO_4)_3$ or $ZnSO_4$ in boiling w contg 1–5% of a Li or Zr doping compd, then evapg to a paste and calcining at 600–1000°, yielding doped oxide agglomerates of 0.5–1 micron particle size

	Increase of Fe_2O_3 Q_c	
Dope Used	% added	Q_c, cal/g
none	–	760
Zr	1.0	780
Zr	5.0	1050
Li	1.0	850
Li	5.0	1100

Refs: 1) Daniel (1902), 16, 133, 134 & 738 2) C.I.B. Hennig, USP 1357865 (1920) & CA **15**, 315 (1921) 2a) A.B. Ray, IEC **18**, 10–17 (1926) & CA **20**, 505 (1926) 3) G.J. Schladt, "Study of the Use of Thermite Type Compositions As Pyrotechnic Illuminants"; PATR **128** (1931) 4) Ibid, "Development of Composition For White Smoke Puff Ground Troop Signals", PATR **134** (1931) 5) Ibid, "Development of Composition For White Smoke Puff Ground Troop Signals", PATR **333** (1933) 6) C.G. Dunkle, "Study Toward Reducing The Smoke Effects From Flash Eliminating Agents", PATR **705**(1936) 7) P. Varrato, "Investigation of the Use of Zinc Oxide as a Setting Inhibitor in Ammonium Nitrate", PATR **1051** (1940) 8) R.D. Sheeline, "Loading of 3" AA Shell with Phosphorus And Zinc Oxide Smoke Charges", PATR **1147** (1942) 9) H.J. Eppig, "Development of AT-15 Airport Flare Composition", PATR **1512** (1945) 10) H.J. Eppig, "The Development of a Smokeless Illuminant Composition For The T-24 Flare", PATR **1527** (1945) 11) W.F. Ehert, "Smith's College Chemistry, Sixth Edn", D. Appleton-Century Co, Inc, NY (1946) 12) A.J. Clear, "Effect of Certain Oxides of Iron and Copper on the Properties of TNT", PATR **1597** (1946) 13) W.M. Latimer & J.H. Hildebrand, "Reference Book of Inorganic Chemistry", MacMillan, NY (1947) 14) A.J. Clear, "Stability of Propellant Powder For The 2.36" Rocket", PATR **1699** (1948) 15) Partington (1949), 656 16) A.C. Hutchinson, USP 2710793 (June 14, 1955) & CA **49**, 14326 (1955) 17) F.B. Clay & R.A. Sohlin, USP 2709129 (1955) & CA **49**, 14326 (1955) 18) R.H. Heiskell, USP 2726943 & 2726944 (Dec 1955) & CA **50**, 5293 (1956) 19) J. Belle & L.J. Jones, "Resumé of Uranium Oxide Data–VII",

WAPD-PWR-PMM-491, USAEC Contract No AT-11-1-Gen-14 (1956) 20) J.K. Davidson et al, "The Fast Oxide Breeder–The Fuel Cycle", General Electric Co, NY, **KAPL-1757**, USAEC Contract No W-31-109 Eng-52 (1957) 21) M. Blais & J.P. Picard, "Effect of Various Physical Properties of Lime On The Purity of White Calcium Cyanamide Made By the Picatinny Process (U)", PATR **2457** (1957) 22) Anon, "Development Leading to a Process For The Manufacture of Large Silica Slabs", Amersil Co, NJ, Detroit Tank A Contract DA 30-069-ORD 1791 (1957) 23) J.C. Clayton & S. Aronsen, "Some Preparation Methods And Physical Characteristics of UO_2 Powders", Westinghouse Electric Corp, Penn, **WAPD-178**, USAEC Contract AT-11-1-GEN-14 (1958) 23a) C.R. Mason et al, "Fused Silica Rocket Nozzles", Engrg Exptl Sta, Georgia Inst of Technology, Ga, **Quarterly Rpt No 1 – Project No A-409**, NAVORD contract No NOrd-18564 (1958) 24) H. Schlüter & R. Meyer, GerP 957195 (Jan 31, 1957) & CA **53**, 10765 (1959) 25) G.R. Cole et al, "Fabrication of Uranium Oxide Fuel Elements", DuPont deNemours & Co, **DP-430**, USAEC Contract AT(07-2)-1, (1959) 26) S.Y. Ek & J.A.D. Eldh, USP 2894864 (July 14, 1959) & CA **54**, 17888 (1960) 27) J.F. Watson & D.R. Wilder, "Roles of Niobium Pentoxide, Vanadium Pentoxide and Titanium Dioxide In The Grain Growth And Sintering of Uranium Dioxide", Iowa State Univ, Iowa, **IS-221**, Contract No W-7405-eng-82 (1960) 28) J. DeMent, USP 2995526 (Aug 8, 1961) & CA **55**, 25100 (1961) 29) R.W. Heinemann, "Development of the SM22 Mod 3 Antipersonnel Mine", PATMR **ORDBB-DR4-40** (1961) 30) A.J. Rothman, "Beryllium Oxide For Nuclear Propulsion Application", **UCRL-7428**, Contract No W-7405-eng-48 (1963) 31) R.W. Heinemann & B.J. Zlotucha, "The Feasibility of Applying The Gravel Concept To Explosive Fuzing Systems (U)", PATM **1102** (1963) 32) R.W. Heinemann & B.J. Zlotucha, "The Feasibility of Artillery Gravel", PATR **1123** (1963) 33) Anon, "Design/Development–Slipcast Fused Silica Radome Assembly", General Dynamics, Calif, PIDBuNavWep Contract Now 64-0505 di (1965) 34) E. Ryshkewitch, "Beryllium Oxide Ceramics–Processes, Properties and Applications", Natnl Beryllia Corp, NJ **AFML TR-65-378**, Contract AF 33 (615)-1621 (May 1966) 35) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry–A Comprehensive Text", Interscience Pub, NY (1966) 36) G.C. MacDonald, USP 3325316 (June 13, 1967) & CA **67**, 66210 (1967) 37) P.E. Streigle, "Activator Investigation For A Silver Oxide–Zinc Battery (U)", Catalyst Research Corp, Md, Rept No **2**, AADLPA Contract No DA-28-017-AMC-3433(A) (1967) 38) Sax (1968), 436–7, 438, 524, 525 & 1107 39) L. Dede et al, HungP 154137 (Nov 22, 1967) & CA **68**, 70811 (1968) 40) M. Roth, "Process Control of Gravel Compositions", PATR **3695** (1968) 41) M. Baer & I. Weisman, "Gravel Mine: Substitution of Quartz for Glass", PATR **3800** (1968) 42) J.E. Niesse & T. Vosilos, "Establishment of a Manufacturing Process For Producing Optically Transparent Armor", Avco Corp, Mass, Rept No **AVSD 0611-70-RR**, AFML Contract F33615-68-C-1552 (Nov 1970) 43) C.D. Greskovich & K.N. Woods, "Yttralox Ceramic Laser", GE Corp, NY, Rept No **S-71-1085**, Contract NOOO14-70-C-0360 (May 1971) 44) P.A. Ormsby & F.H. Brown, "Ceramic Materials Research–Status Report 1971", USAMCRA Report No **RL-TR-71-8**, AD 728816 (1971) 45) Hackh's (1972), 481 46) W.E. Perkins et al, USP 3634153 (Jan 11, 1972) & CA **76**,74449 (1972) 47) W.H. Rhodes & A.J. Delai, "Research on Development and Fabrication of Boron Suboxide Specimens", Avco Corp, Mass, Report No **AVSD-0350-72-CR**, AFML Contract F33615-71-C-1449 (Aug 1972) 48) C.R. Tinsley, "Research and Development Testing of Yttria/Rare Earth Stabilized Zirconia Matrix Bricks in The Pilot Test Unit (PTU) at AEDC", Report No **AEDC-TR-72-161**, Contract F40600-73-C-0004 (Nov 1972) 49) A.D. Kirshenbaum et al, "Gaseous Illuminant Pyrotechnic Systems", PATR **4313** (July 1972) 50) W.L. Phené, "Experimental Studies Aimed at Producing Extruded Propellants Having A Bulk Density of 0.95 grams per cc or Better for 5.56mm and 7.62mm Ammunition", CanIndLtd, Can, FA Contract DAAA25-71-C-0342, CCC No 7MA1-0002 (1972) 51) R.A. Johnson et al, "Development of a Pyrotechnic Metal Oxide Generator (PMOG)", ARC, Alex, Va, Rept No **TR-PL-10092-01-1**, SAMSO Contract F04701-71-C-

0067 (March 1973) 52) H.H. Helms & A.G. Rozner, USP 3695951 (Oct 3, 1972) & CA **78**, 74356 (1973) 52a) C.A. Lipscomb, "The Chemical Reactivity of Ferric Oxide", **NAD-CR-RDTR-249** (1973) 53) C.A. Lipscomb & T.M. Smith, USP 3821120 (June 28, 1974) & CA **81**, 123879 (1974) 54) C.A. Lipscomb, "Chemical Effects of Doping on The Litharge-Silicon System", Rept No **NAD-CR-RDTR-264** (Jan 1974) 55) P.K. Talty, "High Temperature Deformation Behavior of Ceramics", Wright-Patterson AFB Rept No **ARL-75-0156** (June 1975) 56) C.H. Burnside, "Role of Ferric Oxide Surface Area In Propellant Burn Rate Enhancement (First Step Toward Modelling)", Rockwell Intl Corp, Rocketdyne Div, Tex, Rept No **R-4889**, Contract F44620-75-C-0002 (June 1975)

The Following are Selected Inorganic Oxide Entries:

Aluminum Oxide (Alumina, α-Alumina, Corundum, Alandum). Al_2O_3, mw 101.96, v hard white cryst powd, mp 2045°, bp 2980°, d 3.965g/cc. Insol in w, v sl sol in aq alkaline solns. Found in nature as a mineral such as *bauxite*. Lab prepn is by heating aluminum hydroxide to above 1100°. It is used as a chemical reagent, as a smoke and flash reducer and storage stabilizer in NC base propInts, in rubber-base composite propInts as discussed above, and in pyrot compns

The USA Military Specification (Ref 2) contains the following requirements and criteria: (1) form and color; white powder, (2) date of mfg; not older than one year, (3) chloride as AgCl turbidity; 0.010% max, (4) silicates as insol matter after $KHSO_4$ fusion; trace max, (5) sulfate as $BaSO_4$ turbidity; 0.070% max, (6) alkalies and alkaline earths gravimetrically as the sulfate; 0.50% max, (7) heavy metals as PbS turbidity; 0.007% max, (8) Fe as a $Fe(CNS)_3.9KCNS.4H_2O$ red coloration; 0.015% max, (9) H_2O as wt loss on ignition; 5.00% max and (10) w sol substances det by wt loss; 0.75% max

High concns of aluminum oxide dust can cause various types of lung damage such as Shaver's disease, fibrosis, emphysema and pneumothorax

Refs: 1) Gmelin, Syst Nr 35, Teil B (1934), 7–98 2) Anon, "Aluminum Oxide, Ignited Powder, Reagent", **MIL-A-10825** (Cml C) (Jan 1951) 3) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 822 4) Anon, EngDesHdbk, "Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 12–15 5) Merck (1968), 46 6) Sax (1968), 389 7) ChemRubHdb (1975), B-64

Arsenic Pentoxide (Arsenic Acid Anhydride, Arsenic Oxide). As_2O_5, mw 229.84, white amorph powd, mp 315° (decompn), d 4.32g/cc. Sol in alc, acids, alkalies and w. Prepn is by heating a mixt of As_2O_3 with concd HNO_3 (d 1.38g/cc) until the evoln of nitrogen oxides ceases. The soln of H_3AsO_4 is then evapd to dryness, redissolved in w and reevapd until a temp of over 300° is reached. It is used as a chemical reagent

The USA Military Specification (Ref 8) contains the following chemical criteria and requirements: (1) As_2O_5 by sodium thiosulfate–iodine titration; 99.0% min, (2) As_2O_3 by carbonate–iodine titration; 0.05% max, (3) Cl as AgCl turbidity; 0.005% max, (4) heavy metals as PbS turbidity; 0.010% max, (5) Fe as a $Fe(CNS)_3$. $9KCNS.4H_2O$ red coloration; 0.010% max and (6) nitrate as an indigo carmen blue coloration which persists for over 5 mins

Poisonous! LD_{50} (lethal dose to 50% of the animals tested) iu_v (intravenous) in rabbits; 8mg/kg

Refs: 1) Gmelin, Syst Nr 17 (1952), 273–77 2) A. Simon & E. Thaler, ZAnorgChem **161**, 143 (1927) & CA **22**, 1077 (1928) 3) Ibid, **246**, 19 (1941) & CA **36**, 1255 (1942) 4) H. Guérin, BullFr (5) **22**, 1536 (1955) & CA **50**, 3129 (1956) 5) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 601 6) Merck (1968), 102 7) Sax (1968), 438 8) Anon, "Arsenic Pentoxide, Analyzed Reagent", **MIL-A-51313** (May 1969) 9) ChemRubHdb (1975), B-69

Arsenic Trioxide (Arsenous Acid, Arsenous Acid Anhydride, Arsenious Oxide, Arsenic Sesquioxide, White Arsenic). As_2O_3, mw 197.82;

white, amorph, glassy lumps; mp 313°, d 4.32 g/cc. Sol in HCl, alk, alk carbonate and w. Prepn is by heating arsenical pyrite ore in oxygen to produce crude As_2O_3 (Ref 4). Pure As_2O_3 is obtd by reacting crude As_2O_3 with HCl and distg off $AsCl_3$. Any $SbCl_3$ is removed from the distillate by shaking with concd HCl. The pure $AsCl_3$ is then hydrolyzed in agitated boiling w, and pure As_2O_3 crystallizes out on cooling. It is used as a chemical reagent and for evolving smoke in pyrots (see above)

The USA Military Specification (Ref 10) contains the following requirements and criteria: (1) appearance; white powd, (2) As_2O_3 by sodium carbonate–iodine titration; 98.0% min and (3) moisture by wt loss after oven drying; 0.10% max

Poisonous! LD_{50} orally in rats: 138mg/kg

Refs: 1) C.W. Foulk & P.G. Horton, JACS **51**, 2416 (1929) & CA **23**, 4417 (1929) 2) E. Jenckel, ZAnorgChem **182**, 314 (1929) & CA **25**, 5326 (1931) 3) A. Schulman & W.C. Schumb, JACS **65**, 878 (1943); not found in CA 4) W.F. Ehret, "Smith's College Chemistry", D. Appleton Century Co, Inc, NY (1946), 601 5) A.R. Tourky & A.A. Mousa, JCS [1], 1305 (1949); not found in CA 6) I.N. Strauski et al, ZElectrochem **62**, 362 (1958) & CA **52**, 13373 (1958) 7) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 600–1 8) Merck (1968), 182–3 9) Sax (1968), 438 10) Anon, "Arsenic Trioxide, Technical", **MIL-A-10840C** (June 1969) 11) ChemRubHdb (1975), B-69

Barium Oxide (Barium Monoxide, Baryta, Barium Protoxide, Calcined Baryta). BaO, mw 153.36; colorl or white to yelsh-white deliq powd; mp 1923°, bp 2000°, d 5.72g/cc. Sol in dil acids, ethanol, methanol and w (decomps with a large amt of heat being evolved). Prepn is by thermal decompn of $BaCO_3$ under high vacuum. It is a product of the burning of the many barium compds present in pyrots and, as discussed above, it is used as an anti-barrel wear additive in proplnt compns

No USA Military Specification exists for this compd

Poisonous! Max Allowable Concn for an 8 hr day, 0.5mg/cm of air

Refs: 1) G.F. Hüttig & A. Arbes, ZAnorgChem **196**, 403 (1931); not found in CA 2) O. Hönigschmid & R. Sachtleben, ZAnorgChem **178**, 1 (1929); not found in CA 3) E.H. Archibald, "The Preparation of Pure Inorganic Substances", J. Wiley, NY (1932), 77 4) H. Arita, JapP 174523 (April 1947) & CA **44**, 806 (1950) 5) M. Ohshima & H. Arita, JapP 178592 (Apr 1949) & CA **45**, 9403 (1951) 6) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 47–50 7) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 933–4 8) Merck (1968), 121 9) Sax (1968), 451 10) ChemRubHdb (1975), B-71

Beryllium Oxide (Bromellite). BeO, mw 25.01, white amorph powd, mp 2530°, bp *ca* 3900°, d 3.01g/cc. Sol in concd acids and alkalies. V sl sol in w. Prepn is by burning $BeCO_3$ at 900° in a Pt crucible to the oxide. It is used in nuclear reactor fuels and moderators as well as in powder metallurgy, ceramics, fuel cells and coatings (see above)

No USA Military Specification exists for this compd

Extremely poisonous! V small concns are fatal after *brief* exposure

Refs: 1) Gmelin, Syst Nr 26 (1930), 82–91 2) O. Hönigschmid & T. Johannsen, ZNaturforsch **1**, 650 (1946); not found in CA 3) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 893–4 4) Merck (1968), 144 5) Sax (1968), 468 6) ChemRubHdbk (1975), B-72

Bismuth Trioxide. See Vol **2**, B162-R

Boron Oxide. See Vol **2**, B252-L to B253-L

The Bromine Oxides. See Vol **2**, B306-L to B307-L

Cadmium Oxide. CdO, mw 128.41, dk brn infusible powd, mp 900° (decomps), bp subl 1559°, d 8.15g/cc. Insol in w and alk, sol in dil acids and amm hydroxide. Coml prepn is by reacting Cd metal with air during distn, and collecting the oxide in a baghouse. Lab prepn consists of burning the carbonate in air. It is used as a chemical reagent

The USA Military Specification (Ref 4) contains the following requirements and criteria: (1) cadmium by ethylenediaminetetraacetic acid titration; 87.0% min, (2) silver, lead, tin, copper, mercury, zinc and iron by either atomic absorption or emission spectrographic techniques; total 0.050% max, (3) arsenic, antimony and thallium to be detd as in "(2)"; 0.005% max, (4) volatiles by wt loss after oven drying; 0.50% max, and (5) appearance; reddish-brown powd

Poisonous! Human tolerance, 0.1mg/cc of air

Refs: 1) Gmelin, Syst Nr 33 (1925), 69–72; ibid, suppl (1959), 419–36 2) Merck (1968), 187 3) Sax (1968), 518 4) Anon, "Cadmium Oxide", **MIL-C-6151A** (Oct 1969) 5) CondChemDict (1971), 150 6) ChemRubHdb (1975), B-75

Calcium Oxide (Lime, Quicklime, Burnt Lime, Calx, Unslaked Lime, Fluxing Lime). CaO, mw 56.08, white or greyish-white lumps or powd, mp 2580°, bp 2850°, d 3.25–3.40g/cc. Sl sol in w with formation of calcium hydroxide and evolution of large amts of heat; sol in acids, and insol in ethanol. Coml prepn consists of heating calcium carbonate in kilns at 1000–1100° until all of the CO_2 is driven off. Lab prepn is by burning calcium carbonate or calcium oxalate at about 800° using a quartz crucible in an electric furnace

The USA Military Specification (Ref 5) contains the following requirements and criteria for Grade A (bleaching grade) and Grade B (fluxing grade): (1) nonvolatile matter by wt loss after ignition in an electric furnace: Grade A, 94.0% min and Grade B, 98.0% min, (2) calcium oxide by gravimetric procedure (Ref 9): Grade A, 90.0% min and Grade B, 95.0% min, (3) magnesium oxide by gravimetric procedure as magnesium pyrophosphate (Ref 9); Grade B, 1% max, (4) iron and aluminum oxides by gravimetric procedure (Ref 9), Grade B, 1.0% max, (5) silicon dioxide by loss in wt after electric furnace ignition, Grade B, 1.0% max, (4) iron and aluminum oxides by gravimetric procedure (Ref 9), Grade B, 1.0% max, (5) silicon dioxide by loss in wt after electric furnace ignition, Grade B, 1.0% max, and (6) particle size by retention on individual members of a set of US Standard Sieves after agitation on a mechanical shaker – 1.5 sq inch (37.5mm) openings, Grade A – 1.0% max; 1.0 sq inch (25.0mm) openings, Grade A – 7.0% max; 1/8 inch round (3.2mm round) openings, Grade A – 95.0% min; No 3½ (0.223 inch) openings, Grade B – 0.0% max, and No 12 (0.0661 inch) openings, Grade B – 95.0% min

A strong caustic irritant. Dangerous near organic materials. Tolerance, 5mg/cc of air

Besides its use in pyrots, calcium oxide has been used in a number of expl devices such as Jarolimek's igniter, Elliot's "Quicklime Explosive", and the various cartridges of Smith and Moore, Arnould, and Steinau (Ref 1). All of these are presented in greater depth above, together with the current usage of the oxide

Refs: 1) Daniel (1902), 16, 133, 134 & 738 1a) T.W. Richards & O. Hönigschmid, JACS **32**, 1577 (1910) & CA **5**, 840 (1911) 2) E.C. Deforge, RecMatérConst et TravPub Ed C, No **407**, 279–82 (1949) & CA **44**, 805 (1950) 3) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 931 4) Anon, EngDesHdbk, "Properties of Materials in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 75–7 5) Anon, "Calcium Oxide, Technical", **MIL-C-12056B** (Oct 1967) 6) Merck (1968), 194 7) Sax (1968), 525 8) CondChemDict (1971), 158 9) ASTM Stds, **C25-72** (1974), 118–132 10) ChemRubHdb (1975), B-78 & F-147

Ceric Oxide (Cerium Dioxide, Cerium Oxide, Ceria). CeO_2, mw 172.13, white powd, mp *ca* 2600°, d 7.132g/cc at 23°. Sol in concd sulfuric and nitric acids, insol in dil acids and w. Prepn is by dissolving $CeCO_3$ in 16N HNO_3 contg 3% H_2O_2 and then evapg off the nitrate soln followed by thermal decompn. The yield is 97.6% of 99.8% pure CeO_2. The oxide is used in optics, electronics, as a diluent in nuclear fuels (as

above), for fueling gas-generating propulsion units and as an anti barrel wear additive to proplnts

There is no USA Military Specification for this compd

Refs: 1) E.J. Roberts, ZAnorgChem **71**, 305 (1911) & CA **5**, 2231 (1911) 2) C. Duval, AnalChimActa **1**, 341 (1947) & CA **43**, 8952 (1949) 3) R. Bock, AngChem **62**, 375 (1950) & CA **45**, 55 (1951) 4) J.C. Worf, USP 2564241 (1951) & CA **45**, 1314 (1951) 5) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1965), 1132–5 6) Merck (1968), 223 7) Sax (1968), 542 8) CondChemDict (1971), 184 9) ChemRubHdb (1975), B-81

The Chlorine Oxides. See Vol **3**, C243-L to C244-R

Chromic Acid. See Vol **3**, C298-R to C299-L

Chromic Oxide. See Vol **3**, C299-R

The Copper Oxides. See Vol **3**, C522-R to C523-L

The Iron Oxides. See Vol **6**, F15-L to F17-L

The Lead Oxides. See Vol **7**, L9-L to L10-L

Magnesium Oxide. See under Magnesium, M9-L in this Vol

The Manganese Oxides. See under Manganese, M12-L & R in this Vol

Molybdenum Trioxide (Molybdenum Anhydride, Molybdic Oxide, Molybdic Acid Anhydride). MoO_3, mw 143.95, white powd, mp 795°, bp 1155°, d 4.696g/cc at 26/4°. Sl sol in w, sol in acids, alk sulfates and amm hydroxide. Prepn is by first boiling concd nitric acid with NH_4 molybdate to ppt H_2MnO_4. By dehydration at 150° the H_2MnO_4 is then converted to MoO_3. The trioxide is subseq purified by subln in a quartz tube at 780°. The trioxide is used in igniter compns and proplnt compns (see above)

The USA Military Specification (Ref 8) contains the following requirements and criteria: (1) molybdenum trioxide gravimetrically as lead molybdate; 99.5% min, (2) insoluble in dil amm hydroxide as loss in wt; 0.010% max, (3) chloride as silver chloride turbidity; 0.002% max, (4) nitrate as an indigo carmen blue coloration which persists for over five mins; 0.003% max, (5) arsenate, phosphate and silicate (as SiO_2) as a blue coloration in acidified 4-methyl-2-pentanone which should not exceed that in a control; 0.001% max, (6) sulfate as barium sulfate turbidity which should not exceed that of a standard; 0.020% max, (7) ammonium colorimetrically with Nessler's reagent; 0.002% max, (8) lead as PbS colorimetrically; 0.005% max, (9) average particle size using the Fisher Sub Sieve Sizer (Ref 3); 8 ± 4 microns and (10) workmanship by inspection – material to be free flowing and free of lumps, dirt, chips or other foreign mat

The trioxide has a low toxicity; max acceptable tolerance level is 5mg/cc of air (human) and LD_{75} intraperitoneal (ip) in guinea pigs is 400mg/kg

Refs: 1) W.C. Schumb & W.H. Hartford, JACS **56**, 2613 (1934) & CA **29**, 1027 (1935) 2) Anon, "Procedures for Determining Particle Size, Particle Size Distribution, and Packed Density of Powdered Materials", **MIL-STD-1233** (March 1962) 3) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 211–13 4) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **2**, Academic Press, NY (1965), 1412 5) Merck (1968), 699 6) Sax (1968), 941 7) CondChemDict (1971), 593 8) Anon, "Molybdenum Trioxide (For Use in Ammunition)", **MIL-M-48146** (March 1973) 9) ChemRubHdb (1975), B-111

Nitrogen Oxides. See in this Vol, N129-L to N133-L

Potassium Oxide (Potassium Monoxide). K_2O, mw 94.20, white, loose, deliq powd, mp 350° (decompn), d 2.32g/cc at 0°. Reacts with w very readily to form KOH with evoln of 75 kcal/mole. V sol in w, sl sol in ethanol and eth. Prepn is by mildly heating carefully purified K in the presence of pure dry air. Excess K is distd off at 350° under high vacuum. The K_2O is 99.5% pure. Also produced when K compds are burned in pyrots

No USA Military Specification exists for this compd

The oxide is highly caustic and corrosive, and is a moderate fire hazard

Refs: 1) E. Rengade, CR **144**, 754 (1907) & CA **1**, 1526 (1907) 2) E. Zintl et al, ZElectrochem **40**, 588 (1934) & CA **28**, 6604 (1934) 3) Anon, EngDesHdbk, "Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 249–52 4) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 977 5) Sax (1968), 1046 6) CondChemDict (1971), 724 7) ChemRubHdbk (1975), B-125

Silicon Dioxide (Quartz, Lechatelierite, Tridymite, Silica, Silicic Anhydride, Rock Crystal, Cristobalite, Sand). SiO_2, mw 60.08, Sol in HF, v sl sol in alk and insol in w and acids. Found so widely in nature that no mfg or lab procedures are usually needed for impure mat. It is a product resulting from burning Si or Si compds in pyrots. Pure SiO_2 can be prepd in several ways: (1) the transparent or fused variety is manufd by vapzn of sand at 3000° in an electric arc furnace, and (2) amorph SiO_2 is obtd as a fine white powd by decompg pure $SiCl_4$ with w and heating the resulting gel. Its uses (see above) are in detonators, thixotropic control in the manuf of aerial mine expl charges, micromines (Gravel), anti barrel wear additives to proplnts, flares, in cast form as radomes, as well as in such uses as paints, cements, etc

Selected Parameters of the Allotropic Forms of SiO_2

Allotropic Form	Appearance or Crystal Form	Mp, °	Bp, °	Density, g/c
cristobalite	colorl cub or tetrg	1710	2230	2.32
lechatelierite	colorl, amorph, vitreous	–	2230	2.20
quartz	hex	1610	2230	2.653–.66
tridymite	rhombic	1703	2230	2.28 –.33

There are two USA Military Specifications for the use of silica in ammo (Refs 3 & 4). Ref 3 contains the following requirements and criteria for special purpose silica Type I (alkaline), Type II (acid), and Type III (hydrophobic):

	Type I	Type II	Type III
Surface Area, m^2/g[a]	300 ± 50	325 ± 50	130 ± 25
Ignition loss, %[b]	11.0 ± 2.0	11.0 ± 2.0	7.5 ± 2.5
Loss at 105°, %[c]	6.0 max	6.0 max	4.0 max
HF Residue Test, %[d]	3.0 max	3.0 max	3.0 max
pH[e]	8.5 ± 0.5	5.0 ± 0.5	5.0 ± 0.5
No 325 (44 microns) mesh wet sieve residue, %[f]	0.02 max	0.02 max	NA
Water repellency, %[g]	NA	NA	99.5 min
Viscosity, cps at 25°[h]	NA	NA	2000 ± 500

NA – not applicable
a – as the BET (Brunauer, Emmett and Teller) value
b – as the wt loss
c – as the wt loss
d – as the wt loss on ignition
e – as the pH meter reading of a glass electrode vs a calomel std electrode
f – as the wt of the residue
g – as the residue miscible with water
h – as the Brookfield Viscometer measurement

Ref 4 contains the following requirements and criteria for silica: (1) finely divided similar to "Cab-O-Sil", Grade M-5, made by the Cabot Corp of Boston, Mass, (2) surface area as ml of NaOH titrant used to achieve a pH of 9.0; 175 to 225m^2/g, (3) density as the wt of a known vol of silica; 2.3 lbs/cu ft max, (4) moisture as loss in wt; 1.5% max, (5) pH as the measurement made using a Beckman Model G pH Meter with glass vs calomel electrodes; 3.5 min to 4.2 max and (6) suspension as miscibility with fluoroethane after agitation; no settling in 10 mins

Long exposure to SiO_2 dust can result in fibrosis of the lung or silicosis which may eventuate in pulmonary hypertension and cor pulmonale. Susceptibility to tuberculosis is enhanced. The tolerance level for cryst forms of SiO_2 is calculated from the formula $250/(\%SiO_2+5)$, and for amorph forms the tolerance level is 20 millions of particles/cu ft of air

Refs: 1) Partington (1949), 501 2) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 259–65 3) Anon, "Silica, Special Purpose (For Use in Ammunition)", **MIL-S-14771** (May 1968) 4) Anon, "Silica (For Use in Ammunition)", **MIL-S-14760** (May 1968) 5) Merck (1968), 946 6) Sax (1968), 1088–9 7) Anon, "Silica, Colloidal, Synthetic", **MIL-S-12613B** (Oct 1969) 8) CondChemDict (1971), 783 9) Hackh's (1972), 610 10) Anon, "Silica, Pulverized", **MIL-S-24463** (April 1972) 11) Anon, "Silicon Dioxide, Microfine", **MIL-S-47129** (May 1974) 12) ChemRubHdbk (1975), B-133

Silicon Monoxide. SiO, mw 44.09, hard and abrasive, black to brn-black amorph or cubic crysts, mp > 1702°, bp 1880°, d 2.13–.20. Sol in concd aq alk and dil $HF+HNO_3$. Prepn is by subliming finely divided silicon at 1250° under high vacuum for 4 hrs. It is used as a coating for precision optical lenses

The USA Military Specification (Ref 14) contains the following requirements and criteria: (1) a pre-production sample must meet the Spec requirements, (2) silicon monoxide shall be of a high purity grade, (3) chemical compn as detd by the powder–D-C arc semiquantitative technique

of spectrochemical analysis (ASTM E-2 SM 11-2) for: a) iron; 0.01 to 0.10%, b) nickel; 0.02% max, c) aluminum; 0.01 to 0.05%, d) molybdenum; 0.01% max, e) copper, 0.01 to 0.10%, f) manganese; 0.01 to 0.10%, g) magnesium; 0.01 to 0.05%, h) titanium; 0.02% max, i) boron; not detected, j) chromium; 0.03 max, k) free silicon; 0.10% max, l) silicon monoxide; 95.0% min, and (4) workmanship of such a level as to assure a uniform product in Spec compliance

Silicon monoxide has the same toxicity as the dioxide

Refs: 1) K.F. Bonhoeffer, ZPhysChem **131**, 360 (1928) & CA **22**, 1539 (1928) 2) W. Blitz, Naturwissen **26**, 188 (1938); not found in CA 3) E. Zintl et al, ZAnorgChem **245**, 1 (1940) & CA **35**, 1719 (1941) 4) H. Koenig, Optik **3**, 419 (1948); not found in CA 5) G. Grube & H. Speidel, ZElectrochem **53**, 339 (1949) & CA **44**, 4323 (1950) 6) H. von Wartenberg, ZElectrochem **53**, 343 (1949) & CA **44**, 4815 (1950) 7) M. Hoch & H.L. Johnston, JACS **75**, 5224 (1953) & CA **48**, 2436 (1954) 8) G. Jacobs, CR **236**, 1369 (1953) & CA **47**, 9711 (1953) 9) L. Brewer & R.K. Edwards, JPhChem **58**, 351 (1954) & CA **48**, 7373 (1954) 10) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 696–7 11) Merck (1968), 946 12) Sax (1968), 1090 13) CondChemDict (1971), 784 14) Anon, "Silicon Monoxide", **MIL-S-47112** (May 1974) 14) ChemRubHdbk (1975), B-133

Sodium Oxide (Sodium Monoxide). Na_2O, mw 61.98, white-grey deliq powd, mp 1275° (subl), d 2.27g/cc. Combines violently with w, forming NaOH. Sol in w and ethanol with decompn. Reacts with acids to neutralize them. Prepn is by reacting NaOH with Na in a nickel crucible at 320° under high vacuum. Yield is 96%. The oxide is stored under anhyd benz. It is also the product of the ignition of many of the sodium compds found in pyrots. It is used as a chemical reagent for organic polymerization or condensation reactions

No USA Military Specification exists for this compd

The oxide is extremely *corrosive* and should be handled with tongs! Max allowable concn (MAC) is 2mgs/m^3 of air

Refs: 1) A. Klemenc et al, ZAnorgChem **265**, 221 (1951); not found in CA 2) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 975–6 3) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187**, (Oct 1963), 276–8 4) Merck (1968), 963 5) Sax (1968), 1109 6) CondChemDict (1971), 805 7) ChemRubHdbk (1975), B-139

Stannic Oxide (White Tin Oxide, Tin Dioxide, Stannic Anhydride, Flowers of Tin, Stannic Acid, Cassiterite). SnO_2, mw 150.69, white powd, mp 1127°, bp 1800–1900° (subl), d 6.95 g/cc. Sol in concd sulfuric and concd hydrochloric acids, sl sol in hot concd aq KOH or NaOH. Prepn is by reacting Sn with concd nitric acid (d 1.41 g/cc) on a w bath forming β-stannic acid. The β-stannic acid is then heated to a red heat and converted to SnO_2. It is used as a chemical reagent and (see above) as an antifouling, flash and barrel wear reducing additive in proplnts

The USA Military Specification (Ref 7) contains the following requirements and criteria: (1) material as a fine white cryst powd by inspn, (2) volatile content as wt loss on oven drying at 110°; 0.50% max, (3) stannic oxide as $SnCl_2$ by by iodimetric titration to a blue (starch) end point; 98.20% min, (4) Class 1 and 2 types of granulation as the wt of oven-dried (at 105°) material passed thru a sieve when a w-ethanol suspension is w-washed thru a No 200 (74 micron) sieve, Class 1 – 95% min and Class 2 – 95% min; and then, using another sample, thru a No 325 (44 micron) sieve, Class 1 – 85% and Class 2 – 90% min; and (5) acidity as sulfuric acid using NaOH titrant to a methyl red end pt; 0.01% max

The oxide can cause relatively benign pneumoconiosis

Refs: 1) A. Kleinschmidt, Monatsh **39**, 149 (1918) & CA **13**, 2490 (1918) 2) E. Posnaj, JPhChem **30**, 1073 (1926); not found in CA 3) H.B. Weiser & W.O. Mulligan, JPhChem **36**, 3030 (1932) & CA **27**, 1255 (1933) 4) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, Academic Press, NY (1963), 738 5) Merck (1968), 978 6) Sax (1968), 1166 7) Anon, "Stannic Oxide, Technical", **MIL-S-50005A** (Jan 1969) 8) CondChemDict (1971), 822 9) ChemRubHdbk (1975), B-149

Titanium Dioxide (Titania, Titanium White, Rutile, Anatase, Brookite, Titanic Anhydride, Titanic Acid Anhydride, Titanic Oxide). TiO_2, mw 79.90,

Selected Parameters of the Allotropic Forms of TiO_2

Allotropic Form	Appearance or Cryst Form	mp, °	bp, °	Density, g/cc
brookite	white, rhomb	1825	–	4.17
rutile	col, tetr	1830–50	2500–3000	4.26
anatase	brn-blk, octahedrite	–	–	3.84

Sol in hot concd sulfuric acid, HF and alk. The dioxide occurs in nature as Ilmenite (FeO, TiO_2) or rutile. Coml prepn is by extrn of the ore with concd sulfuric acid, followed by heating, filtering, washing and then calcining at 800–1000° to produce anhyd TiO_2. Lab prepn is by mixing a cold soln of aq $TiCl_4$ with a cold HCl buffered soln of concd $(NH_4)_2SO_4$ and then bringing the combined solns to a boil while adjusting the pH to 1.0 using ammonia. The resulting ppt is then dried at 107°, calcined for 1 hr at 800°, ground and washed. Recalcining at 1000° yields a rutile with 99.8% TiO_2 content. The dioxide is also a prod of the combstn of Ti used in pyrots. It is used as an anti barrel wear additive in proplnts, a pyrot smoke generator, a smoke inhibitor in pyrots, and a proplnt burning-rate modifier (see above). It is also used as a paint pigment of great hiding power, when combined with wax it becomes an additive liner for artillery carts, and, in the form of single crysts, as high temp transducers having microsec response

The USA Military Specification (Ref 13) contains the following requirements and criteria: (1) titanium dioxide as the titanous reduced ferrous salt by $KMnO_4$ titration; 98.0% min, (2) coarse particles retained on a No 325 (44 micron) sieve after w washing and brushing; 0.25% max, (3) specific gravity as the wt of kerosene displaced in a pycnometer; 3.8 to 4.2 g/cc at 15.6°, (4) oil absorption as the wt of raw linseed oil used when incorporated by rubbing on a glass plate with TiO_2 using a steel spatula; 20.0 to 40.0 lbs/100 lbs TiO_2, (5) water solubility as the wt of mat recovered by filtn of an aliquot of a boiling w digestion of a sample of the oxide; 0.2% max, (6) hydrogen ion concn as pH using a glass vs calomel electrode; 7.0 to 8.0, (7) moisture by loss in wt after oven drying at 105–10° for 2 hrs; 0.7%, (8) compatibility as detd using M30 proplnt in a 50/50 mixt when heated at 100° for 40 hrs at a press of 5mm; 3ml of gas max, and (9) first article inspection as specified in the delivery contract

The dioxide is considered a nonhazardous respiratory nuisance with a tolerance value for dust 15mgs/m^3 of air

Refs: 1) A.V. Pamfilov et al, ZhObshchKhim **13**, 1310 (1940) & CA **35**, 2432 (1941) 2) W.F. Ehert, "Smith's College Chemistry–Sixth Edition", D. Appleton-Century Co, Inc, NY (1946), 582 3) C.H. Shomate, JACS **69**, 218 (1947) & CA **41**, 2634 (1947) 4) W.B. Blumenthal, CeramicAge **51**, 320 (1948) & CA **42**, 8717 (1948) 5) L. Merker, USP 2760874 (1956) & CA **50**, 16057 (1950) 6) W.L. Faith et al, "Industrial Chemicals", Wiley, NY (1957), 756-60 7) A.W. Czanderna et al, JACS **79**, 5407 (1957) & CA **52**, 1828 (1958) 8) Anon, EngDesHdbk, "Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 307–10 9) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **2**, Academic Press, NY (1965), 1216–18 10) Merck (1968), 1054 11) Sax (1968), 1167 12) CondChemDict (1971), 874–5 10) ChemRubHdbk (1975), B-149–50 13) Anon, "Titanium-Dioxide; Dry", **MIL-T-48149A** (Jan 1976)

Tungsten Dioxide. WO_2, mw 215.92, brn cubic crysts or amorph powd, mp 1851.60° (decompn with ign in air), 1500–1600° (decompn with ign in N), bp *ca* 1430° (subl at 800°), d 12.11g/cc. Sol in acids and aq KOH. Prepn is by heating a mixt of WO_3 and W in a sealed evacuated quartz tube at 950° for 40 hrs. The amorph powd is strongly pyrophoric and is easily oxidized to WO_3

No USA Military Specification exists for this compd

The dioxide is sl toxic upon heavy ingestion (over 10% of the diet) and by dust inhalation to exptl animals

Refs: 1) A. Magnêli et al, AnalChem **24**, 1998 (1952) & CA **46**, 10995 (1952) 2) Anon, EngDesHdbk, "Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963) 3) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **2**, Academic Press, NY (1965), 1421–2 4) Sax (1968), 1214 5) ChemRubHdbk (1975), B-150

Xenon Trioxide. XeO_3, mw 179.30, colorl cryst, trig pyramidol, hygr, mp 30–40° (explds). V sol in w. Prepn (with *care)* is by reacting xenon tetra- or hexafluoride with w at RT under partial vacuum. The compd is stable at RT in aq soln. It explds when dry and is rubbed, pressed, or gently heated. A RH of over 20% decreases the stability of the dry compd

No USA Military Specification exists for this compd

The aq soln is a v strong oxidizing agent and a strong irritant. The compd is highly toxic by inhalation

Refs: 1) D.F. Smith, JACS **85**, 816–17 (1963) & CA **58**, 13417 (1964) 2) D.H. Templeton et al, JACS **85**, 817 (1963) & CA **58**, 13230 (1964) 3) Anon, C&EN **41**, 45–6 (April 1963); not found in CA 4) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, NY (1966), 594–7 5) CondChemDict (1971), 942 6) J.C. Bailar, Jr et al, Eds, "Comprehensive Inorganic Chemistry", Vol **1**, Pergamon Press, NY (1973), 309–15

Xenon Tetroxide. XeO_4, mw 195.30, colorl gas, mp –40° (explds). Prepn is by reacting sodium perxenate with concd sulfuric acid. Compd is v unstable

No USA Military Specification exists for this compd

Refs: 1) J.G. Malm et al, ChemRevs **65**, 199 (1965) & CA **62**, 12765 (1965) 2) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, NY (1966), 594 & 598 3) J.C. Bailar, Jr et al, "Comprehensive Inorganic Chemistry", Vol **1**, Pergamon Press, NY (1973), 321–23 4) ChemRubHdbk (1975), B-152

Zinc Oxide (Flowers of Zinc, Zinc White, Zinc Bloom, Philosopher's Wool, Chinese White, Zincite). ZnO, mw 81.38, white or yellowish-white amorph odorless powd with a bitter taste, mp 1975° (subl and decomps), d 5.47–5.606 g/cc. V sl sol in w, sol in mineral acids, dil acet acid and NH_4OH. Coml prepn is from Zn or ores such as Franklinite or Zinc Blende by vapzn in a CO atm with subsequent oxidation of the vapors with preheated air. Lab prepn is by converting anhyd zinc oxalate to ZnO by heating at 400° for 4 hrs. It is also a product of the burning of Zn in pyrots. Zinc oxide is used as a caking (or setting) inhibitor for AN (expl) compns, an anti barrel wear additive in proplnts, and an ingredient of smoke generating pyrot compns

The USA Military Specification (Ref 7) contains the following requirements and criteria for Grade A (pyrotechnic mixt) and Grade B (stabilizer for XXCC3 impregnite): (1) zinc oxide by titration with a std soln of K ferrocyanide; Grade A – 98.5% min and Grade B – 99.0% min, (2) water-soluble salts as loss in sample wt; Grade A – 0.50% max and Grade B – 0.50% max, (3) sulfur (as SO_3) gravimetrically as $BaSO_4$; Grade A – 0.40% max and Grade B – 0.10% max, (4) lead oxide (as PbO) gravimetrically; Grade A – 0.60% max and Grade B – 0.10% max, (5) loss in wt at 110°; Grade A - 0.30% max and Grade B – 0.50% max, (6) cadmium (as CdO) gravimetrically as CdS; Grade A – 0.20% max, (7) arsenic (as As_2O_3) gravimetrically as As sulfide; Grade A – 0.10% max, (8) antimony (as Sb_2O_3) gravimetrically as Sb sulfide; Grade A – 0.10% max, (9) particle size – as Class 1 (regular grind for both Grade A and Grade B), 99.9% min by (dry) wt shall pass thru US Std Sieve No 140 (105 microns) and 99.0% min thru sieve No 170 (88 microns); and Class 2 (fine grind for Grade A only), average particle size using the Fisher Sub Sieve Sizer (Ref 2a); 5.0 microns max, (10) moisture reabsorption by wt difference; Grade A – 0.15 to 0.54% min and max, and (11) apparent density by pycnometer; Grade A (Class 1) – 0.75g/cc min

Vaporized zinc oxide is sl to moderately toxic on inhalation and can cause "brassfounders ague" or "brass chills". MAC for an 8 hr working day is 15mg/m^3 of air. It is an eye irritant

Refs: 1) Depew, USP 2372367 (1945) & CA **39**, 3405 (1945) 2) W.L. Faith et al, "Industrial Chemicals", Wiley, NY (1957), 810–16 2a) Anon, "Procedures For Determining Particle Size, Particle Size Distribution, and Packed Density of Powdered Materials", **MIL-STD-1233** (March 1962) 3) Anon, EngDesHdbk, "Properties of Materials Used In Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 325–8 4) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **2**, Academic Press, NY (1965), 1664 5) Merck (1968), 1129

6) Sax (1968), 1246–7 7) Anon, "Zinc Oxide, Technical", **MIL-Z-291E(1)** (Aug 1970) 8) CondChemDict (1971), 051 9) ChemRubHdbk (1975), B-154

Written By **H. L. HERMAN**

Oxidized Rosin (Résidée in Fr). An expl material, prepd by E. Steele of Engl by treating a mixt of 90 parts of colophony (rosin) and 10p of starch with 67% nitric acid (42°Be). After washing, drying, and powdering, the résidée was moistened with methylol, mixed with K chlorate (sometimes with other ingredients), and then warmed gently with stirring to evaporate the methylol. The resulting mixts were the so-called "Steelites" (qv), mining expls used in Fr and Engl during the early part of this century
Ref: Davis (1943), 360

Oxinite (Oxinita in Spanish). An expl mixt of Nitroglycol and Dinitrodiglycol prepd by Ohman in Sweden in 1936 directly from ethylene by an electrolytic method

The electrolytic bath consists of two compartments, anodic and cathodic. In the first, Pt gauze is immersed in an acet soln of Ca nitrate which is kept constantly saturated with ethylene, by bubbling ethylene thru it in such a manner that it sweeps over the surface of the Pt gauze. In the cathodic compartment, Al is immersed in a soln of Ca nitrate in nitric acid. The level of the liq in the cathodic compartment is maintained above that of the anodic, and the liq moves from the first to the second compartment as the electrolysis progresses. The discharge of the nitrate ion (NO_3^-) at the Pt gauze anode liberates the free nitrate radical (NO_3), which reacts with ethylene, with the formation of Nitroglycol and Dinitrodiglycol;
1) $CH_2{=}CH_2{+}2NO_3^- \rightarrow CH_2(O.NO_2).CH_2(O.NO_2)$,
and 2) $2CH_2{=}CH_2{+}2NO_3^-{+}[O] \rightarrow CH_2(O.NO_2).$
$CH_2CH_2.CH_2(O.NO_2)$
$\backslash O /$

In the second reaction, the oxygen is supposed to be obtained as a result of the following side reaction; $(NO_3){+}(NO_3) \rightarrow N_2O_5{+}[O]$

After the electrolysis is completed, the cathode soln is fortified with nitric acid for reuse, while the anodic liq is neutralized with slaked lime and distd in vacuo to recover the acet. The residue contains Ca nitrate and a mixt of Nitroglycol and Dinitrodiglycol. After removal of the Ca nitrate, the mixt of expls is water washed and dried

This mixt, called "Oximite", contains up to 15.9% N, and has been proposed for use in low-freezing Dynamites as a substitute for NG
(See also under "Electrochemical Nitrations" in Vol **5** E61-L)
Refs: 1) V. Ohman, ZElecktrochem **42**, 862–72 (1936) & CA **31**, 2106 (1937) 2) Ibid, Svensk-KemiskTid **50**, 84–98 (1938) & CA **32**, 6160 (1938) 3) Davis (1943), 228–9 4) A. Pérez Ara (1945), 282

Oxland Powder. An expl patented in 1860 in Engl, prepd by substituting Na nitrate for a part of the K nitrate in BlkPdr
Ref: Daniel (1902), 593

Oxonite (Oxamite). Brit Sprengel type expl (see Vol **6**, E364-R) invented in 1883 by Punchon and Vizer. It consisted of a cotton bag (cartridge) filled with powdered Picric Acid (PA), inside of which was a glass tube filled with fuming nitric acid. This tube was broken at the moment the cartridge was introduced into a borehole, causing the acid to soak into the PA, and resulting in an expln

The compn of the ingredients varied between 46–58% PA and 54 to 42% fuming nitric acid. Davis (Ref 3) gives the formula PA 58 & nitric acid 42%. According to A. Pérez Ara (Ref 4), the Oxonite proposed by Emmens of New York contained PA 46 & nitric acid 54%. Its expl reaction was given as:
$3C_6H_2(NO_2)_3OH{+}7HNO_3 \rightarrow 16CO_2{+}2CO{+}8H_2O{+}8N_2$
Refs: 1) Daniel (1902), 594–5 2) Colver (1938), 323 3) Davis (1943), 354 4) A. Pérez Ara (1945), 227

Oxonium Compounds. An addition or double compd of an organic oxide with strong acids or their salts, as, $R_2O.HX$ (Refs 5 & 7)

Oxonium nitrates have been known since 1835 (Ref 1). They were originally described as

addition compds of aldehydes and ketones with nitric acid (Refs 1 & 2). Reddelein (Ref 4) represented the structure of the compds diagrammatically as $>C=O \ldots HONO_2$. Hofman et al (Ref 6) recently produced evidence of the oxonium structure of the additive compds, on the basis of infra-red absorption spectra as $C=O^+HNO_3^-$. The products of addition of nitric acid to ethers also possess the same oxonium structure, $>OH^+NO_3^-$

Hofmann et al (Ref 3) obtained the following compds:

diethylene glycol monoperchlorate,

$ClO_4.C_2H_4OC_2H_4OH$ (I)

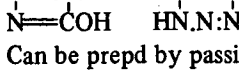
chlorohydrin monoperchlorate,

$ClO_4.CH_2.CHOH.CH_2Cl$ (II)

Compd (I) was obtained by treating ethylene oxide with 60% perchloric acid, and compd (II) by the action of 60% perchloric acid on epichlorohydrin. Both compds are oils immiscible with w, and according to these investigators, both produce an expl effect greater than NG. They are both readily hydrolyzed by w at RT, or in the presence of atm moisture

Refs: 1) J. Dumas & E. Peligot, Ann **14**, 65 (1835) 2) G.J. Mulder, Ann **34**, 165 (1840); J. Kachler, Ann **159**, 283 (1871); J. Collie & K. Tichle, JCS **75**, 710 (1899); F. Kehrmann & M. Mattison, Ber **35**, 343 (1902); J. Schmidt & K. Bauer, Ber **38**, 3758 (1905); K.H. Meyer, Ber **43**, 157 (1910) 3) K.A. Hofmann, A. Zedtwitz & H. Wagner, Ber **42**, 4390 (1909) 4) G. Reddelien, Ber **45**, 2904 (1912); Ibid **48**, 1462 (1915); JPraktChem **91**, 213 (1915); AngChem **35**, 580 (1922) 5) Karrer (1950), 126 6) W. Hofmann, L. Stephaniak & T. Urbański, JCS **1962**, 2343 7) Hackh's (1972), 482-L

5-Oxy-1,5-Azotetrazole ([5-Oxytetrazolyl-(1)]-[Tetrazolyl-(5)]-Diimide). Mw 182.12, N 76.92%



Can be prepd by passing CO_2 thru 5-diazotetrazole, but because the latter compd is very unstable, Thiele and Marais (Ref 2) preferred to start with its salts, which resulted in salts of 5-Oxy-1,5-azotetrazole:

Sodium salt. $Na_2C_2ON_{10}.5H_2O$, yel leaflets. Can be prepd by passing CO_2 thru a boiling aq soln of the Na salt of 5-diazotetrazole. Explds violently on heating

Ba salt. $BaC_2ON_{10}.4H_2O$, yel crysts, difficultly sol in w. As expl as the Na salt

Refs: 1) Beil **26**, 596 2) J. Thiele & J.T. Marais, Ann **273**, 150–55 (1893)

Oxybenzoic Acid, Nitrated Lead Salt (Lead 2,4,6-Trinitro-3-Oxybenzoate, Trinitrométa-oxybenzoate in Fr). H. Ficheroulle and A. Kovache (Ref) prepd and characterized this material

Prepn. Dissolve 2.4g of Pb nitrate in 50ml w at 90–95°, and add with stirring a concd soln of Na benzoate (prepd by neutralizing 2g of benzoic acid with 0.6g NaOH). Evaporate the mixt on a w bath to a small vol while the liq still remains clear. Cool and add 50ml of 95% ethanol. This results in a very fine, light yel ppt, which is separated by vacuum filtration. After drying at 50°, analysis gave 41.82% Pb and 3.40% water

Action of Heat. Explds when brought in contact with flame. The more moisture it contains, the more difficult it is to expld; at 20% moisture level it does not expld. When heated in a liq bath, it explds ca 238°

Compatibility. Mixts of equal amts of Pb trinitro-m-oxybenzoate with PA, TNT, RDX, PETN, K chlorate, AN or Sb_2S_3, when stored for 40 days in a dry atm at 50°, did not show any weight variation

Compatibility with Metals. Strips of metals, kept for 40 days in Pb trinitro-m-oxybenzoate contg 3.40% water, lost the following amts in g/cm^3: Cu 5, steel 10, Al 15, Sn 415, Pb 565, and Zn 965. The least corroded metals were Cu, steel and Al

Hygroscopicity. It is hygroscopic. When stored in atms of different RH levels for periods up to 40 days, it absorbed the following % of w:

% RH	10 days	20 days	30 days	40 days
70	0.44	1.62	2.98	3.30
90	0.50	2.04	3.16	3.78
100	0.84	2.74	3.88	4.88

Impact Sensitivity. Using a 2kg wt:

Height of fall in cm	40	60	80	100
% Detonations for dry product	14	48	60	78
% Detonations for product with 6% water	9	9	6	5

The sensitivity of the wet product is markedly less

than that of dry material

Solubility. In % at 18°: water 0.92, ethanol 0.14, methanol 0.31, petr eth 0.53, acet 0.15, pyridine 0.20, benz 0.06, CS_2 0.05, amyl acetate 0.04, trichloroethylene 0.03, chloroform 0.01, CCl_4 0.01, & eth – insol

Thermal Stability and Volatility. No loss of wt when stored for 300 days at 50°, 150 days at 70° or 50 days at 90°

Uses. Pb trinitro-m-oxybenzoate has not found any practical application in the expls field

Ref: H. Ficheroulle & A. Kovache, MP **31**, 9–10 & 25 (1949)

Oxycellulose and Derivatives

Oxycelluloses. Products obtained by treating cellulose with oxidizing agents, such as hypochlorite, permanganates, hydrogen peroxide, 47.5–60% nitric acid, chlorates, persulfates, ozone, chromic acid, bromine water in the presence of Ca carbonate, by the action of strong sunlight or ultra violet rays, by an electrolytic method, etc. The nature of the oxycellulose depends upon the oxidizing agents used and on the conditions of oxidation. Oxycelluloses should not be confused with the ultimate products of the oxidation of cellulose (see Vol **2**, C95-R ff). Although oxycellulose is not used in te expls industry, it would be advisable to describe it briefly, inasmuch as it is a by-product of the nitration of cellulose (see Vol **2**, C100-L ff)

The discovery of oxycellulose is generally attributed to Witz, who prepd it in 1883 in connection with an investigation of the bleaching of cotton, and who distinguished it from hydrocellulose (see Vol **7**, H213). Prior to this, Kolbe (1868) had shown that linen treated with ozone, produced a modified cellulose, and Jeanmarie (1868) had shown that cotton goods treated with dichromate soln, followed by alkaline treatment, produced a material considerably weaker in strength than the original cotton

The following formulas have been ascribed to oxycelluloses prepd by various methods:

$KMnO_4$ yields $(4C_6H_{10}O_5+C_6H_{10}O_6)$
Bromine yields $(8C_6H_{10}O_5+C_6H_{10}O_6)$
$Ca(MnO_4)_2$ yields $(3C_6H_{10}O_5+C_6H_{10}O_6)$
$KClO_3$ yields $(3C_6H_{10}O_5+C_6H_{10}O_6)$
Bleaching powder yields $(4C_6H_{10}O_5+C_6H_{10}O_6)$

Oxycelluloses differ from cellulose and hydrocellulose in properties, although there is practically no difference in external appearance among the three. The reduction of Fehling's soln has long been recognized as a characteristic of oxycellulose. According to Dorée (Ref 7, p 119), the Cu number for cellulose is 0.28, while for various oxycelluloses it varies between 5.8 and 11. The highest obtained is by the oxidation of cotton with hypochlorite, the lowest for hydrogen peroxide. Oxycellulose prepd by $KMnO_4$ gave a Cu number of 8

Another important characteristic of oxycellulose is the presence of –COOH groups, which may be detd by measuring the amt of CO_2 evolved when oxycellulose is distilled with 12% hydrochloric acid. While, according to Marsh & Wood (Ref 6) and Dorée (Ref 7), the amt of –COOH contained in oxycellulose is between 0.3 and 1.3%, cellulose yields only 0.03% and hydrocellulose 0.04%

There is also a difference in total acidity, as calcd by the ml of 0.1N NaOH required per g of material: for oxycelluloses (10.4 to 41.4), for cellulose (1.8), and for hydrocellulose (4.6) (Ref 7, p 119)

Urbański (Ref 8) states that the properties of oxycellulose depend on its method of prepn. Oxidation in a neutral or acid medium gives a product with definite reducing properties; indicating the presence of aldehyde groups. Oxidation in an alkaline medium gives a product with acidic properties, indicating the presence of carboxylic groups. An oxycellulose of this kind is distinguished from the other by its capacity of being colored by methylene blue

Nitrogen Peroxide Oxycellulose was obtained by Eastman Kodak Co (Ref 3) by the action of NO_2 gas (0.6 to 0.9p) on cellulose at 20°, or below, for 50 hours. It is claimed that oxidation of the terminal carbon took place. This oxycellulose is sol in 2% NaOH

The nitration of oxycelluloses yield products which resemble Nitrocelluloses in properties (see below)

Refs: 1) C.F. Cross, E.J. Bevan & C. Beadle, Ber **27**, 1061–65 & 1456 (1894); JCS **66**, Abs 1, 354 (1894) 2) Daniel (1902), 566 3) Marshall **1**, 154-55 (1917) 4) Stettbacher **1**, 124 (1933) 5) Eastman Kodak Co, USP 2232990 (1941) 6) Marsh & Wood, Cellulose 252–299 (1945) 7) C. Dorée, "The Methods of Cellulose Chemistry", Chapman & Hall, London (1947), 106–143 8) Urbański **2** (1965), 227

Nitroöxycellulose. $C_{18}H_{23}O_{16}(NO_2)_3$, mw 633.39, N 6.64% (theory), 6.48% (found). A white expl substance, prepd for the first time by Cross, Bevan & Beadle (Refs 2 & 3) by nitration of oxycellulose. To obtain this material, they treated the gelatinous product obtained on boiling cellulose with nitric acid, corresponding to the formula $C_{18}H_{26}O_{16}$ (Refs 1 & 3), first with concd nitric to wash it free of w. They then dissolved the anhydr oxycellulose in a mixt of equal vols of nitric and sulfuric acids. The resulting soln was poured in a thin stream into a large vol of cold w, and flakes were obtained of a substance corresponding approx, after drying at 110°, to the above formula. Cross & Bevan (Ref 1) experienced a violent expln while they were heating nitroöxycellulose in a flask, together with $FeSO_4$, as prescribed in Eder's method [Ber **13**, 169 (1880)]

According to Marshall (Ref 4), when dry, powdered oxycelluloses were nitrated with a mixed acid contg H_2SO_4 46.22, HNO_3 42.03, N_2O_4 0.25 & H_2O 11.50%, nitroöxycelluloses contg, on the average, 13% N (12.78 to 13.25) were obtained

Some of the properties of these products are briefly described on pp 156–59 of Ref 4

Refs: 1) C.F. Cross & E.J. Bevan, JCS **43**, 22 (1883) 2) C.F. Cross, E.J. Bevan & C. Beadle, BritP 9284 (1893) 3) Daniel (1902), 566 4) Marshall **1**, 155–59 (1917)

Oxydimercuriacetaldehyde (Hydroxydimercuriacetaldehyde). OHC.C(:Hg).HgOH. It is known only in the form of its salts, some of which are expl:

Chloratodimercuriacetaldehyde. OHC.C(:Hg).HgO.ClO_2, mw 525.70, colorl prisms. Can be prepd by treating an excess of mercuric oxide in an aq soln of chloric acid with an alc soln of acetaldehyde. It is an extremely sensitive expl of the initiating type, exploding even when shaken under liq (Refs 1 & 3)

Nitratodimercuriacetaldehyde. OHC.C(:Hg).HgO.NO_2, mw 504.26, N 2.78%, colorl prisms from alc. Can be prepd by adding an alc soln of acetaldehyde to an aq soln of mercuric nitrate, acidified with nitric acid. Nearly insol in w. Puffs off on heating with evolution of a yellow cloud and Hg (Refs 1, 2 & 3)

Nitritodimercuriacetaldehyde. OHC.C(:Hg).HgO.NO, mw 488.26, N 2.87%, light yel powd. Can be prepd by passing acetylene thru mercuric nitrate and an excess of K nitrite in 1% nitric acid. When dried, it puffs off, either when rubbed or heated (Refs 1 & 3)

Refs: 1) Beil **3**, 606 2) K.A. Hofmann, Ber **31**, 2213 (1898) 3) Ibid, Ber **38**, 2000–04 (1905)

1,1′-(Oxydimethylene)-bis[hexahydro-3,5-dinitro-s-triazine]. CA's name for compd described in Vol **2**, B159-L as Bis(1,3,5-triaza-3,5-dinitro-cyclohexylmethyl)-ether

Oxydine. A safety mining expl, patented by Turpin in 1888 in Fr. It was a mixt of equal parts of Dynamit No 1 (NG 75, kieselguhr 25%) and Zn oxide or sulfide

Refs: 1) E. Turpin, BritP 189428 (1888) 2) J. Cundill, MP **6**, 108 (1893) 3) Daniel (1902), 594

Oxygen Ballance. Oxygen balance (OB) is a measure of the fuel/oxygen ratio in a compound or mixt. In a *qualitative* sense OB has been successfully used in providing guidance to several practical as well as theoretical expl problems. Unfortunately OB has also been misused in attempts to obtain *quantitative* information which it is incapable of providing. Thus the main objective of this article is to point out what type of valid data OB can provide, and to critique published claims ascribing greater utility to OB than this simple concept permits

Basically OB is an index of the deficiency or excess of oxygen, in the compound or mixt, required to convert all the carbon to CO_2 and all the hydrogen to H_2O. For an expl of the generalized molecular formula of $C_aH_bN_cO_d$

$$\text{OB to } CO_2\ (\%) = \left[\frac{d - 2a - 0.5b}{\text{formula weight}}\right] 1600 \quad (1)$$

Occasionally OB to CO is reported in the literature. In this case all the carbon is taken to form CO and all the hydrogen to form H_2O. Consequently

$$\text{OB to CO}\ (\%) = \left[\frac{d - a - 0.5b}{\text{formula weight}}\right] 1600 \quad (2)$$

If the expl contains halogen atoms (X), eg $C_aH_bN_cO_dX_e$, and it is assumed that HX is formed in preference to H_2O, then

$$\text{OB to } CO_2\ (\%) = \left[\frac{d - 2a - 0.5(b-e)}{\text{formula weight}}\right] 1600 \quad (3)$$

One would certainly think that the above assumption concerning HX is valid if X = F, or even if X = Cl. However, published values of OB for halogen-containing expls (Refs 1 & 10) have been calculated via Eq 1, ie, the halogen is ignored

If the expl contains metal atoms it is generally agreed that the stable metal oxide is first formed in preference to H_2O and CO_2. OB is then calculated via Eq 1 corrected for the oxygen required to form the metal oxide

For complex expl mixts such as Dynamites it is convenient to compute OB for the individual ingredients and then calculate the OB for the mixt by algebraic addition. This method is also useful for aluminized expl mixts

In what follows OB will always refer to oxygen balance to CO_2 unless otherwise stated. For convenience the % sign will not be used although it is to be understood that all subsequent OB's are in percent

The following illustrative examples will clarify the computation of OB:

1) *OB of TNT* ($C_7H_5N_3O_6$)

From Eq 1 OB = [6 –(2x7) – (0.5x5)] 1600/227 = –74.0

2) *OB of NG* ($C_3H_5N_3O_9$)

OB = [9 – (2x3) – (0.5x5)] 1600/227 = +3.5

3) *80/20 Tritonal* (TNT/Al)

$$\text{For Al} = Al_2O_3\text{: OB} = \frac{1.5 \times 1600}{27} = -89,$$

and for TNT OB = –74

then OB (Tritonal) = 0.20(–89) + 0.80(–74) = –77.0

4) Mercuric Fulminate ($HgC_2N_2O_2$)

One oxygen atom is required to form HgO, therefore

OB = (1 – 2 x 2)1600/285 = –16.8

Table 1 lists OB for common expls and expl ingredients. Note that most expls have negative OB's

Let us now examine the type of information that OB is capable of providing:

1) *Explosion fumes.* In a qualitative sense, OB can be used to predict the fumes generated by an expl. If the OB is positive, the fumes will contain highly toxic oxides of nitrogen. For negative OB, oxides of nitrogen will be minimal but the fumes may contain a substantial amount of CO. As discussed below, relatively little CO is produced under detonation conditions by high density expls.

Table 1

Oxygen Balance of Common Explosives and Explosive Ingredients

Substance	OB (in %)
NH_4NO_3	+20.0
NH_4ClO_4	+34.0 (a)
	+27.0 (b)
$Ba(NO_3)_2$	+30.6
EGDN	0.0
$NaNO_3$	+47.0
NG	+ 3.5
TNM	+49.0
Al	–89.0
Cellulose ($C_6H_{10}O_5$) or Woodmeal	–118.5
Charcoal	–266.7
Comp B	–43
DEGDN	–40.8
DNT	–114.4
HMX	–21.6
NC (12% N)	–38.7
NC (13.5% N)	–29
NGu	–30.8
NM	–39.0
PETN	–10.0
Pentolite	–42.0
RDX	–21.6
S	–100.0
Tetryl	–47.0
TNETB	–4.2
TNT	–21.6

(a) According to Eq 3
(b) According to Eq 1

However, upon expansion of the detonation products, substantial amounts of CO are formed if the expl OB is negative. This is illustrated in Table 2 by using data from Ref 11

Comparison of the calculated and measured CO concns suggests that considerable expansion takes place even in the highly confined calorimeter samples of these measurements

For many years OB has been used to classify Dynamites into various fume categories (Ref 2). This has been extended recently (Ref 8a) to AN-fuel explosives. It is customary to consider the Dynamite wrapper as part of the expl compn in computing OB, even though it is by no means certain to what extent the wrapper takes part in

Table 2

CO Production During Detonation and Upon Expansion

Explosive	Density (g/cc)	OB (%)	CO moles/mole HE	
			Detonation*	Frozen Equilibrium at 1600°K & 1 atm
PETN	1.74	–10	1.60 (0.13)	1.50
HMX	1.80	–21.6	1.06 (~0.06)	2.54
TNT	1.53	–74	1.98 (0.28)	5.86
NM	1.13	–39.4	0.55 (0.19)	0.75

* Measured by Ornellas (Ref 9) for confined samples; bracketted terms are computed by Mader (Ref 7) and interpolated to the density shown

the detonation

2) *Detonation Product Computation: Effect of Density*

Current views (Refs 7 & 11) of detonation product equilibria in high density oxygen-deficient expls are that the available oxygen goes primarily into forming H_2O and CO_2, and any remaining unoxidized carbon atoms form solid C. These equilibria are highly pressure-sensitive and as packing density decreases (which proportionately reduces the detonation pressure), increasing amounts of CO are produced. However, if the OB is positive or slightly negative, the amount of CO will vary only mildly with change in packing density. Thus OB provides qualitative information on the variation of CO production with HE packing density

3) *Explosive "Power"*

At best, expl power is a somewhat nebulous quantity. If we consider relative power as measured in a *Ballistic Mortar* or *Trauzl Block,* then OB correlates reasonably well with relative power, *provided* these comparisons are made for *similar expls.* This is illustrated in Fig 1, where Ballistic Mortar measurements are respectively correlated with OB for nitro, nitramine, nitrate ester and aluminized expls. In general Ballistic Mortar measurements are more reproducible than Trauzl Block data. Consequently we have shown these in preference to Trauzl Block measurements. Correlation between Trauzl block data and OB are reported in Refs 1 & 8

In the past, there have been a number of attempts to ascribe quantitative significance to correlations of OB with various detonation parameters (Refs 1, 3, 5, 6 & 8). In recent years these vain attempts appear to have subsided (see note at end of Refs)

Lothrop & Handrick (Ref 1) claimed to have correlated OB with "Power and Brisance", with detonation velocity, and with heat of expln

Martin & Yallop (Ref 3) have proposed a "corrected" OB and claim quantitative correlation (to within 2%!!) of their corrected OB with detonation velocity

Glowiak (Ref 5) claims that detonation velocity, heat of combustion and Trauzl Block test all correlate with a "true" OB for 25 nitro compounds (some containing diazo or azido groups). This writer has not seen his original publication & CA does not specify intelligibly what is meant by "true" OB

Pagowski (Ref 6) proposes an "effective" OB (again undefined in CA) and claims a linear correlation of "effective" OB and detonation velocity

Mustafa & Zahran (Ref 8) prepared a series of substituted Tetryls, Pentyls, Hexyls & Nonyls. For each series they claim a correlation between the Martin & Yallop "corrected" OB, and impact or friction sensitivity, and Trauzl Block "power". Their impact and friction sensitivity data appear to be monotonic functions of corrected OB, but the relation between corrected OB and Trauzl Block data appears to be complex

Price (Ref 4) has shown convincingly that OB (garden variety, "corrected", "effective", or "true") cannot per se determine the heat of expln or detonation. Using modern values of the heat of detonation, Q, this writer has convinced himself that there is not even fortuitous correlation between OB and Q

Price also showed that detonation velocity, D, cannot be a linear function of OB, and even less

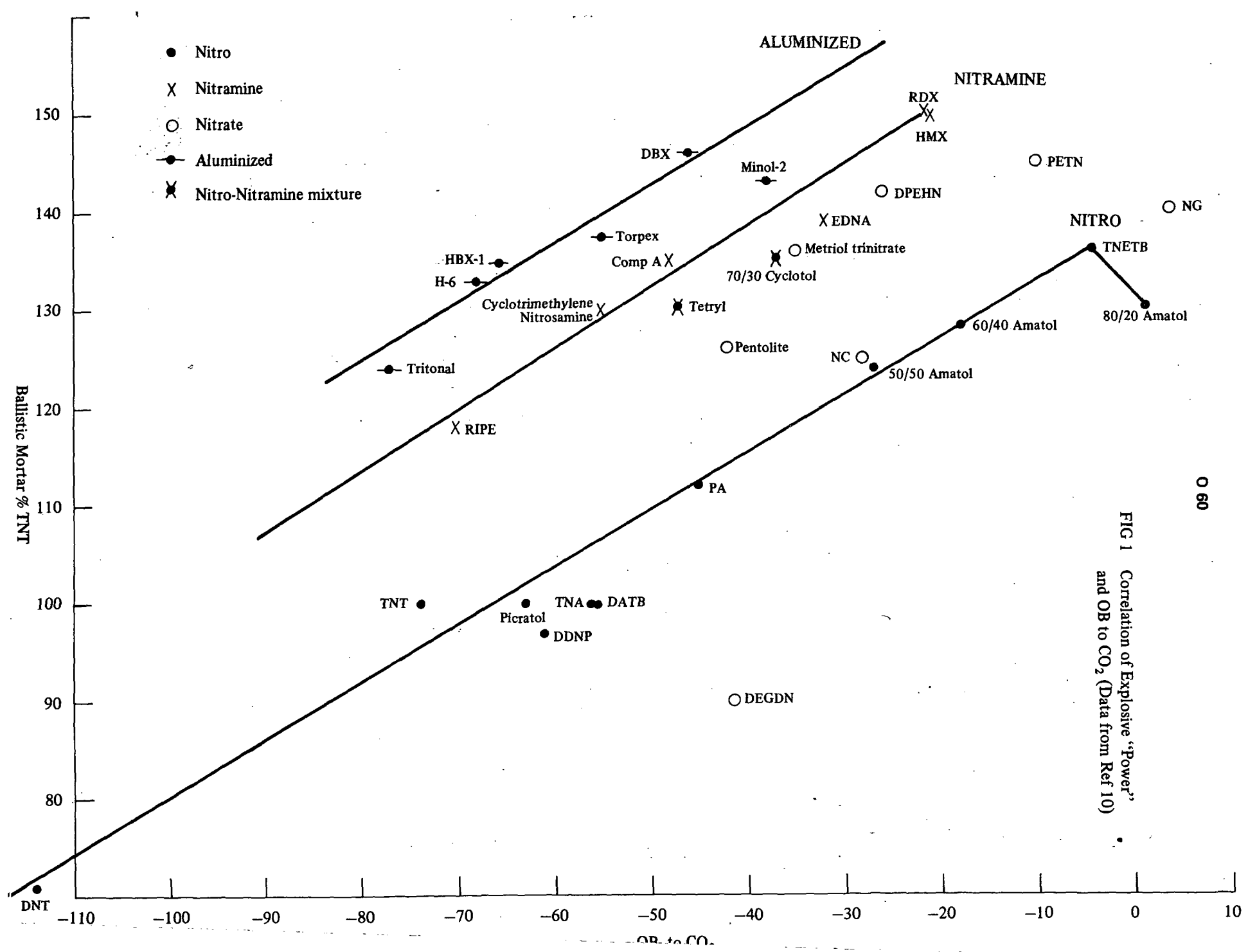


FIG 1 Correlation of Explosive "Power" and OB to CO_2 (Data from Ref 10)

Table 3

Martin & Yallop Correlation of OB and Detonation Velocity

Explosive	Density g/cc	Corrected OB*	Detonation Velocity (m/sec) Observed	Calculated**	%Error
HMX	1.90	−14.3	9100	9162	+0.7
RDX	1.80	−14.3	8750	8799	+0.6
RDX	1.00	−14.3	5980	5929	−0.9
TNT	1.64	−50.0	6950	7001	+0.7
Tetryl	1.71	−34.0	7850	7790	−0.8
HNS	1.70	−50.0	7000	7210	+3.0
NGu	1.55	−18.2	7650	7680	+0.4
NM	1.13	−21.4	6300	6195	−1.7
DATB	1.65	−38.6	7500	7430	−0.9
BTF ($C_6N_6O_6$)	1.859	−33.3	8485	8320	−1.9
PETN	1.70	−12.25 (a)	8300	8525	+2.7
DEGDN	1.38	−42.8 (a)	6760	6400	−5.3
DDNP	1.60	−58.8 (a)	6900	6570	−4.8
NC (13.45% N)	1.20	−33.3 (a)	7300	6110	−16.3
TNETB	1.76	−15.0 (a)	8290	8623	+4.0
LX-04	1.86	−19.8	8460	8830	+4.4
Comp B	1.72	−28.1	7990	8110	+1.5
Pentolite	1.66	−33.3	7465	7650	+2.5
EGDN	1.48	0	7300	8110	+11.0
EGDN	1.48	−14.3 (b)	7300	7650	+4.8
BTNEU	1.60	0	8100	8570	+5.8
BTNEU	1.60	−6.2 (b)	8100	8360	+3.2
1 mole NM/ 0.5 moles TNM	1.40	0	6780	7810	+15.0
NG	1.59	+17.5 (a)	7580	9108	+18.8
Nitromannite	1.73	+21.05 (a)	8260	9810	+20.0
TNM	1.64	+46.1	6360	10290	+61.8

* "Corrected" OB = $\Omega = (d-2a-0.56)100/n \pm 100w/n$

where n = number of atoms in the molecule

w = summation of O atoms according to their linkages, thus

w = 0 for nitro or nitramine oxygens

w = 1 for nitrate (–O–N–) oxygens

w = 1.8 for carboxyl oxygens

w = 2.0 for alcohol oxygens

± take + if first term is +

± take – if first term is –

Other symbols as defined for Eq 1

** $D_{calc} = 2509 + 3793\rho + 13.25\Omega + 12.81\rho\Omega$

where ρ = packing density of expl

(a) w term included in Ω computation

(b) w term included in Ω computation but negative sign is used for ±

likely a linear function of OB and packing density

However, as shown in Table 3 (assembled by this writer from data in Refs 7, 10 & 12 and the Martin & Yallop equation), computed and measured D's agree surprisingly well for a variety of expls having negative "corrected" OB, although agreement is not within the 2% claimed by Martin & Yallop. However, correlation between "corrected" OB and D breaks down completely (as shown in Table 3) for expls with positive OB. Also, the correlation for the nitrate esters (second grouping from top of Table 3), is not as good as for the other oxygen-deficient expls

To sum up, OB is a concept that can provide useful qualitative information. It should not be used for quantitative correlations except (and then only judiciously) for correlation between chemically similar expls

Written by **J. ROTH**

Refs: 1) W.C. Lothrop & G.R. Handrick, ChemRev **44**, 419 (1949) 2) J. Taylor, "Detonation in Condensed Explosives", Oxford Press, (1952), Chap 2 3) A.R. Martin & H.J. Yallop, TransFaradSoc **54**, 257 (1958) 4) D. Price, ChemRev **59**, 801–25 (1959) & CA **54**, 897 (1960) 5) B. Glowiak, ChemStosowana **6**, 133 (1962) & CA **57**, 3687 (1962) 6) W. Pagowski, BullAcadPolonSciShim **10**, 475 (1963) & CA **58**, 7780 (1963) 7) C.L. Mader, **LA 2900** (1963) 8) A. Mustafa & A.H. Zahran, JChemEngData **8**, 135 (1963) & CA **58**, 5444 (1963) 8a) H. Poeschl, Bergakademie **17**, 742 (1965) & CA **63**, 17784 (1965) 9) D.L. Ornellas, JPhysChem **72**, 2390 (1968) 10) Anon, "Properties of Explosives of Military Interest", EngDesHndb, **AMCP 706-177** (1971) 11) Anon, "Principles of Explosive Behavior", EngDesHndb, **AMCP 706-180** (1972), Chap 3 12) B.M. Dobratz, "Properties of Chemical Explosives & Simulants", **UCRL-51319**, Lawrence Livermore Lab, Univ of Calif (1974)

Note: CA was searched from 1964–1975 but no refs to OB were found

Oxygen Fluoride (Oxygen Difluoride, Fluorine Monoxide). OF_2, mw 54.00; colorl, unstable gas; mp −224°, bp −145°, sl sol in w and alc. It has been suggested as an oxidizer for rocket proplnts (Ref 1)

OF_2 explds on contact with w, air and reducing agents. It reacts vigorously with Al chloride, As trioxide, Cr oxide, P pentoxide, and ammonia. OF_2 and H_2S expld on mixing. Liq OF_2 and 60/80 mesh silica gel at about 254mm press and −196° expld. The presence of moisture was suspected (Ref 2)

OF_2 is more toxic than fluorine, attacking the lungs with the delayed appearance of symptoms. It is a dangerous disaster hazard; when heated to decompn it emits highly toxic fluorine fumes (Refs 3 & 4)

Refs: 1) CondChemDict (1971), 651 2) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, **491M-296**, Natl Fire Protection Assoc, Boston, Mass (1975) 3) Sax (1975), 773-L 4) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 392

Oxyliquit. There is some confusion regarding this term; it is sometimes applied to *liquid air explosives* and sometimes to *liquid oxygen explosives.* However, there is no doubt that it was applied to *liquid air explosives* prior to the appearance of commercial liquid oxygen

According to Marshall (Ref 2), "Oxyliquit" refers to an expl invented by Linde in 1895 (Ref 1) which consisted of liquid oxygen absorbed in wadding, charcoal, or other organic material

Barnett (Ref 3) calls "Oxyliquit" the "liquid air explosive"

Davis (Ref 4) states, "Liquid oxygen explosives were invented in 1895 by Linde, who developed a successful machine for the liquifaction of gases. The **'Oxyliquits'**, as he called them, prepared by impregnating cartridges of porous combustible material with liquid oxygen or liquid air . . .". Also according to Davis, "Liquid oxygen explosives were at first made from liquid air, more or less self-enriched by standing; the nitrogen (bp −195°) evaporating faster than the oxygen (bp −183°) but it was later shown that much better results followed from the use of pure liquid oxygen"

Cooke (Ref 5) defines "Oxyliquit" as a blasting expl formed by rapidly mixing liquid air, rich in oxygen, with powdered charcoal, petroleum residues, or cotton wool

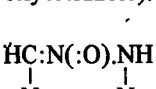
In conclusion, it may be said that, if the original term "Oxyliquit" was applied to "liquid air explosives", it might be well to leave it so, especially as "Liquid Oxygen Explosives" have been given the

convenient acronym **"LOX"**

Also see under Liquid Air and Liquid Oxygen Explosives in Vol **7**, L19-R to L26-L

Refs: 1) G. Linde, Ber **32**, 925 (1899) 2) Marshall **1** (1917), 44; **2** (1917), 572 3) Barnett (1919), 108 4) Davis (1943), 355–6 5) E.I. Cooke, "Chemical Synonyms and Trade Names", CRC Press, Cleveland (1968), 479-R

1-(or N)-Oxytetrazole (1-Oxy-isoTetrazole, Isooxytetrazole). CH_2N_4O, mw 86.01, N 65.11%, OB to CO_2 –37.20%, crysts from ethyl acetate, mp 155°, bp starts to decomp at about 160°. Easily sol in w, methanol and alc; diff sol in eth, insol in benz



It was first prepd by Palazzo by the interaction of hydrazoic acid and fulminic acid at low temp. Can also be prepd by acidifying Na oxy-iso-tetrazole with dil sulfuric acid (Refs 1, 2 & 4)

It explds on strong impact, and forms salts, some of which are expl:

Sodium salt. $NaCHON_4.3H_2O$. According to Rosati (Ref 3), this salt occurs in two cryst forms; 1) as pale-yellow crysts and 2) as colorl tablets; both belonging to the pinacoidal class of the triclinic system; mp, loses its water at 120–130° and explds at 240°. Easily sol in w, diff sol in aq alc, insol in abs alc and other org solvents

It was first prepd by Palazzo as a by-product in the prepn of 1-hydroxytetrazole from hydrazoic acid (2 mols) and Na fulminate (1 mol) (Refs 1, 2 & 4). The Na salt may serve for the prepn of free iso-oxytetrazole, as well as its salts, such as:

Mercury salt. White solid, expl. Can be prepd by treating the Na compd with a sol Hg salt

Silver salt. White solid, expl. Can be prepd by treating the Na compd with a Ag salt

Refs: 1) Beil **26**, (109) 2) F.C. Palazzo, AttiR-AccadLincei **19**, (I), 218–19 (1910); Ibid, JCS **98**, (I), 342 (1910) 3) A. Rosati, AttiRAccadLincei **21**, (II), 645–48 (1912); Ibid, JCS **104** (I), 207 (1913); Ibid, Gazzchimital **43**, (I), 72 (1913) 4) F.C. Palazzo & G. Marogna, Gasschimital **43**, (I), 75–6 (1913); Ibid, JCS **104**, (I), 300 (1913)

Ozobenzène (Fr) (Ozobenzene). $C_6H_6O_6$, white amorph product. Prepd by A. Renard by passing a current of dried ozone at a temp below 10° thru a test tube contg a few ml of pure benz (obtained from Ca benzoate), until the contents became a translucent jelly. After removing the excess benz by dry air aspiration, the solid product could be stored in a dry atm

It is decompd by moisture or on slow heating to about 50°. When heated rapidly to ca 50°, it detonates. It is extremely sensitive to friction, and sometimes detonates on removing the cork from its container. It also detonates on contact with concd sulfuric acid, concd KOH or ammonia

Ref: L. Gody, "Traité des Materières Explosifs", Namur (1907), 531

Ozocerite or Ozokerite (Mineral Wax, Fossil Wax, Native Paraffin). In purified form known as Ceresine Wax (see under Waxes). Waxlike hydrocarbon mixt, yel brown to black or green, translucent when pure and having a greasy feel. D 0.85–0.95g/cc, mp 55–110°, usually about 70°. Sol in light petr hydrocarbons, benz, turpentine, kerosene, eth, CS_2; sl sol in alc, insol in w. Combustible, non-toxic (Refs 1 & 3)

It has been used, especially in Europe, as a substitute for beeswax, carnauba wax, etc. Its use in expls dates to the sixties or seventies of the last century, when A. Nobel included ozocerites in the compn of some of his Dynamites in order to render them less hygroscopic, as well as to prevent the exudation of NG. (It should be noted that ozocerites, as well as paraffins, stearin and naphthalene, dissolve in NG even at room temp) (Ref 2)

Ozocerites have also been used as a coating for substances such as AN to render them non-hygroscopic, and as a coating for HE's such as RDX and PETN to render them less sensitive to impact

Refs: 1) Colver (1918), 34 2) Davis (1943), 333 3) CondChemDict (1971), 652

Ozone. O_3, mw 48.00, triatomic oxygen, the most reactive form of oxygen; a bluish, expl gas or blue liq. It is found in the atm in varying proportions (about 0.05ppm at sea level), since it is produced continuously in the outer layers of the atm by the action of solar UV radiation on the oxygen of the air. In the laboratory ozone is prepd by passing dry air between two plate electrodes connected to an alternating current source of several thousand volts. Machines for the production of ozone,

known as ozonizers, are marketed commercially. More generally, ozone is formed whenever oxygen is subjected to intense photochemical or electrical radiation (Ref 5)

At ordinary temps ozone is a blue gas, but at the concns at which it is normally produced the color is not noticeable unless the gas is viewed thru considerable depth. At −112°, ozone condenses to a dark-blue liq which is easily expld, as are concd ozone-oxygen mixts (above about 20% ozone), in either the liq or the vapor state. Explns may be initiated by minute amounts of catalysts or organic matter, shocks, electric sparks, sudden changes in temp or pressure, etc (Ref 4). Other properties of ozone are given in Table 1

Table 1
Properties of Pure Ozone (O_3) (From Ref 4)

Melting point, °C	−192.5 ± 0.4
Boiling point, °C	−111.9 ± 0.3
Critical temperature, °C	−12.1
Critical pressure, atm	54.6
Critical volume, cm^3/mole	111

Density and vapor pressure of liquid

temperature, °C	density, g/cm^3	vapor pressure, torr
−183	1.574	0.11
−180	1.566	0.21
−170	1.535	1.41
−160	1.504	6.73
−150	1.473	24.8
−140	1.442	74.2
−130	1.410	190
−120	1.378	427
−110	1.347	865
−100	1.316	1605

Density of solid ozone, g/cm^3, at 77.4°K	1.728
Viscosity of liquid, cP, at 77.6°K	4.17
at 90.2°K	1.56
Surface tension, dyn-cm, at 77.2°K	43.8
at 90.2°K	38.4
Parachor at 90.2°K	75.7
Dielectric constant, liquid, at 90.2°K	4.79
Dipole moment, debye	0.55
Magnetic susceptibility, cgs units, gas	0.002×10^{-6}
liquid	0.150
Heat capacity of liquid from 90 to 150°K	$C_p = 0.425 + 0.0014(T-90)$
Heat of vaporization, kcal/mole, at −111.9°C	3410
at −183°C	3650

Heat and free energy of formation

	ΔH_f, kcal/mole	ΔG_f, kcal/mole
gas at 298.15°K	34.15	38.89
liquid at 90.15°K	30.0	–
hypothetical gas at 0°K	34.74	–

Liq ozone is miscible in all proportions with $CClF_3$, CCl_2F_2, CH_4, CO, F_2, NF_3 and OF_2 liquids, and forms two-layer systems with A, CF_4, N_2 and O liquids. The limited miscibility of ozone in oxygen is of practical importance because the dense, ozone-rich layer which settles to the bottom, is easily expld. The mutual solubility of the two liqs decreases when the temp is reduced. Thus, liq ozone and oxygen are completely miscible above 93.2°K (at which temp the total pressure is 1.25 atm), but at 90.2°K (the atm-bp of liq oxygen), there is separation into two layers, containing 17.6 and 67.2 mole % ozone, respectively. At still lower temps, the separation becomes even more pronounced (Ref 4)

Uses. In terms of ordnance application, during WWII, German scientists worked overtime on an ozone-propelled rocket designed to bombard New York City from European launching platforms. However, they were unable to handle the material without spontaneous detonation (Ref 1). Later investigations into the possibility of using liq ozone or, strictly speaking, mixts of liq oxygen with liq ozone, were corried out by the Armour Research Foundation. According to Platz and Hersh (Ref 2), liq ozone or a mixt of liq ozone and oxygen may be obtained by introducing oxygen, carefully purified from organic impurities, into an ozonizer, where the mixt is irradiated and the ozone liquified (−111.9° under atm press); the oxygen escapes thru an exit pipe. If a mixt of liq ozone with oxygen is to be obtained, the gases discharged from the ozonizer are introduced into the liq oxygen after being cooled

A.G. Streng (Ref 3), in an excellent review article on the combustion and explosive properties of ozone, states, "In recent years ozone has attracted attention as a high energy chemical with a potential use in powerful propellant and explosive systems. Being an endothermic compd and a highly active oxidizer, ozone can burn and detonate by itself and in combination with various fuels. Ozone alone represents the simplest combustible and explosive system. It has often been used as a model in the theoretical interpretation of detonation and combustion phenomena, but inability to handle highly concentrated ozone in the past has prevented its experimental investigation for a long time. When combined with fuels, ozone produces systems with much higher energy content than does oxygen." Streng covers flammability or explosibility limits, burning and detonation velocities, and dangerous characteristics of gaseous, liq and solid ozone, both alone and in admixture with fuels

Toxicity and Hazards. The odor of ozone can be detected in concn as low as several parts per hundred million by vol (pphm). The threshold limit value (TLV) is 0.1ppm or 0.2mg/m^3; its toxic dose level (TDL), 50% kill concn is 2ppm (Ref 6)

Pure 100% liq ozone may be kept safely at 90°K (cooled by liq oxygen) for indefinite periods of time, but the smallest provocation, such as a spark or fast warming, even only up to bp (161°K), causes detonation. The evapn of liq ozone, for example, in the process of the prepn of pure gaseous ozone is, therefore, a dangerous procedure (Ref 3, p 224)

Liq ozone in concns greater than 30% by wt is extremely unstable, and may expld on contact with even minute traces of organic matter. Not only all precautions for handling liq oxygen, but also extra precautions for a sensitive expl must be observed (Ref 4, p 430)

Solid ozone is very expl, and at its freezing pt is very sensitive. If liq ozone in a tube is suddenly immersed to the full length of the ozone layer into solid nitrogen, detonation usually occurs. This probably is due to the fact that ozone crystals appear over the entire height of the tube, and by friction of one set of crystals against another, enough heat is developed to initiate ozone detonation. On the other hand, if only the bottom of the ozone tube is inserted into solid nitrogen, the crystallization of solid ozone proceeds slowly from the bottom toward the top and no detonation takes place (Ref 3, p 225)

Hazardous reactions reported in the literature between ozone and aniline, benz, bromine, diallyl methyl carbinol and acetic acid, diethyl ether, dinitrogen pentoxide, ethylene, hydrogen bromide, hydrogen iodide, nitric oxide, nitrogen dioxide, nitrogen trichloride, nitrogen triiodide, NG, organic liquids, organic matter, and stilbine are detailed with pertinent refs in Ref 7

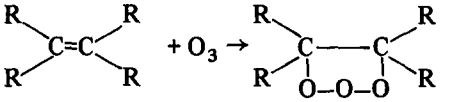
Refs: 1) Anon, Ordnance **36**, No 187 (July–Aug 51), 108–110 2) G.M. Platz & C.K. Hersh, I&EC **48**, 742 (1956) 3) A.G. Streng, Explosivst **10**, 218–25 (1960) (in English) & CA **55**, 8862 (1961) 4) Kirk & Othmer **14**, 2nd Ed (1967), 410–32 5) Merck (1968), 777-R 6) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical

Information Institute, Tokyo (1975), 393
7) Anon, "Fire Protection Guide on Hazardous Materials", **491M**, 6th Ed, National Fire Protection Assoc, Boston (1975), 297–99
8) J.S. Murphy & J.R. Orr, Eds, "Ozone Chemistry and Technology, A Review of the Literature: 1961–1974", The Franklin Institute Press, Phila, Pa (1975)

Ozone Explosives or Ozonides

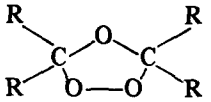
The principal organic reaction of ozone is its addition to the carbon-carbon double bond of an ethylenic compd. The resulting ozone-olefin addition compd is known as an *ozonide*. Decompn of the ozonide gives a mixt of oxygenated products containing carbonyl compds and acids. Ozone also adds to the carbon-carbon triple bond of acetylenic compds, the usual products being diketones and carboxylic acids. In polynuclear aromatic compds, the various carbon bonds and atoms have different reactivities. The reaction with ozone is more complex and the compn of products is difficult to predict

The reaction of ozone with an unsaturated organic compd was reported more than a century ago (Schönbein, JPraktChem **66**, 282 (1855)), however, complete explanation of this reaction has not been made until recent times. In 1905, Harries (Ref 1) postulated that the addition of ozone to an olefin resulted in the formation of an ozonide according to the formula:



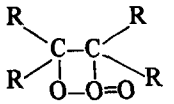
A compd of this structure should on reduction, give a glycol. However, many attempts by various investigators failed to give the expected reduction product

About twenty years later, Staudinger (Ref 2) suggested that ozonides had the following structure:



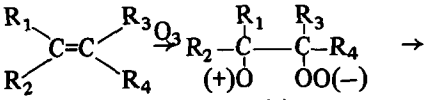
(1)

He called this compound (1) an *isozonide*. Since the carbon-carbon bond was broken, glycols would not be formed, and the decompn products would be those which had already been observed. As the primary ozone-olefin addition product, Staudinger postulated a *molozonide* to which he ascribed formula (2),

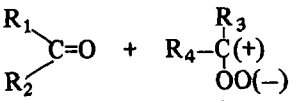


(2)

The molozonide was unstable and would either rearrange into the isozonide or form polymers. While Staudinger's theory explained the formation of the major products, some of the by-products could not be accounted for. The greatest step toward complete elucidation of the ozonolysis reaction was made by Criegee (Ref 3) in the 1950s. From a study of ozonolysis in various solvents and the constitution of the products, Criegee proposed these reactions:



(3)



(4) (5)

The primary ozone-olefin addition product splits into a molozonide zwitterion (3). The zwitterion (3) then stabilizes by splitting into a carbonyl compd (4) and another zwitterion (5). The observed ozonolysis reaction products could now be explained by the reaction of the zwitterion (5) with itself and other reactive compds present in the reaction mixt (Ref 4)

Because ozonides are active oxygen compds, they can be used as oxidizing agents, polymerization catalysts, bleaching agents, and germicides. But their instability makes it difficult to prepare them in good yields and to use them safely in reactions. Ozonides or ozonolysis products have at times expld on standing. Ozonolysis products are also thermally unstable. One must maintain the reaction at a certain temp in order to prepare and react these compds. Moreover, since the ozone addition reaction is highly exothermic, reactors must be cooled to maintain the desired temp (Ref 4)

Following below are some expl ozonides, reported primarily in the older literature

Refs: 1) C.D. Harries, Ann **343**, 311 (1905); Ibid **374**, 288 (1910); "Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen", J. Pringer, Berlin (1916) 2) H. Staudinger, Ber **58**, 1088 (1924) 3) R. Creigee,

Papers, 120th ACS Meeting, New York (Sept 1951) 4) Kirk & Othmer, 2nd Ed, **14**, 416–19 (1967)

Acetyleneozonide. $C_2H_2O_3$, has never been isolated. According to Briner et al (Ref 3), ozonization of acetylene in gaseous form resulted in explns. However, when the ozonization was conducted in an anhydr solvent by one of the methods described by Harries (Ref 2) for ozonization of unsaturated hydrocarbons, Briner was able to obtain some crystals which were unstable and exploded before they could be examined. When the solvent used in the prepn was rapidly evaporated, the residue exploded

Refs: 1) Beil, not found 2) C.D. Harries, Ann **374**, 288 (1910) 3) E. Briner & R. Wunenburger, Helv **12**, 786 (1929) & CA **23**, 5156 (1929)

Allylacetone-oxo-ozonide (Hexen-(1)-on-(5)) ozonid in Ger). $C_6H_{10}O_5$, syrup, d 1.1814g/cc. Can be prepd by treating allylacetone with ozone. It is very expl

Refs: 1) Beil **1**, 734 2) C.D. Harries & K. Langheld, Ann **343**, 348 (1905)

Amyleneozonide (Trimethylethyleneozonide). Harries et al (Ref 2) claimed to have prepd two expl products on treating trimethylethylene (C_5H_{10}) with ozone. The first corresponded to the formula $C_5H_{10}O_3$, while the second, more expl than the first, $C_5H_{10}O_4$ (amylene-oxo-ozonide). Both substances were syrups of different densities and refractive indices (values not given)

Refs: 1) Beil, not found 2) C.D. Harries & K. Haeffner, Ber **41**, 3099 (1908)

Benzene Triozonide (Ozobenzene, Benzoltriozonid in Ger). $C_6H_6O_9$ (probable structure given by Beilstein, Ref 1); white, amorph, sl volatile solid; sol in benz, insol in alc, eth, chlf, CS_2 and ligroin. Prepd by Renard (Ref 2) and Harries et al (Refs 3 & 4) by passing ozone thru pure benz (thiophene free), cooled to 5–10°

It is an extremely expl compd. It detonates violently on impact, heat or when brought into contact with warm water, concd sulfuric acid or concd K hydroxide. When treated with ice water, it is transformed into a crystalline material which explds at the slightest touch

According to A. Pérez Ara (Ref 6), it detonates when heated to as low as 50°, and Stettbacher (Ref 5) states that 1 kg develops about 2,000kg cal on expln

Refs: 1) Beil **5**, 197 2) A. Renard, CR **120**, 1177 (1895); JCS **68**, I, 593 (1895) 3) C.D. Harries & V. Weiss, Ber **37**, 3431–2 (1904) 4) C.D. Harries et al, Ann **343**, 311–74 (1905); **374**, 288–368 (1910); **390**, 235–268 (1912); **410**, 1–116 (1915) 5) Stettbacher **1**, 30–1 (1933) 6) A. Pérez Ara (1945), 465 7) Mellor **1**, 911 (1946–47) 8) R.W. Murray, AccChemRes **1**, (10), 313 (1968)

Biphenyl (or Diphenyl) Tetraozonide. $C_{12}H_{10}(O_3)_4$. It was first prepd in 1905 by Harries (Ref 1), and again in the USA during WWII, where it was found to be too unstable and too sensitive for military or commercial use as an expl

Ref: 1) C.D. Harries, Ann **343**, 337 (1905)

n-Butadienecaoutchouc Ozonide (n-Butadienerubber Ozonide, Normaler Butadienkautschuk in Ger). $(C_4H_6O_3)_x$(?). Was prepd by the oxonization of a polymer called "Normaler Butadienkautschuk" in Beilstein (Ref 1), dissolved either in chlf or CCl_4. The caoutchouc was prepd by Harries (Ref 2) by heating butadiene-1,3 (also called divinyl or erythrene) in a sealed tube for 10 days at 110–120° with acetic acid

When chlf was used as solvent in the ozonization, the resulting ozonide was an expl oil. When CCl_4 was used as solvent, the resulting product was a non-expl solid.

Several other ozonides were prepd from butadiene polymers, but it was not stated whether or not they were expl

Refs: 1) Beil **1**, (109) 2) C.D. Harries, Ann **383**, 206 (1911)

Butylene-oxo-ozonide Dimer (Dimeres Butylenoxozonid in Ger). $(C_4H_8O_4)_2$, oil, mp –80°, d 1.1604g/cc at 19/19°, RI 1.43167 at 19°. Was obtained together with other products on treating β-butylene, $CH_3.CH{:}CH.CH_3$, dissolved in methyl

chloride, with 14% ozone. Easily sol in petr eth and w. When carefully heated, it goes to monomeric butyleneozonide (see below), but expl̈ds very violently when heated to about 125° (Ref 2).

The same investigators prepd butylene-oxo-ozonide monomer, to which they assigned the formula $CH_3.CH.CH.CH_3$ (with O_4 bridging the two CH groups). This oily material was not examined for expl properties

Refs: 1) Beil **1**, (85) 2) C.D. Harries & F. Evers, Ann **390**, 245–247 (1912)

β-Butyleneozonides (Buten-(2)-ozonid, Pseudo-butylen-ozonid, or α, β-Dimethyl-äthylen-ozonid in Ger). The following compns were prepd by Harries et al (Refs 1 & 2):

Butylene Ozonide Monomer (Monomers Normales Butylenozonid in Ger). $C_4H_8O_3$, very vol oil, bp 15–16° at 20mm, d 1.0217g/cc at 22/22°, RI 1.3855 at 22°. Was prepd by Harries and then by Briner et al (Ref 3) by ozonization of β-butylene. Briner prepd it by dissolving β-butylene in methyl chloride, cooling the soln to −80°, and passing ozonized air thru it

The compd is fairly stable at room temp and is only slowly decompd by cold w. It reacts with hot w (70–75°), yielding CH_3COOH, HCOOH and CH_4. It is sol in org solvents; explds violently when heated under confinement to about 125°; burns quickly when unconfined and touches with a flame or hot object

Butylene Ozonide Dimer (Dimers Normales Butylenozonid in Ger). $(C_4H_8O_3)_2$, thick syrup, sol in org solvents. Was obtained, together with the monomer, by treating β-butylene with 8–10% ozone; could not be distilled. Expld on heating in a tube to about 125°

Briner and Meier (Ref 3) prepd ozonides of all three butylenes (α, β and iso) by ozonization in the dil gaseous phase, both in the presence and absence of w. The same compds were obtained by ozonization at low temps of butylenes, dissolved in non-aqueous solvents. The resulting ozonides, only sl sol in w, were very expl

Refs: 1) Beil **1**, (85) 2) C.D. Harries & F. Evers, Ann **390**, 241–44 (1912) 3) E. Briner & R. Meier, Helv **12**, 529–53 (1929) & CA **23**, 5155 (1929)

Iso-Crotonicacidozonide (Isocrotonsäure-ozonid in Ger). $C_4H_6O_6$, clear syrup, decompd by w or on standing; extremely expl. Was prepd by the action of ozone on a chloroformic soln of iso-crotonic acid, $CH_3.CH:CH.COOH$

Note: Crotonic acidozonide was prepd by Briner and Franck (Ref 3)

Refs: 1) Beil **2**, 414 2) C.D. Harries & K. Langheld, Ann **343**, 351 (1905) 3) E. Briner & D. Franck, Helv **22**, 587–9 (1939)

Cyclohexene-oxo-ozonide Polymer (Polymeres Cyclohexen-oxo-ozonid in Ger). $(C_6H_{10}O_4)_x$, amorph substance, mp 115–120° decompn, insol in org solvents. Was prepd, together with polymeric cyclohexeneozonide (see below), by passing ozone thru a soln of cyclohexene in chlf or CCl_4 (Ref 3). Although its expl properties were not examined, it might be presumed that, inasmuch as the polymeric ozonide $(C_6H_{10}O_3)_x$ is a strong expl (see below), the compd $(C_6H_{10}O_4)_x$, with with one additional oxygen per each six carbons, should be even a stronger expl

Cyclohexene-oxo-ozonide Dimer (Dimeres Cyclohexen-oxo-ozonid in Ger). $(C_6H_{10}O_4)_2$, solid, mp 115–120°. Obtained in small quantities by passing strong ozone thru a chlf soln of cyclohexene. Its expl properties were not examined

Refs: 1) Beil **5**, (32) 2) C.D. Harries & H. von Splawa Neymann, Ber **41**, 3555 (1908) 3) C.D. Harries & H. Wagner, Ann **410**, 35 (1915)

Cyclohexene Ozonides:

Monomeric Cyclohexeneozonide. $C_6H_{10}O_3$, bp 59-60° at 12mm, difficultly sol in cold w, easier in hot w (with decompn). Was prepd by Harries & Seitz (Ref 2), together with polymeric forms, by treating cyclohexene dissolved in hexane with ozone

Polymeric Cyclohexeneozonide. $(C_6H_{10}O_3)_x$, solid compd, mp 60–65°; sol in boiling alc, insol in eth & chlf; explds violently on heating to 140–150°. Can be prepd, together with the monomer (see above) and the polymer (see below) by passing ozone thru cyclohexene dissolved in cooled hexane, chlf or CCl_4

Polymeric Cyclohexeneozonide. $(C_6H_{10}O_4)_x$, amorph substance, mp 115–120° (with decompn), insol in org solvents, explds on heating. Can be

prepd, together with the two ozonides above, by passing ozone thru cyclohexene dissolved in cooled chlf or CCl_4

Some cyclohexeneozonides were prepd and studied in the USA during WWII, but were found to be too unstable and insufficiently powerful to be used as expls (Ref 6)

Refs: 1) Beil **5**, (32) 2) C.D. Harries et al, Ann **343**, 311–74 (1905); Ibid **374**, 288–368 (1910); Ibid **390**, 235–68 (1912); & Ibid **410**, 1–116 (1915) 3) C.D. Harries & H. Neresheimer, Ber **39**, 2848 (1906) 4) C.D. Harries, Ber **45**, 941 (1912) 5) C.D. Harries & H. Wagner, Ann **410**, 24–28 & 35 (1915) 6) Blatt, OSRD **2014** (1944)

Cyclopentene-oxo-ozonides. A **monomer**, $C_5H_8O_3$, was prepd (Ref 2) by the ozonization of cyclopentene dissolved in CCl_4. It is a yel, volatile liq with a penetrating odor; sol in chlf, ethyl acetate and acetic acid; is decompd explosively by concd sulfuric acid; explds on heating

The **polymer**, $(C_5H_8O_4)_x$, was prepd (together with some monomer) on passing ozone thru a chloroformic soln of cyclopentene. It is a cryst compd, insol in org solvents; reacts violently with concd sulfuric acid; a powerful expl

Refs: 1) Beil **5**, (30) 2) C.D. Harries & H. Wagner, Ann **410**, 31–5 (1915)

Cyclopentene Ozonides. The **monomer**, $C_5H_8O_3$, was prepd by passing a small quantity of ozone thru cyclopentane dissolved in hexane cooled with an ice-salt mixt (Ref 2). A liq, bp 60–62° at 10mm, it sometimes expld on distillation

The same investigators obtained the **polymer**, $(C_5H_8O_3)_x$, by treating cyclopentane dissolved in ethyl chloride, with ozone. A cryst compd, insol in most org solvents, it expld at 94°

Refs: 1) Beil **5**, (30) 2) C.D. Harries & H. Wagner, Ann **410**, 29–31 (1915)

Cyclopentadieneozonide (Polydicypentadiene diozonide, Polycyclopentadieneozonid in Ger). $(C_5H_6O_3)_x$ or $(C_{10}H_{12}O_6)_x$; amorph powd, mp 120–125° (starts to sinter at 114°). The polymeric ozonide is insol in common org solvents, dissolves in boiling AcOH with decompn, is decompd by boiling w. It is very expl

Was prepd by Staudinger & Bruson (Ref 2) by saturating a CCl_4 soln of dicyclopentadiene, $C_{10}H_{12}$, with 5% ozone

Refs: 1) Beil **1**, 459, (238) & [391]; Ibid **5**, [78] 2) H. Staudinger & H.A. Bruson, Ber **58**, 1095 (1925)

Diallyldiozonide (1,5-Hexadienediozonide, Hexadien-1,5-diozonid in Ger). $C_6H_{10}O_6$, syrupy, explds strongly on heating. Was prepd by Harries & Turk by treating a cooled chloroformic soln of diallyl, $CH_2:CH.CH_2.CH_2.CH:CH_2$, with ozone (Ref 2)

Refs: 1) Beil **1**, 254 2) C.D. Harries & H. Turk, Ann **343**, 360 (1905)

Iso-Dicyclopentadienediozonide (Isocyclopentadienediozonid in Ger). $C_{10}H_{12}O_6$, white hygr powder, mp 95–98° (explds on heating above mp), decomps in humid air. It is easily sol in acet & pyridine, sol in acetic acid; sl sol in ethyl acetate, benz, CCl_4 and CS_2; insol in eth & petr eth

Was prepd by passing 5% ozone thru an ethyl acetate soln of dicyclopentadiene, $C_{10}H_{12}$ (Beil **5**, 495, (238) & [391]), for 20 hours

Refs: 1) Beil **5**, [391] 2) H. Staudinger & H.A. Bruson, Ber **58**, 1094 (1925)

Iso-Dicyclopentadiene-oxo-diozonide. $C_{10}H_{12}O_7$; white, hygr solid; mp 105–108° (explds on heating above mp); solubility similar to above compd

Was prepd by passing 5% ozone for 48 hrs thru dicyclopentadiene dissolved in ethyl acetate

Refs: 1) Beil **5**, [392] 2) H. Staudinger & H.A. Bruson, Ber **58**, 1095 (1925)

2,5-Dimethylhexadiene-1,5-diozonide. $C_8H_{14}O_6$, thick yel syrup, decomps on standing, explds violently on heating. Prepd from 2,5-dimethylhexadiene-(1,5) and ozone

Refs: 1) Beil **1**, 259 2) C.D. Harries & H. Turk, Ann **343**, 367 (1905)

Diphenyltetraozonide. $C_{12}H_{10}O_{12}$; colorl, very volatile crysts; explds violently on heating. Prepd by treating a chloroformic soln of diphenyl with ozone

Refs: 1) Beil **5**, 579 & [482] 2) C.D. Harries

& V. Weiss, Ann **343**, 374 (1905) 3) V.I. Vaidyanathan, IndianJPhys **2**, 427–28 (1928); Ibid, ChZtr **1928**, II, 1895 & CA **22**, 4349 (1928)

Ethylene Ozonide. $C_2H_4O_3$; colorl, unpleasant-smelling oil; mp, becomes lustrous at –80°; bp, 18° at 16mm, 20° at 17mm; d 1.265g/cc at 17.5/17.5°. Was first prepd by Harries & Koetschau (Ref 2) by passing ozonized (7%) air thru a soln of ethylene in methyl chloride, cooled to –70°

Ethylene ozonide explds violently on heating, impact or friction, or when poured into concd caustic soln (Ref 3)

Refs: 1) Beil **1**, 184–5 2) C.D. Harries & R. Koetschau, Ber **42**, 3305–11 (1909) 3) E. Briner & E. Schnorf, Helv **12**, 151 & 181 (1929) & CA **23**, 2149 (1929) 4) A. Rieche, "Alkylperoxide und Ozonid", Steinkopf, Dresden (1931), 80 (Reproduced by Edwards Bros, Ann Arbor, Mich) 5) A. Rieche & R. Meister, Ber **66**, 718 (1933)

Ethylozonide (Called Ethylperoxide by Berthelot). Berthelot obtained a fruity-smelling liq by passing ozone, in an atm of CO_2, thru well-cooled (ice-salt mixt) absolute ether. After removing the ether by vac, the residue was distilled at 20mm, and a fraction at 40–50° was collected. It was a colorl mass, which gave colorl crysts on strong cooling (Ref 1)

According to Berthelot, the formula of this compd is $(C_2H_5)_4O_3$, which requires C=58.54%, H = 12.19% and O = 29.27%. The substance expld during the last stages of the work

Harries and Weiss (Ref 2) repeated Berthelot's expt, but obtained a product of lower C and H content (C = 15.3 to 25.6%; H = 6.5 to 7.1%), and higher O content (O = 67.9 to 77.7%). The material expld when heated on a Pt foil

Refs: 1) M. Berthelot, CR **92**, 895 (1881) 2) C.D. Harries & V. Weiss, Ann **343**, 375 (1905)

Iso-Eugenolozonide. $C_{10}H_{12}O_5$, yel oil from ethyl acetate & petr ether. Can be prepd by passing 1% ozone thru isoeugenol dissolved in hexane. This gave a ppt of heavy syrup, which was a weak expl, insol in ethyl acetate, hexane or petr ether. After evapg the hexane at 20° and reduced pressure, a small quantity of highly expl yellow oil was obtained. It was not further examined

Refs: 1) Beil **6**, (470) 2) C.D. Harries & R. Haarman, Ber **48**, 36 (1915)

Fumaric Acid Ozonide. $C_4H_4O_7$, a very expl compd, prepd by treating a soln of fumaric acid in methanol, cooled to –60°, with ozone

Ref: E. Briner & D. Franck, Helv **21**, 1297–1313 (1938) & CA **33**, 535 (1939)

α-Hexylene Ozonide (Hexen-(1)-ozonid in Ger). $C_6H_{12}O_3$, colorl oil, bp 60° at 12mm, d 0.9709 g/cc at 18/18°, RI 1.4059 at 18°. This product was isolated by Harries et al from an oil having a compn between $C_6H_{12}O_3$ and $C_6H_{12}O_4$. The oil was prepd by ozonization of a chlorethylic or hexanic soln of α-hexylene, $CH_3(CH_2)_3.CH{:}CH_2$. The ozonide $C_6H_{12}O_3$ was sol in common org solvents with the exception of petr ether, in which it was difficultly sol; it was also difficultly sol in w. It is an expl compd

Another substance isolated from the crude oil was also an expl; bp ca 60° at 12mm, d 0.9938g/cc at 22.5/22.5°, RI 1.3947 at 22.5°. It probably was hexylene-oxo-ozonide, $C_6H_{12}O_4$

Refs: 1) Beil **1**, (90) 2) C.D. Harries & K. Haeffner, Ann **374**, 331–35 (1910)

Isoprene Rubber Ozonides (Isoprenkautschuk-ozonid or Künstlicher Isoprenkautschuk Diozonid in Ger). $(C_5H_8O_3)_X$, several products correspond-to this formula are known:

Normal-Isoprene Rubber Ozonide (Ozonid des Normaler Isoprenkautschuk in Ger). A very thick oil, sol in hot w; puffs off violently on heating. Prepd by Harries et al by passing 12% ozone thru a chlf or CCl_4 soln of n-isoprene rubber for several hours

α-Isoprene Rubber Ozonide (Ozonid des Natrium-isoprenkautschuk in Ger). A thick, colorl oil from ethyl acetate & petr eth. It is a more powerful expl than the above compd. Prepd by passing 6–7% ozone thru a chloroformic soln of α-isoprene rubber

Refs: 1) Beil **1**, (116) 2) C.D. Harries, Ann **383**, 201–6 (1911) 3) C.D. Harries & M. Hagedorn, Ann **395**, 234–42 (1913) 4) C.D. Harries, Ann **406**, 178–81 (1914)

D-Limonenediozonide Polymer (Diozonid des d-Limonens in Ger). $(C_{10}H_{16}O_6)_x$, white, solid, mp 60–65°, explds on heating to about 85°. Sol in w, alc, eth, benz; v sol in chlf, ethyl acetate and AcOH. Prepd by ozonization of d-limonene, $C_{10}H_{16}$, dissolved in chlf or CCl_4
Note: Limonenediozonide was first described by H. Neresheimer, Dissertation, Kiel (1907)
Refs: 1) Beil **5**, (71) 2) C.D. Harries & H. Adam, Ber **49**, 1035 (1916)

Mesityloxideozonide. $C_6H_{10}O_4$, liq, d 1.0754 g/cc at 18.5/18.5°, RI 1.3941, sol in most org solvents except petr ether. Prepd by passing dil ozone (12–14% concn) and CO_2 thru well cooled mesityleneoxide. Decomps on heating, but is fairly stable at room temp
Refs: 1) Beil **1**, (383) 2) C.D. Harries & H. Turk, Ber **38**, 1631 (1905) 3) Ibid, Ann **374**, 340 (1910)

Mesityloxideperozonide. $C_6H_{10}O_5$, green syrup, highly expl, catches fire spontaneously on standing at room temp. Prepd by saturating mesityloxide with ozone at very low temp
Refs: 1) Beil **1**, 738 & **7**, 953 2) C.D. Harries et al, Ber **36**, 1933 (1903) 3) Ibid, **38**, 1631 (1905)

Methyleugenolozonides. Mono- and triozonides are known:
Monozonid des Eugenolmethyläther. $C_{11}H_{14}O_2(O_3)$, a thick syrup which puffed off on heating. Prepd by Majima (Ref 2) by passing 6% ozone thru a cooled chloroformic soln of methyleugenol
Triozonid des Eugenolmethyläther. $C_{11}H_{14}O_2(O_3)_3$, a semi-solid, very expl compd. Prepd by Majima (Ref 2), and then by Harries & Haarmann (Ref 3) by passing 15% ozone thru a cooled chloroformic soln of methyleugenol
Refs: 1) Beil **6**, 963 2) R. Majima, Ber **42**, 3668 (1909) 3) C.D. Harries & R. Haarmann, Ber **48**, 40 (1915)

Naphthalene Diozonide. $C_{10}H_8(O_3)_2$, white crysts, very expl. It was first prepd by Harries & Weiss (Ref 2), and again during WWII in the USA. It was found to be too sensitive and unstable to be used as an expl
Refs: 1) Beil **5**, 540 & [444] 2) C.D. Harries & V. Weiss, Ann **343**, 372 (1905) 3) V.I. Vaidyanathan, IndianJPhys **2**, 427 (1928); Ibid, ChZtr **1928**, II, 1757 & CA **22**, 4349 (1928)

Phenanthrene Diozonide. $C_{14}H_{10}(O_3)_2$, colorl crysts, very expl. Prepd by passing ozone thru a cooled chloroformic phenanthrene soln
Refs: 1) Beil **5**, 670 & [583] 2) C.D. Harries & V. Weiss, Ann **343**, 373 (1905) 3) V.I. Vaidyanathan, IndianJPhys **2**, 427 (1928); Ibid, ChZtr **1928**, II, 1985 & CA **22**, 4349 (1928)

Phoronediozonide (Sym-Diisopropylideneacetone-ozonide). $C_9H_{14}O_7$, light green syrup, very expl, self-flammable on standing in air. Was prepd by Harries & Turk by passing ozone thru a well cooled chloroformic soln of phorone [2,4-dimethyl-heptadien-(2,5)-on-(4)], $(CH_3)_2C{:}CH.CO.CH{:}C(CH_3)_2$, followed by vacuum removal of chlf at 20°
Refs: 1) Beil **1**, 753 & (390) 2) C.D. Harries & H. Turk, Ber **38**, 1634 (1905); Ibid, Ann **374**, 349 (1910)

Pineneozonide and Pineneoxoozonide. A compn corresponding to something between $C_{10}H_{16}O_3$ and $C_{10}H_{16}O_4$ was obtained by Harries & Neresheimer (Ref 2) on treating right-rotary turpentine with weak ozone. It could be sepd into thick oily (80–90% of the total) and solid fractions. The mixt was insol in common org solvents, and puffed off when heated on a spatula

The oily fraction was supposedly the ozonide, $C_{10}H_{16}O_3$; bp 50° at 15mm; d 1.31g/cc at 20/4°; sol in org solvents except hexane; explds on heating
Refs: 1) Beil **5**, 152 & (79) 2) C.D. Harries & H. Neresheimer, Ber **41**, 38 (1908)

Polydihydrodicyclopentadiene Ozonide. $(C_{10}H_{14}O_3)_x$, white solid, mp 125–130°, explds on heating. Sol in benz, CCl_4, CS_2; insol in eth and petr ether; decompd by w. Obtained by passing 5% ozone thru dihydrodicyclopentadiene (Beil **5**, [330])
Refs: 1) Beil **5**, 331 2) H. Staudinger & H.A. Bruson, Ber **58**, 1095 (1925)

Propylene-oxo-ozonide ($C_3H_6O_4$) and **Propylene Ozonide** ($C_3H_6O_3$). An expl oil, having a compn somewhat between these two compds, was prepd by Harries & Haeffner (Ref 2) by passing ozone thru an ethyl chloride soln of propylene, cooled in a mixt of solid CO_2–ether. This oil was very expl and possessed the following properties; d 1.1541g/cc at 22/22°; RI 1.4034 at 22°

When this oil was distilled in vac (18mm), the fraction collected between 28° and 34° corresponded almost exactly to the **oxo-ozonide**, $C_3H_6O_4$; d 1.070g/cc at 22/22°; RI 1.3798 at 22°. It expld on heating with great violence. The residue of the distillation was also an expl, and it was assumed to be the **ozonide**, $C_3H_6O_3$. It was not analyzed by Harries et al

According to Briner & Schnorf (Ref 3), propylene ozonide can be prepd by passing ozone thru a soln of propylene in hexane, cooled to –80°. Briner & Meier (Ref 4) prepd an expl compd by treating propylene in a dil gaseous phase with ozone, either in the presence or absence of H_2O, or in a non-aq solvent, as previously used by Harries et al

Refs: 1) Beil **1**, (82) 2) C.D. Harries & K. Haeffner, Ann **374**, 335–38 (1910) 3) E. Briner & P. Schnorf, Helv **12**, 154 & 181 (1929) & CA **23**, 2149 (1929) 4) E. Briner & R. Meier, Helv **12**, 529–53 (1929) & CA **23**, 5155 (1929)

α-Terpineol Ozonide. $C_{10}H_{18}O_4$, solid; sol in ether, benz and hexane; insol in petr ether. Was first prepd by Harries (Ref 1), and then by Briner et al (Ref 2) by passing ozonized air thru a soln of α-terpineol in hexane

This compd is one of the most stable among the ozonides. Its Q_c is about 1500cal/g, and the calcd Q_f is about 90cal/g. It is only a mild expl

In addition to α-terpineol ozonide, Briner et al prepd and investigated other ozonides. Their conclusion was, that, although some of the ozonides are powerful expls, there is absolutely no advantage in employing them as commercial or military expls, because of their extreme sensitivity to impact and poor storage stability

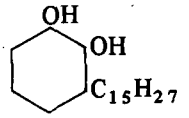
Refs: 1) Beil **6**, (41) 2) E. Briner, M. Mottier & H. Paillard, Helv **13**, 1030–5 (1930) & CA **25**, 2137 (1931)

Toluene Ozonide. Colorl crysts or glutinous mass; stable at 0° but decompd at 8°; extremely expl. First prepd in 1891 by Dieckhoff

Ref: C.D. Harries et al, Ann **343**, 314 (1905)

Urushioldimethyletherozonides

Urushiol is the liq secretion of Rhus vernicifera used in Japan lacquer. It contains an unbranched, unsaturated side chain in the ortho position to the hydroxyl of pyrocatechol (Ref 3)



Urushioldimethyletherdiozonide (Diozonid des Urushiol-dimethyläthers in Ger). $C_{22}H_{34}O_2(O_3)_2$, oily liq; explds on heating or by flame, but not as strongly as the tri- or tetraozonides, described below. Prepd by Majima (Ref 2) by passing 6% ozone thru a chloroform soln of dimethylurushiol, cooled in ice, for 6 hours

Urushioldimethylethertriozonide (Triozonid des Urushiol-dimethyläthers in Ger). $C_{22}H_{34}O_2(O_3)_3$, light-yel oily liq, explds on heating or on exposure to flame. Prepd by Majima (Ref 2) by passing 6% ozone thru a chloroform soln of dimethylurushiol, ice cooled, for 16 hours

Urushioldimethylethertetraozonide (Tetra-ozonide des Urushiol-dimethyläthers in Ger). $C_{22}H_{34}O_2(O_3)_4$, yel, semi-solid substance; explds violently when heated to about 60°, or when touched by a flame. Prepd by Majima (Ref 2) by passing 15% ozone thru a chloroform soln of dimethylurushiol, cooled in ice, for 10 hours, After removal of the chlf in vac, the residue was dissolved in ether and pptd by hexane

Refs: 1) Beil – not found 2) R. Majima, Ber **42**, 3667–72 (1909) 3) P. Karrer, "Organic Chemistry", Elsevier, Amsterdam (1950), 436

Ortho-Xylene Ozonide. $C_8H_{10}O_6$ (probable structural formulae are shown in Ref 2), colorl crysts. Was prepd by passing 15% ozone thru a soln of o-xylene in acetic anhydr-ether, cooled to about

–25°. On pouring the resulting yellowish soln into ice-w, a ppt of the ozonide was obtained which proved to be very expl

The ozonide can also be obtained using petr ether as the solvent for o-xylene. In this case, the ozonide ppt separates during ozonization, because it is insol in petr ether. An expln can occur during removal of the ppt from the ether. For this reason, Levine & Cole (Ref 2) considered it more convenient to use acetic anhydr as solvent for o-xylene

Refs: 1) Beil – not found 2) A.A. Levine & A.G. Cole, JACS **54**, 338–41 (1932)

P

"P" (Explosifs de mine). Older Fr mining expls which were also used for military purposes. Typical of these were No 1: AN 80, Guncotton 20%; No 2: AN 90.5, Guncotton 9.5%
Ref: Daniel (1902), 595

"P" (Explosives). Brit permitted expls categorized as P1, P2, P3, P4 and P5. See under Permissible and Permitted Explosives in this Vol
Ref: S. Fordham, "High Explosives and Propellants", Pergamon Press, NY (1966), 90–96

"P" (Pebble Powder). Blk Pdr in the form of cubes, used by the Brit Army until 1876, and later replaced by EXE Powder (see Vol **6**, E348-R)
Refs: 1) Daniel (1902), 595 2) Marshall **1**, 29 (1917)

P-2. Designation for 50/50 cast Pentolite charge
Ref: Cook (1958), 251-L

PA. Abbreviation for Picric Acid

"P.A." Explosives. A variety of expl blends, patented by the firm of Bombrini-Parodi-Delfino of Rome, consisting of PETN desensitized with pentaerythritol acetate. These expls can be cast below 100°, are less sensitive to shock than PETN, but more sensitive than TNT. Although they are less powerful and brisant than PETN, they are more so than TNT. Their stability is less than that of TNT. Their advantage in comparison with RDX formulations lies in the uniformity of the blend
Ref: Vivas, Feigenspan and Ladreda **2** (1946), 288–9

"P.A." (Poudre). Prismatic BlkPdr used by the Fr at the end of the last century
Ref: Daniel (1902), 595

Packaging of Ammunition and Explosives

The term *Packaging* can be defined in a military sense as including preservation, packaging, packing, marking (see in this Vol, M18-L), and omni-transport loading of ammo and expls (Refs 4–7, 24–26, 29a, 29b and 31–33). A non-military definition also includes minimum overall costs plus the concept of product advertising as being included in the marking of the packages (Refs 8 and 18). Under either aegis (military or civilian), packaging must satisfy five divergent sets of requirements as stated in developed guide lines covered in the indicated references and articulated by the appropriate Mil Specs. These requirements represent a compromise between the goals of the manufacturer, who would like to minimize overall costs and increase efficiency by using packaging machinery wherever possible; the ammo design engineer, who would like ease of use of the item ("ready-for-use in the package" concept), and the relative advantages of either environmentally degradable or reusable containers; the transportation specialist, who would like a rugged, shock and vibration resistant package of convenient size and minimum wt which can be palletized and handled by fork lift truck; the safety engineer, who would like not only an omni-shock, fire and vibration resistant package, but one that can be ventilated and conveniently undergo surveillance for deterioration in storage; and the user, who would like a package with easy access requiring only simple hand tools, of limited wt, sabotage-proof, tamper-proof, theft-proof, with a 10-yr storage life under adverse environmental and weather conditions over temp ranges of from –80°F to 160°F, easily identifiable contents, and being amenable to camouflage (Mil) and accurate record keeping (Refs 4, 6, 15–18, 29 and 36)

In order to comply with all of the objectives which have been stated above, plus international, Federal, state and local regulations, a concerted effort has been made to evolve new packaging materials, new packaging techniques, and to develop new containers (Refs 1–4, 8–10, 12, 14–23, 25–30 and 32). [See also "Loading and Fabrication of Explosives" in Vol **7**, L46-L to L57-L]. These efforts have resulted in an applied packaging technology outlined below for selected ammo end items and expls:

Ammunition For Artillery usually consists of a complete round packaged in strong wooden, especially designed plastic or metal containers (Refs 29a, 29b, 33 and 34)
Ammunition For Small Arms (Mil) is packaged in strong wooden or metal containers. Within these containers it may be loose, in bandoleers, in magazines (clips), or in belts of 200 rounds. The gross wt of the outside containers must not exceed 175 lbs (Refs 17, 33 and 34). Civilian purpose small arms ammo is usually packaged in polyethylene or polyurethane foam cushioned cardboard boxes of from 20 to 50 rounds. A number of these boxes are then over-packaged in a larger cardboard box. The content of the larger box varies with the type of ammo packaged, ie, 50 boxes of rifle ammo, 25 boxes of shotgun ammo, and 2000 rounds of pistol ammo (subdivided in boxes of from 20-50 rounds depending on the round caliber). The popularity of .22 cal ammo is such that transparent plastic containers are used with individual cavities for 100 rounds per box (Ref: Interviews with the store managers of both "Dover Sport", Dover, NJ and "Lester Edelman's" of Wayne, NJ on June 14, 1976)
Explosive Bombs, Mines, Projectiles, Torpedoes or Grenades. If the item exceeds 90 lbs in wt and 4.5 inch diam it may be securely fastened to a pallet. Other items are secured in strong wooden or metal boxes (Refs 33 and 34)
Fireworks (Pyrots). These devices are usually packaged in fiber boxes or drums of not over 65 lbs gross wt. If wooden boxes are used gross wt is not to exceed 150 lbs. For many types of individual items "tin" cans, fiberboard boxes, or self-contained special prepacking is used. Packaging is usually limited to 150 boxes per over-box (Refs 33 and 34)
Fuzes and Tracers are individually wrapped in pasteboard or plastic tubing. No more than 50 of these individual packets are to be in the next outer, usually pasteboard, carton. Special provisions are made for securing individual packages of fuzes or tracers against movement. The over-package container is a strong, tight wooden or fiberboard box. Gross wt of a wooden or triple wall fiberboard box is not to exceed 150 lbs, and of a fiberboard box, 65 lbs (Refs 30, 33 and 34)
High Explosive Gels (up to 30% liq expl) are contained in cartridge casings or shells of polyethylene-paper; a small number being placed in grease-proof paper bags. These bags are contained in wooden boxes with liq expl absorbtive sawdust or cellulose sheet linings (Refs 33 and 34)
High Explosive Liquids. Strong metal containers of 10 quart capacity are used with wooden box overpacking (Refs 33 and 34)
Solid High Explosives such as TNT or Pentolite are packaged in fiber drums (200 lbs gross wt), or in wooden boxes over strong paper or cloth bags (100 lbs gross wt) (Refs 33 and 34)
Initiating High Explosives such as LA or LSt are packaged with 20 to 40% w or an antifreeze mixt of ethanol/w in a 4 oz duck bag, which is then overwrapped with a strong grain bag. The outer container is a metal barrel or drum. The dry wt of the expl is not to exceed 150 lbs (Refs 33 and 34)
Nuclear Weapon Major Assemblies are packaged for shipment in accordance with the applicable service technical manuals; viz, Army-TM's (Technical Manuals) (Ref 35), Navy-SWOP's (Special Weapons Operational Procedures), and Air Force-TO's (Technical Orders), etc.
Liquid Propellants can be packaged in 12 gallon polyethylene drums inside of strong, tight metal drums (Refs 33 and 34)
Solid Propellants are packaged, for example, in tight metal drums, gross wt not to exceed 200 lbs (Refs 33 and 34)
Rocket Ammunition with Explosively Loaded Projectiles are packaged, for example, in specially designed preformed fiberglas resin impregnated or Al containers (Refs 33 and 34)

Written by **H. L. HERMAN**

Refs: 1) Anon, "Rules For Handling, Storing, Delivering, and Shipping Explosives", Inst of Makers of Expls, **Pamphlet No 5**, NY (1939) 2) Anon, "Regulations Governing Transportation of Military Explosives on Board Vessels During Present Emergency", **NAVCG 108**, Wash, DC (1945) 3) Anon, "Explosives or Other Dangerous Articles on Board Vessels", **USCG 187**, US Govt Printing Off, Wash, DC (1950) 4) Anon, "Packing and Packaging of Ammunition and Related Material at Picatinny Arsenal 1946–1954", PicArsn (1954) 5) Anon, "Packaging Requirements Code", **MIL-STD-726** (1960) 6) Anon, "Ammunition Packing De-

sign Criteria", FRL, PicArsn (1961) 7) Anon, "Packaging Standards, Preparation and Use of", **MIL-STD-647 (ORD)** (1962) 8) F.A. Paine, Ed, "Fundamentals of Packaging", Blackie & Son, London (1963) 9) Anon, "Care, Handling, Preservation, and Destruction of Ammunition", **TM 9-1300-206** (1964) 10) Anon, "The Carriage of Dangerous Goods and Explosives In Ships", Ministry of Transport, HMSO (1965) 11) Anon, "Packaging and Materials Handling Packaging Cost Manual", **TM 38-275** (April 1966) 12) Kirk & Othmer, 2nd Ed, Vol **14** (1967), 432–461 13) G. Jones, "Packaging Information Sources", Gale Research Co, Detroit (1967), 135–143 14) S.E. Mautner, "Military, Electronics, and Aerospace Handbook on Reuseable Protective Packaging", Kayar Publg Co, USA (1967) 15) G.R. Buck et al, "A Survey of Packaging Systems For Artillery Ammunition", PATR **4124** (1970) 16) M.G. Baldwin et al, "New Directions in Packaging", Management Assocn, Inc, NY (1970) 17) S.J. Porter, Coordinator, "Proceedings of Ammunition Packaging Seminar", USA Mucom, PicArsn, Dover, NJ (1970) 18) J.F. Hanlon, "Handbook of Package Engineering", McGraw-Hill, NY (1971) 19) H.F. Wreden & E.X. Petrocco, "Preliminary Stage of Improved Packaging For Three 152mm Cartridges . . .", PATR **4212** (1971) 20) J.P. Flynn, "Dangerous Materials Study For The Packaging Evaluation Agency", Dow Chem Co, Mich, **AD-759289**, WPAFB, AF Packaging Evaluation Agency Contract F33601-70-C-0653 (1971) 21) H. Weiner, "Improved Plastic Container For Cartridge 81mm, HE, M374A2", PA Engrs Product Improvement **GG 37280** (1971) 22) Anon, "Technical Advances In Packaging With Flexible Barrier Materials", **ASTM Special Technical Publ 548**, ASTM, Phila (1972) 23) Anon, "Packaging, Handling, Storage, and Transportation System Dimensional Constraints, Definition of", **MIL-STD-1366** (1972) 24) Anon, "Packaging and Pack Engineering", EngrgDes-Hdbk, **AMCP 706-121** (1972) 25) Anon, "Packaging, Handling, Storage, And Transportability Program Requirements [For System And Equipments]", **MIL-STD-1367**, (1972) 25a) B.D. Rossi & Z. Pozdnyakov, "Commercial Explosives And Initiators", Rept No **FSTC-HT-23-587-73**, Translation of "Promyshlennye Vzryvchatye Veshchestva I Sredstva Vzryvaniya-Spravochnik", Moscow, 1971 (Oct 1973) 25b) Anon, "TNT (Trinitrotoluene) For Industrial Explosives", **Rept No FSTC-HT-23-1067-73**, Translation of Russ Std **GOST 4117-67**, 1967 (1973) 25c) Anon, "Packaging (Ordnance)", Rept No **DDC-TAS-73-20** (1973) 26) Anon, "Parts and Equipment, Procedures For Packaging and Packing of", **MIL-STD-794D** (1973) 27) F.A. Niehaus & J.A. Wiegand, "Investigation of Environmentally Degradable Materials", NAVAMMODEPOT **RDTR-275** (1974) 28) Anon, "Packaging Requirement Codes", **MIL-STD-726E** (1974) 29) Anon, "1975 Packaging Machinery Directory", Packaging Machine Mfg Inst, Wash (1974) 29a) Anon, "Preservation And Packaging", Vol **1, TM 38-230-1** (1974) 29b) Anon, "Packing", Vol **2, TM 38-230-2** (1974) 30) Anon, "Packaging, Packing and Marking For Shipment of Artillery Type and Rocket Fuzes: General Specification For", **MIL-P-60412A (PA)** (1975) 31) Anon, "Packing, Handling and Transportability In System/Equipment Acquisition", **MIL-P-009024H (USAF)** (1975) 32) Sax (1975), 264, 338–40, 760 & 762 33) Anon, "Packaging and Materials Handling, Preparation of Hazardous Materials For Military Air Shipment", **TM 38-250** (1976) 34) Anon, Relevant Mil Specs for individual Ord items (various dates) 35) Anon, "Operators and Organizational Maintenance of the (Individual) Weapons System", **TM 9-1100-1115-XXX-12** or **20** (various dates) 36) Anon, "Minutes of the Explosives Safety Seminar (Held Yearly) . . .", Armed Services Expl Safety Board, Wash, DC (various dates)

Paléine or Paléina. Dynamites patented by Langfrey in Engl in 1878 contg nitrated straw ("fulmi-paille"). One of the formulations contd: NG 35.0, Nitrostraw 18.6, saltpeter 32.5, sulfur 4.6, and potato starch 9.3%. Part of the sulfur could be replaced with hardwood charcoal, and dextrin could be substituted for the starch

These Dynamites were stable and fairly insensitive to shock. Incorporation of hydrocarbons rendered them still less sensitive, and suitable for military purposes

Refs: 1) Daniel (1902), 596 2) Gody (1907), 471 3) Giua, Trattato **6** (1) (1959), 386

Palmer's Explosive. AN or AP 50, DNT 14, Na or K nitrate 31, and paraffin wax (mp > 120°) 5%. For a quicker expl, the proportions used are 70, 13 and 7%, respectively
Refs: 1) W.H. Palmer, BritP 20214 (1909) & CA **3**, 2507 (1909) 2) Ibid, USP 990585 (1911) & CA **5**, 2332 (1911)

Panclastites (see also under Anilite or Anilithe in Vol **1**, A443-R). Liq expls of the Sprengel type, patented in France by Turpin in 1881, contg liq N_2O_4 as oxidizer and CS_2 as fuel. Later, petroleum, benz, toluene, xylene, aniline, mixts of CS_2 and NB, naphthols, pitch, and vegetable and animal oils were also proposed as fuels. Some of these substances were nitrated (Ref 8)

Panclastites were inexpensive and easy to prepare, and were very powerful, some possessing a greater brisance and higher detonation velocity than either TNT or PA

All the Panclastites were extremely sensitive to shock, and for this reason the ingredients could not be mixed in advance and transported to the work site. Mixing had to be done just prior to use, this being a major disadvantage in their utilization. In addition, N_2O_4 is a corrosive liq, and requires special vessels for its transportation

Following are examples of some of the most commonly used Panclastites:
1) Liq N_2O_4 64.3, CS_2 35.7% by wt. Decomps on expln as follows: $2CS_2+3N_2O_4 \rightarrow 2CO_2+4SO_2+3N_2$. Some characteristics, as given in Ref 5 are: "force specifique" 6455 vs 8910 for TNT; abs temp of expln in °K, 3731 vs 3423 for TNT; vol of gas developed by 1 kg of expl, w calcd as vapor, at 760mm and 0°, 459ℓ vs 688ℓ for TNT. According to Stettbacher (Ref 4), it has a Trauzl test value (power) of 330cc vs 305cc for PA, and a crusher test value (brisance) of 3.3mm vs 3.05 for PA
2) Liq N_2O_4 81.8, benz 18.2% by wt. Decomps on expln, according to A. Pérez Ara (Ref 7), as follows: $C_6H_6+3N_2O_4 \rightarrow 3CO_2+3CO+3H_2O+3N_2$
3) Liq N_2O_4 69.8, NB 30.2% by wt. Decomps on expln as follows: $8C_6H_5NO_2+25N_2O_4 \rightarrow 48CO_2+20H_2O+29N_2$. According to Stettbacher (Ref 4) this mixt has a d of 1.38g/cc, heat of deton of 1777cal/g, vel of deton of 8000m/sec, is more brisant (crusher test value 5.05mm vs 4.9mm) and more powerful (Trauzl test value 505cc vs 490cc) than NG or even Pentrinit (50/50 PETN/NG). According to Pascal (Ref 2) the vel of deton of a 65/35 N_2O_4 / NB mixt is 7650m/sec
4) Liq N_2O_4 about 68, 65/35 NB/CS_2 about 32% by wt. This mixt gave a Trauzl test value of 432cc and a crusher test value of 4.3mm, vs 490cc and 4.9mm for NG, respectively

Panclastites were tested in the 1880's by the Ger navy in marine torpedoes. For this, two thick, sealed glass vessels, one contg N_2O_4 and the other CS_2, were placed in each warhead. The set-back forces produced on firing a torpedo broke both vessels, resulting in the formation of an expl mixt which was detonated by an impact fuze when the torpedo reached the target. Although the results of the trials were favorable, Panclastites were not adopted by the Ger navy because of the inconvenience of handling the ingredients, and the danger of premature breakage of the glass vessels in the warhead

Although Panclastites are very powerful and brisant expls, their use was very limited (even as commercial expls), and with the appearance of many new expls at the end of the last and beginning of the present century, their use was discontinued. They were, however, resurrected during WWI, because of the shortage of such conventional expls as TNT, PA, DNB, TNB, Nitronaphthalenes, etc, and used extensively in weapons which had just begun to come into vogue, namely, "aeroplane drop bombs". Fr used Panclastites under the name "Anilite" (qv) in a specially designed bomb with two compartments. Italy also seems to have used Panclastites (N_2O_4-benz) to some extent, since, in 1921 or 1922, they experienced an expln at Brodio involving 4500kg of N_2O_4 and 1500kg of benz (Ref 5)

Panclastites were even used in WWII, in some of the heaviest Brit aircraft bombs (Fliegerbomben in Ger). These bombs had two compartments, as described under "Anilite" [Ref 2 (1948)]

Refs: 1) Daniel (1902), 596–98 2) Pascal (1930), 193–4; (Russian ed, 1932), 137 3) Vennin, Burlot & Lécorché (1932), 533 4) Stettbacher (1933), 182–4; (1948), 70 5) J. Pepin Lehalleur (1935), 359–60 6) Davis (1943), 355 7) A. Pérez Ara (1945), 228–9 8) D.G. Morrow, USP 2355817 (1944) & CA **39**, 194 (1945) 9) V. Mannheimer, "Some Explosive Properties of Panclastite", MAF **28**, 505–16 (1954) & CA **49**, 2733 (1955) 10) H. Muraour, MAF **28**, 517–21 (1954) & CA **49**, 2735 (1955) (Notes on Ref 9)

Panclastites-Guhr. In order to avoid the problems inherent in using liq expl ingredients, Turpin, in 1881–82, invented expls in which the N_2O_4 was absorbed by guhr (see Vol **6**, G174-L) or other materials. Such "solid" N_2O_4 was mixed with either a solid fuel or a liq fuel absorbed on a solid compd
Refs: 1) M. Turpin, FrP 146497 (1881) & 147676 (1882) 2) Daniel (1902), 598

Pandora. A WWII code name for the Long Aerial Mine, which consisted of an expl charge attached to 2000 ft of cable. The object of this RAF innovation was to tow the charge behind a Havoc aircraft and train it in the path of Ger bombers. It did not prove successful, and the idea was abandoned in November 1941
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973)

Pannonit. An Austrian pre WWI permissible low-freezing mining expl contg NG 25.5, NC (collodion cotton) 1.5, AN 37, dextrin 4, glycerol 3, MNT 5, & Na or KCl 24%. It was fired with a special detonator contg TNT, and replaced the previously used "Progressit" (qv)
Refs: 1) Anon, SS **8**, 398 (1913) 2) Marshall **1** (1917), 398 3) Naoúm, NG (1928), 417

Pantopolit. An older Dynamite, manufd at the end of the last century by the Rheinische Dynamit Gesellschaft at Opladen, near Köln, Ger. It contained NG dissolved in naphthalene 67–70, guhr 20–23, Ba sulfate 7 & chalk 3%. The naphthalene content was to increase the gas vol produced on expln
Refs: 1) Daniel (1902), 599 2) PATR **2510** (1958), Ger 122-R 3) Giua, Trattato II (1) (1959), 345

Panzerfaust. Ger WWII antitank projectile weapon utilizing a shaped charge expl and a tungsten carbide core. It was lighter than an earlier version *(Panzerschreck),* and could be handled by one person. Its trajectory was flatter than the Panzerschreck, with a range of 150 meters
Refs: 1) L.E. Simon, "German Research in World War II", J. Wiley, NY (1948), 187–8 2) Stettbacher (1948), 134

Panzergranate. Ger for a WWII projectile used against armor plate, or an AP (armor-piercing) projectile. According to Stettbacher (Ref), they were of one piece construction with a solid, sharp nose. They were effective against softer armor, but not against hardened steels
Ref: Stettbacher (1948), 401

Panzerschreck. A Ger WWII weapon, similar to the American *Bazooka.* It fired an 88mm projectile, which was about 50% larger than the Bazooka, but its trajectory was more curved and its range shorter. Two persons were required to operate the weapon. Later in the war, the rocket size was increased to 100mm. This resulted in better penetration, but made the weapon too heavy to use, and it was superseded by the *Panzerfaust.*
Ref: L.E. Simon, "German Research in World War II", J. Wiley, NY (1948), 188

Panzerwurfkannone. A Ger smooth-bore 80mm mortar developed during WWII by Rheinmetall for firing hollow-charge projectiles at longer ranges than the *Panzerschreck* or *Panzerfaust.* It fired an 18-inch finned projectile weighing 6 lbs at a muzzle velocity of 1700 fps to an effective range of 700 meters. The projectile penetrated 140mm of armor at a 60° angle of impact
Ref: L.E. Simon, "German Research in World War II", J. Wiley, NY (1948), 188

Paper Chromatography, Paper Partition Chromatography. See under Chromatography in Vol **3**, C289-L to C298-L

Papers, Explosive. See under Explosive Papers or Pyropapers in Vol **6**, E424

Papite. Fr designation for acrolein (see Vol **1**, A96-L), used during WWII in some artillery shells and gas grenades. It was intended to serve as a powerful lachrymator which contained neither bromine nor acetone, both being in short supply in Fr during this period. Its toxic effects were comparable to phosgene
Ref: C. Wachtel, "Chemical Warfare", Chemical Publishing Co, NY (1941), 168–70

Paraffin (Paraffin wax, Hard paraffin). A mixt of solid hydrocarbons having the general formula C_nH_{2n+2}, obtained from petroleum. Colorl or white; somewhat translucent, tasteless, odorless solid; greasy feel; burns with a luminous flame. D 0.880–0.915g/cc, mp 47–65°, flash p 390°F, autoignition temp 473°F, non-toxic (Refs 8 & 9)

Insol in w, alc and acids; sol in benz, chlf, eth, ligr, turpentine, CS_2 & oils; miscible when melted with wax, spermaceti & fats (Refs 8 & 9)

The use of paraffin in the expl industry is extensive, not only as a moisture protecting agent, but as a desensitizer. Paraffin can be incorporated either directly with ingredients of expl compns (at a temp above its mp), or one or more ingredients can be coated separately with molten paraffin and then mixed. When hygroscopic substances, such as AN, Na nitrate, etc, are coated in such a manner, they are rendered less hygroscopic, and, when the same procedure is applied to sensitive compds or expls (K chlorate, RDX, PETN, etc) their sensitivity can be markedly reduced

One of the first to use paraffin in expls was A. Nobel, who incorporated small quantities in some of his Dynamites

In the 1880's, the Fr prepd and tested a series of "paraffined nitrocelluloses" (Refs 1 & 2). Several mixts were prepd by incorporating various amts of paraffin (5 to 20%) into hot, wet NC, followed by extrusion into cartridges and drying. It was found that while mixts contg 5% paraffin could be detonated with a cap contg 1.5g of MF, mixts with 10% or more paraffin required a "cartouche-amorce auxiliaire" (booster). Cartridges contg 5% paraffin burned without detonation on bullet impact. Cartridges of NC desensitized with paraffin were used extensively in Europe as late as WWI for demolition purposes

H. von Bezold (Ref 3) details many uses of paraffin in the expls industry, and gives methods of analysis as well

In addition to being used in many commercial expl compns (such as Cheddites, Minêlite Explosifs, Gesteins-Koronit, etc), paraffin has been used for military purposes. Paraffined AP in the compn AP 86, paraffin 14% was used in Fr in 75mm artillery shells, but was found to be too sensitive, causing prematures. It was, however, suitable for loading mortar shells, hand grenades and aircraft bombs. As an example, the following mixt was used for loading 58mm trench mortar rounds: AP 61.5, paraffin 8.5 & Na chlorate 30% (Ref 6, p 366)

Paraffin is also used for impregnating paper used for cartridging expls, as well as moisture proofing paper cartridges already loaded with hygroscopic Dynamites

In the pyrot area, paraffin is widely used in the manuf of book and wooden matches, as a protective coating to counteract possible surface deterioration of metal powders, as a lubricant and waterproofing agent for the interior surfaces of kraft paper flare and signal cases, and as a binder which tends to fill interstices between particles on press loading (Ref 7, pp 69, 71, 302 & 316)

A US Federal Specification, "Wax, Paraffin, Technical", **VV-W-95A** (31 May 1968) contains requirements for procurement of this material. It covers two types and six grades of paraffin wax:

Type I – Fully Refined
Grade AA - mp 145–150°F
Grade A - mp 125–140°F
Grade B - mp 130–134°F
Grade C - mp 123–127°F

Type III – White Crude Scale
Grade B - mp 124–128°F
Grade C - mp 118–122°F

The min-max mp ranges for each grade are

detd by the cooling curve method described in **ASTM Standard D87-66**

Color (liq), Saybolt: Type I, +25 min; Type I, Grade AA, +23 permitted; Type II, no requirement. The procedure is described in **ASTM Standard D156-64**, "Saybolt Color of Petroleum Products"

Oil content, %, as described in **ASTM Standard D721-65T**, "Oil Content of Petroleum Waxes":

	Type I	Type III
	% Maximum	% Maximum
Grade AA	0.5	–
Grade A	0.5	–
Grade B	0.5	3.5
Grade C	0.8	3.5

Workmanship: The finished wax shall be clean, homogeneous in appearance, and free from dirt, and other foreign matter

Refs: 1) Commission des Substances Explosives, MP **1**, 468 & 483–4 (1882–3); Ibid, **2**, 586–7 & 605 (1884–89); Ibid, **5**, 73 (1892) 2) Daniel (1902), 600 3) H. von Bezold, NC **3**, 119–21 (1932) & CA **26**, 4954 (1932) 4) A. Stettbacher, NC **7**, 181–3 (1936) 5) Bebie (1943), 113 6) Davis (1943), 333, 338, 361, 364, 366 & 391 7) Ellern (1968), 69, 71, 302 & 316 8) Merck (1968), 782-R 9) CondChemDict (1971), 657-L

Paraffin Oil (Mineral Oil, Liquid Petrolatum). Colorl, tasteless, transparent liq, consisting mostly of liq paraffin hydrocarbons; bp 330–390°, d 0.84–0.94g/cc. Insol in w, cold alc and glycerin; sol in eth, chlf, CS_2, benz, petr eth, gasoline & boiling alc

It is obtained by distn of high-boiling petroleum fractions, followed by purification. The latter operation consists of treatment with concd sulfuric acid, then concd Na hydroxide soln, and filtration thru decolorizing carbon. In order to reduce the solid paraffins, the oil is chilled and filtered

Paraffin oil has been used in several Nitrostarch blasting expls (Ref 1, p 276), as well as in some smokeless powders, for example, in "bulk sporting powders". A typical compn is NC (12.90% N) 87.00, K nitrate 6.0, paraffin oil 4.0, Ba nitrate 2.0, and diphenylamine 1.0% (Ref 1, p 289)

Refs: 1) Davis (1943), 276 & 289 2) CondChemDict (1971), 657

Nitroparaffins, Explosives Derived From. Although mononitroparaffins are generally not expl, they can be used for the prepn of expls

Aaronson (Ref 1) nitrated nitroisobutylglycerin to Nitroisobutylglycerintrinitrate, 2-nitro-2-methyl-1,3-propane diol to 2-Nitro-2-methyl-1,3-propanedioldinitrate, and 2-nitro-2-methyl-1-propanol to 2-Nitro-2-methyl-1-propanolnitrate. Their prepn and characterization follow:

Nitroisobutylglycerintrinitrate. $O_2N.C(CH_2ONO_2)_3$, mw 286.14, N 19.58%, OB to CO_2 0%

Preparation of *Nitroisobutylglycerin.* Several procedures for the preparation of this compd are given in the literature. Of those tried, that described by Stettbacher [Nitrocellulose **5**, 162 (1934)] gave the best results. The method of prepn follows:

Into a three-necked, 1-liter reaction flask set into a water bath placed on a hot plate were added 150g of Nitromethane (Eastman Kodak No 189 – Distillation Range 98–101°) and 2g of K carbonate ($K_2CO_3.\frac{1}{2}H_2O$). A total of 675g of 37% formaldehyde of reagent grade were slowly added. The formaldehyde content was determined by oxidizing to formic acid in a measured amt of standard alkali soln and titrating the excess alkali (See Scott's Standard Methods of Analysis, 5th Ed, p 2149). Addition of the formaldehyde raised the temp, and the rate of addition was adjusted and the cooling bath regulated so that the temp was maintained below 30°, until about 200g of the formaldehyde had been added. The heat of reaction was then permitted to raise the reaction mixt to about 80°, while the remainder of the formaldehyde was added in about one-half hour and then heated at about 90° for two hours. The yellowish soln was concd under reduced press (about 4 inches). It smelled strongly of formaldehyde. Water was added and the soln again concd as before to remove some of the formaldehyde. Dilution and concn were again repeated. On cooling an almost solid mass of crystals, reeking strongly of formaldehyde, separated. This red colored mass was filtered, but filtration was very slow due to the viscous sticky character of

the filtrate. After several hours, the mass was dissolved in hot alc and recrystallized. By repeated recrystns from ether there was finally obtained material melting at 165° and above. The various mother liquors were similarly recrystd in order to accumulate sufficient material for nitration

Preparation of **Nitroisobutylglycerintrinitrate.** The procedure followed was that given by Stettbacher, [Nitrocellulose **5**, 183 (1934)]. 50g of the nitrobutylglycerin were gradually added with mechanical stirring to 304g of a mixed acid having the composition sulfuric acid 60%, nitric acid 38%, and water 2%. The temp was maintained below 15° by means of a cooling bath and the acid added in about ½ hour. The mixt was stirred for an additional ½ hour, during which the temp fell to +5°. After transferring to a separatory funnel and allowing the mixt to stand for awhile, the heavier spent acid was drawn off. The residual product was washed with water, then with Na bicarbonate soln until it was alkaline, and then with water to neutrality to litmus (2 washes). The washings were added to the separated spent acid, extracted thoroughly with ether, the ether extract washed with water to neutrality and then added to the main separated product. The ether was removed from the product by evaporating and then drying in a vacuum desiccator. A yield of 95% of the theoretical was obtained. The nitrate nitrogen was determined by the nitrometer and gave a result of only 14.02%. The product was renitrated exactly as above except that the temp was held at just below 20° for 1 hour. After extraction with ether, washing and drying as above, the nitrate nitrogen was raised to 14.12%

Using the material thus obtained, a number of tests and determinations were made with the results given in Table 1. The Drop Test, de-

Table 1

Properties of Nitroisobutylglycerintrinitrate Compared with Nitroglycerin

	Nitroisobutyl-glycerintrinitrate	Nitroglycerin
Nitrate nitrogen, %	14.07 (theory 14.68)	18.50 (theory)
Drop Test, 2 kg wt	25 cm	44 cm
Temp required for decomposition in 5 secs	185° without detonation	–
Sand Test, sand crushed by 0.2g [a]	28g	30g
82.2° KI Heat Test	2 minutes	Specification minimum 15 minutes
Effect of flame when sealed in capillary tube	Detonation	Detonation
Volatility at approx 25°:		
Loss in g per sq cm per 24 hrs	0.127×10^{-3}	0.153×10^{-3}
Freezing point	Below −50°	About +12°
Refractive Index (D line)	1.4896 at 25° 1.4874 at 30°	1.4713 at 25° 1.4693 at 30°
Gelatinizing action on Nitrocellulose	Slight	Strong
Toxicity	Slight, decidedly less than NG	Very marked
Soluble in	Methyl and ethyl alcohols, acetone, ether, ethylene-dichloride, chloroform and benzene	Most organic solvents
Insoluble in	Water, carbon disulfide, petroleum ether	Water (practically insol) petroleum ether

[a] When absorbed by 0.2g of kieselguhr

composition temp, and the 82.2° KI Heat Test were made according to procedures standard at PicArsn. In order to determine the brisance value of the Nitroisobutylglycerintrinitrate, it was mixed with an equal weight of kieselguhr and 0.4g of the mixt hand pressed into the detonator cap. The volatility at approx 25° compared with NG was determined by exposing approx equal wts of the materials in similar dishes to the air and weighing daily for a number of days. The refractive index was determined by means of an Abbé refractometer over the range 24–33°. Whether the compd had any gelatinizing action on NC was determined by adding a few drops to a small amt of NC and mechanically working to determine whether or not gelatinization had taken place

A study of the results showed that Nitroisobutylglycerintrinitrate was a powerful expl of the same class as NG, but that it was much more sensitive to impact and much less stable, as judged by the 82.2° KI Test. Stettbacher [Nitrocellulose **5**, 203 (1934)] reported the low stability of this material, but attempted to minimize this important defect by ascribing the low heat test values to long drying at 40–60° in order to remove the ether. In this work, the ether was removed by a current of air at room temp and then by holding the expl under reduced pressure in a vacuum desiccator until there was no further loss in weight. In spite of those precautions very low 82.2° Heat Test values were obtained. Its gelatinizing action on NC was too slight to permit the use of Nitroisobutylglycerintrinitrate as a solvent unless large quantities were employed. Aaronson (Ref 1) concluded that it was too unstable to be of military value

2-Nitro-2-methyl-1,3-propanedioldinitrate.

$CH_3.\overset{NO_2}{C}(CH_2ONO_2)_2$, mw 225.14, N 18.67%, OB to CO_2 −24.87%

Purification of *2-nitro-2-methyl-1,3-propanediol.* This material was purchased from the Commercial Solvents Corp and had a melting point of 135–136°. By recrystallizing twice from 95% alc the mp was raised to 151.2°. This purified material was used for nitration

Preparation of **2-Nitro-2-methyl-1,3-propanedioldinitrate.** 50g of the dry ground diol prepd above was sifted into a mixt of 300g of a mixed acid having the compn nitric acid 40% and sulfuric acid 60%, while the mixt was mechanically agitated and the temp maintained at about 15°. After the addition, the temp was allowed to rise to 20° and maintained for ½ hour. After standing for an hour, the mixt was transferred to a separatory funnel and the spent acid drawn off. The residual oily liq was washed twice with warm (about 45°) aq Na sulfite soln and then with warm distd w until neutral to litmus. The liq was dried in a vacuum oven at 50°, and then chilled. A milk white waxy mass was obtained, yield 76.0% of theory. The properties of this material were obtained and the results shown in Table 2. The washings were added to the spent acid and the whole extracted thoroughly with ether. The ether extracts were combined, washed with w, evaporated and dried to constant wt in a vacuum desiccator. Yield 16.2% of theory, which made a total nitration yield of 92.2%

Table 2
Properties of
2-Nitro-2-methyl-1,3-propanedioldinitrate

Nitrate nitrogen	12.39% (theory 12.45%)
Melting point (while waxy solid)	37.4°
Drop Test, 2 kg wt	11 cm
Temp required to cause decompn in 5 secs	200° (without detonation)
Sand Test, sand crushed by 0.4g[a]	53g
82.2° KI Heat Test	9 minutes
Gelatinizing action on Nitrocellulose	Practically nil
Toxicity	Similar to Nitroglycerin
Soluble in	Alcohol, acetone, ether, carbon tetrachloride, and petr ether. Slightly sol in water

[a] When initiated by 0.24g of Mercury Fulminate and 0.08g of Tetryl

The 2-nitro-2-methyl-1,3-propanediol purified by recrystn was of high purity as indicated by its melting point of 151.2°, which compared with 150° reported by Vanderbilt and Hass [Ind&EngChem **32**, 36 (1940)]. Nitration of the above compd yielded 2-Nitro-2-methyl-1,3-propanedioldinitrate in 92% total yield as a milk-white waxy solid melting at 37.4°. It was an expl with a brisance value about equal to that of Tetryl. However, it was very sensitive to impact, having a Drop Test value of only 11 cm with a 2-kg hammer. This was not in agreement with the statement by J.A. Wyler [USP 2195551 (1940)] to the effect that it was very insensitive to impact and that a "10 kg weight dropping 100 cm does not cause a detonation." Like the other nitroparaffins, 2-Nitro-2-methyl-1,3-propanedioldinitrate showed very poor stability in the 82.2° Heat Test even after repeated and careful stabilization. It had practically no gelatinizing action on Nitrocellulose. Aaronson (Ref 1) concluded that it was too unstable to be of military interest

2-Nitro-2-methyl-1-propanolnitrate.

$CH_3.\overset{NO_2}{\overset{|}{C}}.CH_2ONO_2$, mw 164.14, N 17.07%, OB to CO_2 −68.23%

Purification of *2-nitro-2-methyl-1-propanol.* Material melting at 86–87° and made by the Commercial Solvents Corp was recrystd from benzene and dried in a vacuum desiccator. The mp was about 88° (not sharp). This material was used for nitration

Preparation of *2-nitro-2-methyl-1-propanolnitrate.* 50g of the 2-nitro-2-methyl-1-propanol purified as above were sifted into a mixt of 58.5g of 90.5% nitric acid and 241.5g of 103.1% sulfuric acid (oleum) while the well-agitated mixt was maintained close to 15°. Stirring was continued for 1 hour and the mixt allowed to stand for ¼ hour. No separation of the nitration product occurred and the mixt was poured over cracked ice. An oily layer separated. The mixt was transferred to a separatory funnel, washed with water, Na bicarbonate, and twice with water to neutrality. The separated diluted spent acid together with the washings were thoroughly extracted with ether; the ether extract washed to neutrality and added to the main product. The ether was removed by evaporation and the residue dried in a vacuum desiccator. The yield was 34.8g or 50.5% of the theoretical. Table 3 gives the results of the tests made on this material

Table 3
Properties of
2-Nitro-2-methyl-1-propanolnitrate

Nitrogen	16.99% (theory 17.07%)
Drop Test, 2 kg wt	100+ cm
Temp required to cause decompn in 5 secs	200–205° without detonation
Sand Test [a]	Not detonated by 0.35g of Lead Azide and 0.2g of Tetryl, or by 0.5g of Mercury Fulminate
82.2° KI Heat Test	6 minutes
Gelatinizing action on Nitrocellulose	Good
Toxicity	Similar to Nitroglycerin
Soluble in	Alcohol, ether, acetone, benzene, and CCl_4
Insoluble in	Water and petr ether

[a] Test charge consisted of 0.2g of 2-nitro-2-methyl-1-propanolnitrate absorbed by 0.2g of kieselguhr

2-nitro-2-methyl-1-propanol was obtained in good quality by recrystn from alc. The mp of the material used, 88°, should be compared with 89.5–90.0° given in the literature [Ind&EngChem **32**, 36 (1940)]. On nitration 2-nitro-2-methyl-1-propanolnitrate was obtained in about 50% yield. It was not detonated by the fall of a 2 kg hammer from a height of 100 cm, and was insensitive to initiation by strong detonating agents. It caused headaches similar to those caused by Nitroglycerin, and it was a good gelatinizing agent for Nitrocellulose. However, like the other nitroparaffin derivatives discussed above, it was quite unstable, giving a very low 82.2° Heat Test value. It, therefore, was considered to be unsuitable for military use (Ref 1)

Blatt (Ref 3) gives the following additional test data for this compd from other sources:

Impact Sensitivity. 2 kg at 100 cm gives 0/2 shots
Power. 75% of blasting gelatine by Ballistic Mortar
Stability. 82.2° KI Heat Test, 4 and 8 minutes (two sources)
Remarks. Gelatinizes blasting soluble Nitrocotton rapidly at room temp

In a final summary report on the prepn of Nitroparaffins (Ref 2), the following compds were synthesized: Tetranitromethane; 1,1-Dinitroethane; 1,2-Dinitroethane; Hexanitroethane; 1,1-Dinitropropane; 2,2-Dinitropropane; 2,2-Dinitrobutane; 2,2-Dimethyl-1,3-dinitropropane; 2,2,3-Trinitrobutane; 2,2,3,3-Tetranitrobutane; 2-Methyl-2,3,3-trinitrobutane; 2,3-Dimethyl-2,3-dinitrobutane; 2-Methyl-2,3,3-trinitropentane; 3-Methyl-2,2,3-trinitropentane; and 3-Ethyl-2,2,3-trinitropentane. However, it was concluded that none possessed properties satisfactory for military expls. This disqualification generally resulted for the following reasons: 1) low mp or high vap press, 2) those compds contg α-hydrogens were strongly acidic, and 3) certain arrangements of nitro groups were thought to be inherently unstable

The following compds could not be synthesized: 1,1,1-Trinitropropane; 1,3-Dinitrobutane; 2,3-Dinitrobutane; 2-Methyl-1,1,2-trinitropropane; 2,2-Dimethyl-1,1,1-trinitropropane; 2,2-Dimethyl-1,1,3-trinitropropane; 1,3-Dinitro-2-methyl-2-(nitromethyl) propane; 2,2-Dimethyl-1,1,1,3-tetranitropropane; 2,2-Dimethyl-1,1,3,3-tetranitropropane; 2,2-Bis (nitromethyl)-1,3-dinitropropane (sym-tetranitroneopentane); 3,3-Dimethyl-1,1,4-trinitrobutane; 2,2,5,5-Tetranitrohexane; 3,3,4,4-Tetranitrohexane; 2-Methyl-2,3,3,4-tetranitropentane; 3-Methyl-2,2,3,4,4-pentanitropentane; 3,3-Dimethyl-2,4-dinitropentane; 2-Methyl-2,3,3-trinitrohexane; 3-Methyl-2,2,3-trinitrohexane; 2,2-Dimethyl-1,4,4-trinitropentane; 2-Ethyl-1,2,3-trinitropentane; 3,3-Dimethyl-2,2,4,4-tetranitropentane; 2,3-Dimethyl-1,4-dinitro-2,3-bis (nitromethyl) butane; 2,5-Dimethyl-2,3,3,4,4,5-hexanitrohexane; 3,4-Dimethyl-2,2,3,4,5,5-hexanitrohexane; and 2,2,4,4-Tetrakis (nitromethyl) pentane. Ref 2 details a listing of a variety of methods attempted in these unsuccessful syntheses

The above Ref also lists reactions which either succeeded or failed to yield poly-nitroparaffins, salts of methazonic acid and polynitroparaffins, nitroolefins and their polymers, nitrates of nitrohydroxy compds, and nitrated alcohols

Written by **S. M. KAYE**

Refs: 1) H.A. Aaronson, "Study of Explosives Derived from Nitroparaffins", PATR **1125** (1941) 2) Anon, "Final Report on The Preparation of Nitroparaffins", OSRD **2016** (1943) 3) Blatt, OSRD **2014** (1944)

Paraformaldehyde. $(CH_2O)_n$, mw $(30.03)_n$; white, cryst powder; mp 64°, bp sublimes, range of polymerization n=8 to 100. *Note:* Paraformaldehyde is not the same as sym-trioxane, which melts at 150–60°. Slowly sol in cold, more readily in hot w, with evolution of formaldehyde; insol in alc & eth; sol in fixed alkali hydroxide solns. Obtained by concentrating formaldehyde soln. At ordinary temps, it gradually vaporizes, yielding formaldehyde gas

Paraformaldehyde Explosives.

When paraformaldehyde is treated with hydrogen peroxide, expl compds, similar to those obtained by treating formaldehyde with H_2O_2 (methylol hydrogen peroxide or dimethylol peroxide) are obtained. According to Bamberger and Nussbaum (Ref 2), mixts of solid paraformaldehyde and 60% H_2O_2 are brisant expls which detonate on heating or under the influence of a blasting cap. This mixt detonates spontaneously when left in contact with Pb for a short time, presumably from the heat generated by the oxidation of the Pb. Expl crysts of mp 50° were sepd from paraformaldehyde-peroxide mixts. See also under Formaldehyde Polymers and Formaldehyde and Derivatives (Explosives Obtained Therefrom) in Vol **6**, F164-L to F167-L

Refs: 1) Beil **1**, 566 & [635] 2) M. Bamberger & J. Nussbaum, SS **22**, 125–8 (1927) & CA **21**, 4070 (1927) 3) J.F. Walker, "Formaldehyde", Reinhold Publ Co, NY (1944) 4) Merck (1968), 782-R

Paragón. Mixt of K perchlorate 60, nitro compds 10, sawdust or cereal flour 20, Na chloride 6, and powdered Zn-Al alloy 4%
Ref: A. Pérez Ara (1945), 218

Paraldehyde. See under Acetaldehyde and Derivatives in Vol **1**, A14

Paraldol. See under Acetaldol and Derivatives in Vol **1**, A15-R

Parammons (Perammons). Perchlorate expls used by the Fr during WWI for loading aerial bombs:

	No I	No II	No III
Ammonium perchlorate, %	86	90	92
Paraffin, %	14	10	8

Of these, No II had an OB to CO_2 of close to zero, and its power by Trauzl test was 470cc. It was about as sensitive to impact as the Cheddites, and could be expld by rifle bullet. According to Stettbacher (Ref 3), mixt No II was used again during WWII for military purposes
Refs: 1) Naoúm, Expls (1927), 135 2) Stettbacher (1933), 316 3) Stettbacher (1948), 91

Paraplex. A trademark for a group of alkyd type polymeric materials known as polyester resins. These resins are primarily long chain polybasic acids esterified with polyhydric alcohols such as glycol sebacate, glycerol, or ethylene glycol. Some are oil-modified while others are unmodified polyesters

Paraplex resins are manufd by Rohm & Haas Co, Phila, Pa

Some Paraplex resin mixts, such as Paraplex P-10 containing Paraplex resin AP-31 and styrene, are used by the Aerojet Engrg Corp, Azusa, Calif as an ingredient of JATO proplnts (see below). The same resin has been used as a constituent of resin-bonded expls (also, see below), while still other Paraplex resins are used to fabricate ceramic-faced composite armor (Ref 4)
Refs: 1) L.H. Eriksen, "Study Stability and Sensitivity Characteristics of Paraplex Propellant", PATR **1629** (1946) 2) E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR **2062** (1954) 3) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vol **11**, J. Wiley, NY (1964), 129–168 4) J.E. Gulbierz & L.E. Day, "Development of Reinforced Plastic Backing for Ceramic-Faced Composite Armor (U)", PATR **3226** (C) (1965)

Paraplex P-10. One of the P-series of Paraplex resin mixts which contain resins such as Paraplex Resin AP-31 together with varying amounts of styrene to form solns of unsaturated polyesters. Paraplex P-10 contains a 50/50 mixt of Paraplex Resin AP-31/styrene. It is a thermosetting mixt but can also be cured at RT (or higher using steam) with a peroxide catalyst such as benzoyl peroxide to either a flexible, semi-rigid, or rigid compd. It finds use in low pressure laminating, casting and molding applications. Specific military applications for Paraplex P-10 are in expls as a binder with RDX (see below), and in proplnts as a liner compn with asbestos fiber (Ref 1), and as a fuel with $KClO_4$ (see below)
Refs: 1) W.E. Campbell Jr, "Report No 1 on Restricted Propellant Charges Containing Paraplex Resin Fuel", Aerojet Engrg Corp, Azusa, Calif, **Report No 183**, Contract NOa (S) 5350 (1946) 2) E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR **2063** (1954) 3) CondChemDict (1971), 658

Paraplex Propellants. A series of JATO proplnts (the PF-series) developed by the Aerojet Engrg Corp, Azusa, Calif using Paraplex P-10 resin-styrene mixt as a fuel ingredient in the amt of approx 26.5%. Other ingredients are AN or K perchlorate, 73.0%, and small amts of t-butylhydroperoxide or benzoyl peroxide, 0.1 to 0.5% (as a polymerization catalyst) (Ref 2)

The Paraplex proplnts have a specific impulse of 199 lb/(lb/sec) at 2000 psia chamber press. They exhibit great thermal stability above 150°F and great impact strength at −20°F. Measured parameters of interest ($KClO_4$ content, PF-6 Proplnt): A loading d of 1.86g/cc; an expln temp of 600°; a friction pendulum test of 10 unaffected in 10 trials using a steel shoe; Q_e 965cal/g; an impact test using PA apparatus with

a 2 kg wt of 14 inches (TNT=12); a storage stability of over 90 days at 80°; and a vac stability of 0.05ml gas at 90° for 40 hrs (Ref 3)
Refs: 1) W.E. Campbell Jr, "Report No 1 on Restricted Propellant Charges Containing Paraplex Resin Fuel", Aerojet Engrg Corp, Azusa, Calif, **Report No 183**, Contract NOa (S) 5350 (1946) 2) Ibid, "Smokeless Propellant Investigations", Aerojet Engrg Corp, Azusa, Calif, **Report No 192**, Contract NOa (S) 7968 (1946) 3) L.H. Eriksen, "Study Stability and Sensitivity Characteristics of Paraplex Propellant", PATR **1629** (1946) 4) D.M. French et al, "Evaluation and Characterization of Binder Constituents", **NAVORD ES 12-3-1-71** (1971)

Paraplex Resin-Bonded Explosive. Usually consists of Paraplex P-43/RDX/Al/Styrene monomer/ Lupersol DDM (as a polymerization catalyst) in the following percentages, viz; 6.0/65.0/ 20.0/9.0/0.5. Density 1.65g/cc. The material is mixed and polymerized using the usual procedure for polyester resins and Plastic Bonded Expls (see in this Vol)

The following parameters were measured for the above formulation. A brisance of 71.6g sand crushed; a deton rate of 7291m/sec; an expln temp of 280°; a friction pendulum result of 3 partial detons in 10 trials using a steel shoe; a 100° heat test result of no weight loss in 48 hrs and no expln in 100 hrs; an impact sensy of 17 inches in a PA appar using a 2 kg wt (TNT= 14-15 inches), and 5.3 ft in a BurMines appar at the 50% pt using a 2kg wt (TNT = 11.2 ft); power by BalMort of 119 (TNT=100), and by Trauzl test of 157 (TNT=100); a rifle bullet impact test of 1 sample flashed, 3 smoked and 1 unaffected out of 5 trials; a sensy to initiation of 0.300g LA; an excellent storage stability (wet and dry storage plus JAN-cycles); and a vac stability of 0.25ml after 40 hrs at 100°
Ref: E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR **2062** (1954)

Paravane. A protective underwater device, invented during WWI by C.D. Burney of the Brit Navy, which, when towed with a wire rope from a fitting on the bow of a ship, rides out from the ship's side and cuts the cables of anchored mines. The mines will then rise to the surface, where they can be seen and destroyed. Another version, called "explosive paravane" contains an expl charge which is towed at some distance from a vessel. If a submarine is suspected of being nearby, the charge is detonated electrically
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 340

Parazol. A mixt consisting mainly of p-dinitro- and o-dinitro-dichlorbenzenes, N 11.8%, yellowish crysts, mp 63–85°, cast d 1.694g/cc. It can be prepd by the nitration of commercial dichlorbenzene. Parazol is nearly insol in w; very difficultly sol in cold alc; easily sol in hot alc; sol in eth, benz and CS_2

It is an expl, less powerful, brisant and sensitive than TNT. Its thermal stability is satisfactory (Abel Test at 65.5°, 60 minutes; German Test at 135°, 120 minutes). Parazol does not ignite at temps as high as 340°. When hand packed, it compresses a Pb block 27% vs 39% for TNT

The power of Parazol, as detd by Cope (Ref 1), is about 86% of TNT (Bal Mort Test, consisting of detg the quantity of Parazol required to cause deflection equal to the deflection from 10g of TNT). It is less sensitive to detonation than TNT and, when confined, requires a very powerful detonator

According to Davis (Ref 6), the chlorine in dinitrochlorbenzene is active, while that in monochlorbenzene is unreactive. It yields dinitrophenol by hydrolysis, dinitroaniline by reaction with ammonia, and dinitromethylaniline by reaction with methylamine. These and similar materials may be nitrated to produce expls, because introduction of a third nitrogroup is done very easily after the chlorine has been replaced by a more strongly ortho-para orienting group. Tetryl, as well as hexanitrodiphenylamine, have been produced starting with dinitrochlorobenzene

Parazol was used in Europe during the early days of WWI for filling projectiles. According to Davis (Ref 6), this was done because of a shortage of toluene, necessary for the manuf of TNT; an abundance of chlorine, produced during

manuf of caustic soda by an electrolytic process; and the ready availability of benz

In order to utilize the chlorine, large amts were used for the chlorination of benz to produce chlor- and dichlorbenzenes, used at that time as insecticides and moth exterminators. At the same time, attempts were made to nitrate the dichlorbenzene, which proved to be expl. When mixed with TNT in HE shells, it did not detonate completely, but presented interesting possibilities because the unexploded portion, atomized in the air, was a vigorous itch-producer and lachrymator, and because the exploded portion yielded phosgene

After WWI, Babcock (Ref 2) patented a mixt similar to Parazol for use in military expls. PA can be incorporated in such mixts

Toxicity. The crude material is more toxic than the purified. The crude material, when applied to the human skin for 2 hours, produced hyperemia and finally small vesicles, which developed into blisters contg a clear fluid after 48 hours. After 4 days, the latter started to heal. The dust and fumes were also toxic, and the irritant action of the fumes increased with temp (Ref 5)

Refs: 1) W.C. Cope, IEC **12**, 870 (1920) 2) J.H. Babcock, USP 1336048 & CA **15**, 947 (1921) 3) Marshall **3**, 72 & 238 (1932) 4) L. Wöhler & O. Wenzelberg, AngChem **46**, 173 (1933) 5) W.F. von Oettingen, "The Aromatic Amine and Nitrocompounds, Their Toxicity and Potential Dangers", US Public Health Bull **No 271**, Washington, DC (1941), 105 6) Davis (1943), 140

Paris Guns. See under Big Bertha, Paris Gun and Other German Big Guns of WWI and WWII in Vol **2**, B113-R

Parkes' Absorbent for Nitroglycerin. Materials patented in 1898 by Parkes, manufd by Chemische Fabrik at Winkel-on-Rhine, Ger, for use in Dynamites as absorbents for NG in lieu of the previously used kieselguhr. The absorbents were rubber-like materials, prepd by the action of sulfur chloride, S_2Cl_2, on vegetable oils. It was claimed at the time that Dynamites prepd with Parkes' absorbent were so insensitive, they could be used for loading shells

The absorbents could also be used for coating sensitive expls such as MF, PA, etc. For this, the powdered expl was mixed with a soln of Parkes' absorbent, and then gradually dried to eliminate the excess solvent

See also under Bielefeld's Gelatinization Method in Vol **2**, B113-L and Chemische Fabrik Dynamites in Vol **2**, C178-R

Ref: Daniel (1902), 134

Parlon (Chlorinated Rubber, Tornesit, Alloprene). A proprietary trade name (Hercules Powder Co) for a rubber chlorinated polyisoprene, $[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2]_x$, chlorinated approx 67% Cl by wt. A white coarse amorph inelastic or poorly crystd granular powder; mp 140° (softening point of film); d 1.56g/cc (solid), also given as 1.64g/cc and up. Sol in CCl_4, esters, aromatic hydrocarbons and ketones; insol in acet; unaffected by strong or weak acids or alkalies, salt spray, aliphatic alcs and hydrocarbons

The chlorination of rubber results in a complete reaction. There is not only addition and substitution of chlorine, but also cyclization along the polymer chains. The theoretical chlorine content for the completely chlorinated isoprene unit, $C_5H_6Cl_4$, is 68.5%. Parlon is marketed in five viscosity types. Stabilized Parlon usually contains 1% of an epoxy compd as a stabilizer to improve resistance to heat, ultraviolet light and moisture. Sunlight causes discoloration and embrittlement in unpigmented, unstabilized films. Parlon is resistant to dampness, soaps, molds and mildew

Parlon is nontoxic and nonflammable. It will ignite in the flame of a bunsen burner, but the flame is self-extinguishing. On burning, it melts, giving off bubbles of gas and chars

Parlon has been used in pyrotechnic tracer formulations as a color intensifier and binder (Ref 4). It is also employed as a base for rapid drying concrete paints and alkyd enamels (Ref 5)

Refs: 1) G.F. Bloomfield, JChemSoc **1943**, 289 2) "Parlon, Properties and Uses", Hercules Powder Co, Inc, Wilmington, Del (1957) 3) Anon, EngDesHndbk, "Military Pyrotechnics Series, Part Three–Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 221–22 4) Ellern (1968), 125 & 194 5) W. Gardner & E.I. Cooke, "Chemical Synonyms and Trade Names", CRC Press, Cleveland (1968), 488

Parone Explosive. A mixt consisting of 2p K chlorate and 1p CS_2, prepd in Italy at the end of the last century. On its first exptl firing in a 240mm mortar, it burst the mortar tube
Refs: 1) Cundill (1889) in MP **6** (1893) 2) Daniel (1902), 601 3) A. Pérez Ara (1945), 206

Parr Calorimeter (Parr Bomb). A device invented by S.W. Parr in 1912, and improved since then by the Parr Instrument Co of Moline, Illinois. It can be used to detn the heats of combustion of energetic materials by burning them with oxygen under pressure. Exptly, a weighed sample is ignited in an O_2 atm by an electrically heated wire in a closed combustion chamber or "bomb". The heat evolved during combustion is absorbed by a weighed quantity of water surrounding the combustion chamber. By observing the temp rise of the water, and knowing the energy equivalent of the calorimeter, the amt of heat released from the sample can be calcd (Ref 3)

It should be noted that, prior to Parr, other calorimeters existed which used oxygen under pressure for combustion in closed vessels, namely, those of Berthelot (1881) and its modifications and variations, Berthelot-Vieille, Moreau, Landrieu-Malsallez, and of the "Commission des Substances Explosives". Later bombs were those of Mahler (1892), Attwater (1899) and Kast (constructed at Chemisch-Technische Reichsanstalt, New-Babelsberg, near Berlin, Ger)

Parr not only improved the design of the above existing bombs, but reduced their cost by variations in mechanical details and by the use of new materials for the combustion chamber

See also under Calorimeter, Calorimetry and Calorimetric Determinations in Vol **2**, C10-L to C12-R
Refs: 1) Vennin, Burlot & Lécorché (1932), 62–66 2) Anon, "Van Nostrand's Scientific Encyclopedia", 4th Ed, D. Van Nostrand Co, Princeton, NJ (1968), 263–4 3) Anon, Fisher Scientific Co Catalog **74** (1974), 73

Parrott Gun. A type of muzzle-loading cast-iron rifled gun with a wrought-iron band shrunk around the breech for extra strength. It fired cylindroconical projectiles including shot, shell, case shot, and canister. Guns of this type, in calibers ranging from 2.9 to 10 inches, were used in the US Civil War era. They were invented by an American, R.P. Parrott
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 340

Particle Size Effects in Detonation. The raison d'etre for particle size effects in detonations was clearly stated many years ago in the following quotation from Eyring (Ref 1):

"All solid explosives in actual use are composed of grains. These grains may range in size from a few microns upward to single crystals some centimeters across. The granular structure is sometimes produced intentionally by milling the explosive, but even cast explosives are granular polycrystalline materials, as may easily be seen under the microscope or inferred from the fact that the density of cast explosives is below the single-crystal density

At first glance, it might be supposed that the granular nature of an explosive would be of no significance, that the high temperature in the detonation wave would first vaporize all the explosive, which would subsequently react according to the kinetic laws for homogeneous reactions. But this is not so. In the short time during which the explosive grain is exposed to the high temperature (a microsecond, more or less) the heat is unable to penetrate deeper than the surface layers. Consequently, each grain of explosive begins reacting at its hot surface, and the reaction progresses layer by layer until it reaches the center of the grain. The reaction for each grain within the reaction zone of a detonation is thus a sort of "cigarette burning", in which one layer of molecules is not ignited until the previous layer is consumed

This *grain-burning theory* is supported by two kinds of arguments: the first from the impossibility of heat conduction through a grain, and the second from the experimentally observed effect of grain radius on the reaction time"

Eyring et al then deduced the following eqns: The time τ required for complete reaction is merely the time required for the reaction to traverse the grain radius Rg:

$$\tau = \frac{1}{kr}\,\frac{Rg}{\lambda} \qquad (1)$$

Since the extent of reaction $N = 1 - (R/Rg)^3$, the rate law for grain-burning becomes:

$$\frac{dN}{dt} = \frac{3kr\lambda}{Rg}(1-N)^{2/3} \qquad (2)$$

where kr is the specific reaction rate (reciprocal mean life) for one molecule and λ is the molecular diameter. If grain-burning occurs in the detonation process, then according to Eq 1, the reaction time τ of such a process should be proportional to Rg the grain radius of the expl. There is a considerable body of circumstantial evidence that this is indeed the case (Refs 1, 8, 12, 13 & 15). Some of this evidence will be discussed below

Regardless of any theory, there is firm exptl proof that the particle size of a granular expl affects its steady detonation properties as well as its initiation behavior. In particular, the detonation velocity as well as the critical diameters of many granular expls depend on their particle size. The shock sensitivity of granular expls is also influenced by particle size. These effects will now be described

Steady Detonation.

Fig 1 (presented by Cook in Ref 3 for TNT at a bulk density of about 1 g/cc) shows that at a given diameter the detonation velocity, D, decreases as Rg increases. Note, however, that particle size effects disappear at larger column diameters

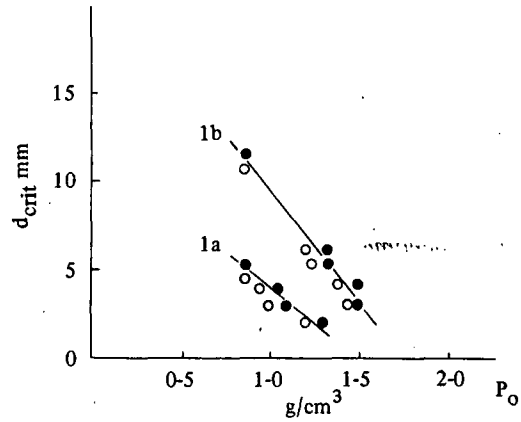


Fig 2. Critical diameter of TNT as a function of initial density. 1. Pressed or powder after Andreev and Belyaev (1960) (Ref 6). Grain size: (a) 0.01–0.05mm; (b) 0.07–0.2mm

For the more "sensitive" expls like PETN, the influence of particle size effects on D are much less pronounced that for TNT (unpublished work by the writer and Ref 2)

The critical diameter, d_c, of many "insensitive" granular expls increases with increasing particle size. This is shown in Fig 2 for TNT and the following tabulation for Picric Acid and for Ammonium Perchlorate

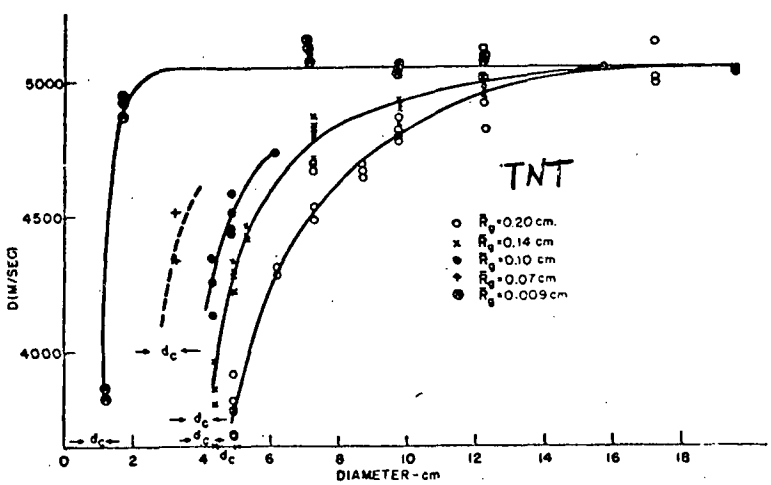


Fig 1. Theoretical versus Experimental D(d) Curves for TNT

	ρ_o (g/cc)	grain size (mm)	d_c (mm)
Picric Acid	0.95	0.1-0.75	9.0
(Ref 5)	0.95	"small"	5.5
Ammonium	1.00	0.006	1.9
Perchlorate	1.00	0.013	3.0
(Ref 10)	1.12	0.175	14

Initiation Phenomena.

A common test for the sensitivity, ie, the initiation susceptibility, of an expl is the detn of the *minimum priming charge* required to produce detonation. Baum et al (Ref 4) present the following tabulation to show that the min priming charge for several aromatic nitro compds decreases with their decreasing particle size

Name of Explosive	Min charge of Lead Azide, g	
	For particles passing thru a sieve with 2500 holes/cm^2	For particles obtained by pptn from a soln in water
Trinitroxylene	0.34	0.08
Trinitrobenzene	0.19	0.06
Trinitrotoluene	0.10	0.04

In initiating PETN by sparks generated by a *condenser discharge,* Romanov & Sten'gach (Ref 14) found that discharge energies for 50% expln increased with increasing PETN particle size. Similar effects are reported for several other expls (see Vol **5**, E43)

The effect of particle size on *DDT* (deflagration-to-detonation) transition is complex. Andreev & Chuiko (Ref 7) claim that the pressure above which PETN combustion becomes unsteady and accelerates decreases with increasing PETN particle size. Other studies suggest that there is an optimum particle size for DDT (see Sect VII of *Propellants, Solid* in this Vol). In a recent study, Bernecker et al (Ref 16) found that at a given degree of compaction, 20-micron Tetryl had a longer run-up to detonation, ℓ, than 470-micron Tetryl. This is shown in Fig 3

Exploding bridgewire initiation of PETN was studied by Blackburn & Reithel (Ref 9). They observed that transition to detonation is aided by fineness (actually increased specific surface) of the PETN particles

Probably the most studied initiation phenomenon is that of *impact initiation* (see Vol **7**, I35-R). Particle size does not appear to influence

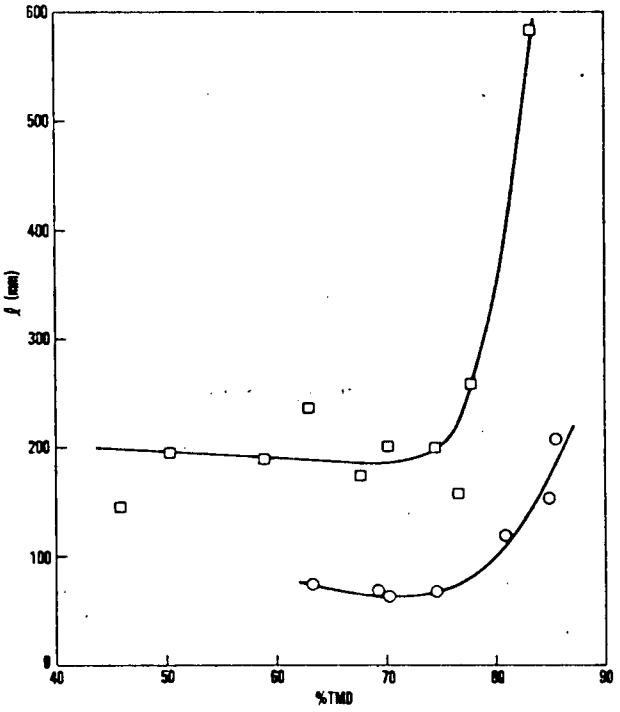


Fig 3. Effect of Compaction on Predetonation Column Length of Tetryl. (□ 20μ, ○470μ)

the impact sensitivity of granular expls. There is some evidence, however, that decreasing particle size makes impact more reproducible

Several studies have shown that the *shock sensitivity* of granular expls depends on expl particle size. The consensus is that the threshold shock pressure to initiate detonation in a given expl is *less* for large particles than for small particles. However, the converse is true when one considers run-up distances (or run-up times) to detonation. Thus at some pressure above the threshold for both large and small particles, run-up to detonation is smaller for small particle charges than for large particle charges

The above effects were observed for Tetryl by Seely (Ref 8); for RDX by the writer (Ref 12); for PETN, RDX & Tetryl by Scott (Ref 13); and for RDX & TNT by Dremin & Shvedov (Ref 15). The latter used a novel technique to demonstrate that small particles, once initiated, attain steady detonation more readily than larger particles. Their results for RDX are summarized in Fig 4. The insert graph shows the measurement method used, wherein u, the particle velocity, is observed as a function of time t

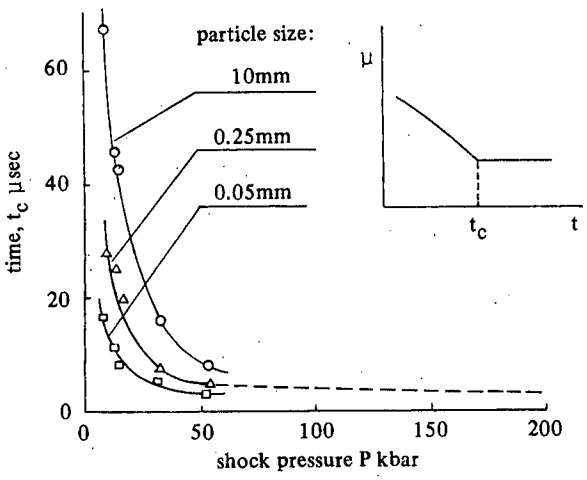


Fig 4. (From Dremin & Shvedov, Ref 15)

Blackburn & Seely (Ref 11) recorded the light given off during detonation of granular expls. They found that for coarse Tetryl or PETN, light was produced in discrete bursts whose dimensions were roughly equivalent to the dimensions of the interstices of the granular charges

To summarize, the particle size of a granular expl influences both its initiation and steady detonation behavior. Grain-burning provides an explanation for some of these effects. However, the lower shock threshold or discrete detonation for coarse-grain expls cannot be explained in terms of grain-burning. Possibly, as suggested by Seely (Refs 8 & 11), the operative mechanism in the latter is some form of flow stagnation

Written by **J. ROTH**

Refs: 1) H. Eyring et al, Chem Rev **45**, 144–46 (1949) 2) M.A. Cook, JACS **79**, 32 (1957) 3) Cook (1958), 129 4) Baum, Stanyukovich & Shekhter (1959), 83 5) Ibid, 349 6) Andreev & Belyaev (1960) 7) K.K. Andreev & S.V. Chuiko, ZhFizKhim **37**, 1304 (1963) & CA **59**, 6190 (1963) 8) L.B. Seely, Jr, Paper 23, Proc4thElectricInitiatorSymp (1963) 9) J.H. Blackburn & R.J. Reithel, ProcExploding-WirePhenomena 3rd, Boston, 153 (1964) & CA **63**, 9736 (1965) 10) W.E. Gordon, 4thONR-SympDeton, 184 (1965) 11) J.H. Blackburn & L.B. Seely, Jr, TransFaradSoc **61**, 537 (1965) 12) J. Roth, 5thONRSympDeton, 219 (1970) 13) C.L. Scott, Ibid, 266 (1970) 14) I.D. Romanov & V.V. Sten'gach, ZhPriklMekhTekhn-Fiz **1972**, 152 & CA **78**, 99953 (1973) 15) A.N. Dremin & K.K. Shvedov, Preprint 6thONRSympDeton (1976) 16) R.R. Bernecker et al, Ibid

PARTICLE SIZE MEASUREMENTS OF SOLID PROPELLANTS, EXPLOSIVES, AND PYROTECHNICS

The term "particle" and "particle size" are so highly ambiguous as to require precise definition. As used in this article "particles" will be limited by size to those distinct entities which have physically detectable boundaries in any direction within the limits of 0.05 and 10^4 microns (1 micron, μ = 0.001mm). This size range covers those particles which can be directly measured without magnification down to those which exhibit colloidal behavior

The performance characteristics of solid expls, proplnts, and pyrots, depending as they do on surface reactions, are strongly influenced by the size of the component particles. If a particle is a sphere its size is uniquely determined by its diameter in microns. Only rarely are powdered materials composed of spherical particles because on crushing or grinding, a laminated or bedded material always tends to produce slabs, monoclinic crystals tend to produce acicular particles, while isometric crystals tend to produce cubicle particles. Crystal form tends to be preserved regardless of fineness of subdivision of individual particles. If a particle is non-spherical the size is usually regarded as an equivalent spherical diameter (ESD), ie, the diameter of a sphere with the same volume as the non-spherical particle. Such a measurement is not always convenient to make; accordingly, the diameter of a circle whose area is equal to the projected area of the particle is generally the dimension used to express the sizes of irregular particles. This is the projected area diameter (da). These diameters are conveniently measured in the microscopic range (0.2 to 5.0μ diameter) with the ocular micrometer (graticule) invented by Patterson and Cawood (Ref 3). The graticule consists of a rectangle and a series of ten numbered circles and

corresponding discs engraved on glass. When inserted in the focal plane of a (X12) compensating microscope eyepiece, the rectangle, circles, and discs appear super-imposed on the field of view of the microscope. If a deposit of particles to be measured is placed on a microscope slide and properly focused in the field of the microscope, the images of the particles contained within the rectangle can be rapidly matched by eye against the discs or circles and their sizes determined from the parameters of the microscope and the known dimensions of the graticule. It is recommended that the deposit be so dispersed on the microscope slide that the number of particles observed within the rectangle averages about 6, and no particles overlap. The optical measuring technique is thus a fairly precise, absolute method of measuring particle size

When all the particles of a system are composed of the same-sized particles the system is mono-disperse, whereas different-sized particles compose polydisperse particle systems. The occurrence of monodisperse particle systems is rare, polydisperse particle systems are the most common. Thus, the particle sizes of any material are associated with their frequency of occurrence and a particle size distribution which can be determined by some form of particle size analysis.

The frequency of occurrence may be reported either as the number of particles or as the weight greater than or smaller than a stated range of sizes (Ref 38)

Two methods for representing size distribution graphically are given in Fig 1. The frequency distribution plot gives the fraction of particles (on whatever basis is desired) that lie in a given narrow size range as a function of the average size of the range (or of some function Ψ (D) of the average size). The lower curve of Fig 1 is a cumulative distribution curve, the integral of the frequency curve. Being an integral, the method of choosing size increments need not be selected or specified

The shape of a frequency distribution curve will depend on how the size increments were chosen. With the common methods for specifying increments, the curve will usually take the general form of a skewed probability curve with a single peak. However, it may also have multiple peaks, as in Fig 2. There are various analytical relationships for representing size distribution. One or the other may give a better fit of data in a particular instance. There are times, however, when analytical convenience may justify one. The log-probability relationship is particularly useful in this respect

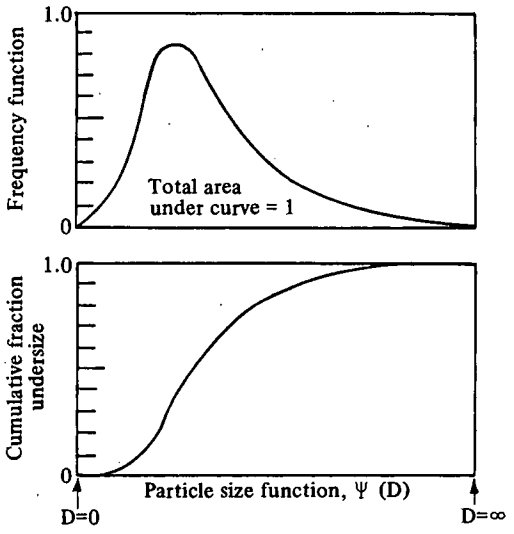


Fig 1 Frequency and Cumulative Distributions of Size

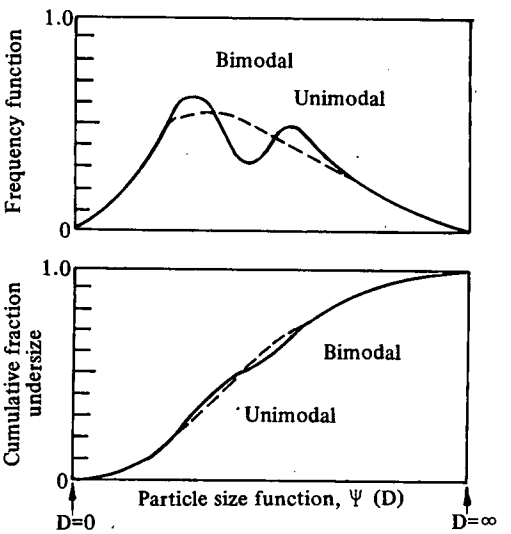


Fig 2 Comparison of Unimodal and Bimodal Distributions

The log-probability frequency distribution is given by Eq (1):

$$\frac{d\phi_x}{d\ \ell n\ (D/D_{mx})} = \left[\frac{1}{(\sqrt{2\pi})\ \ell n\ \sigma}\right] \exp\left\{-\left[\frac{\ell n\ (D/D_{mx})}{(\sqrt{2})\ \ell n\ \sigma}\right]^2\right\} \quad (1)$$

with ϕ_x = the cumulative fraction smaller than size D on a basis corresponding to x; D = the particle diameter; σ = the standard geometric deviation; and D_{mx} = median diameter on the basis of a property corresponding to x

The values of σ and D_{mx} are characteristic constants for a given size distribution. If a material follows a log-probability distribution on one basis (x), it also does on any other basis (y) – with the same value of the standard geometric deviation (σ) but a different value of median size (D_{mx}) corresponding to the new basis (y). This is a unique property of log-propability distribution (See Eq 2):

$$D_{mx} = D_{my} \exp\left[(x-y)\ \ell n^2\ \sigma\right] \quad (2)$$

A graph paper based on this type of relationship can be obtained. It permits convenient graphical representation of size distribution data (as shown in Fig 3) even if the distribution does not follow a log-probability relationship. In addition, the assumption of a log-probability distribution as an approximation permits simple conversion from one basis of representing size distribution, mean size, or median size to another basis

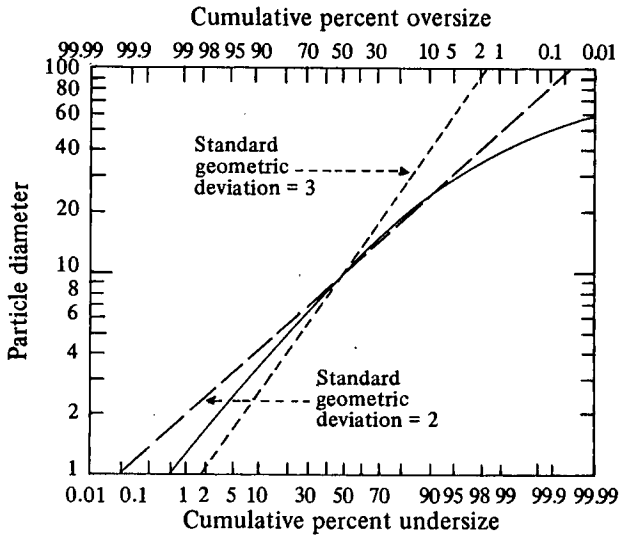


Fig 3 Typical Size Distributions Compared to Ideals

The solid line typifies the shape of curve shown by actual materials on this type of plot. If a material obeys a log-probability relationship, the plot on this graph paper is a straight line, as shown by the two dashed lines, and can be completely characterized by two numbers: (1) a median diameter, corresponding to the 50% cumulative size, and (2) a standard geometric deviation, a number equal to or greater than unity that is the ratio of the 84.13% to the 50% or the 50% to the 15.87% cumulative size

The median diameter is a measure of the general size level, whereas the standard geometric deviation is a measure of the degree of uniformity. A completely uniform material (all particles the same size) would show up as a horizontal line in Fig 3 and have a standard geometric deviation of 1.0. A completely heterogeneous material would be represented by a vertical line which would have a standard geometric deviation of infinity

Most materials will tend to approximate log-probability distributions at the fine end (usually with standard geometric deviations in the range of 2 to 3) and to level off at some upper limiting size, as indicated by the solid curve. Approximating the data by a straight line either in the fine range or over the entire range may, at times, be expedient because of the ease with which certain properties of the material can be ascertained analytically

Before beginning a size determination, it is customary to look at the material, preferably under a microscope. This examination reveals the approx size range and distribution of the particles, and especially the shapes of the particles and the degree of aggregation. If microscopic examination reveals that the ratios between max and min diameters of individual particles do not exceed 4, and indirect technique for particle size distribution based on sedimentation or elutriation may be used. Sedimentation techniques for particle size determination were first used by Hall (Ref 2) in 1904. He showed that the rate of fall of individual particles in a fluid was directly related to the particle size by the hydrodynamic law derived by Stokes from Newton's law of fluids in 1849 (Ref 1). This basic equation of the motion of a particle suspended in a fluid assumes that when subjected to constant driving force the particle acceleration is opposed by the

resistance of the fluid to motion. In Stokes Law as usually stated, the force of resistance to motion F_1 of a sphere is:

$$F = 3\pi\eta vd \qquad (3)$$

where d is the diameter of a sphere, η is the viscosity of the fluid, and v is the velocity of the particle. Although Stokes' Law is strictly applicable only to spherical particles, it has been shown by Irani and Callis (Ref 26) to apply to particles whose max-to-min-diameter ratio does not exceed 4 with only small error. When applied to non-spherical particles settling under the driving force of gravity, particle diameter in equation (3), d, is replaced by the Stokes diameter, d_{st}, which is the particle diameter averaged over all possible orientations of settling. In addition, particles smaller than 200μ settling in a viscous medium almost instantaneously reach a terminal velocity at which point the driving force (gravity) becomes equal to the resistance:

$$\frac{\pi}{6} d_{st}^3 \ (\rho_1 - \rho_2)g = 3\pi\eta v d_{st} \qquad (4)$$

where ρ_1 and ρ_2 are the densities of the particle and the suspending medium respectively, and g is the acceleration of gravity, which in turn reduces to:

$$d_{st} = \left(\frac{18\eta v}{(\rho_1 - \rho_2)g}\right)^{1/2} \qquad (5)$$

For particles smaller than 2 microns, settling times under gravitational forces become extremely long and subject to errors because of Brownian movement, so that in such cases centrifugal sedimentation must be employed. Stokes' equation holds strictly only at extremely slow motion in the hydrodynamic region of laminar or streamline flow (for Reynolds' number ($\leq$0.1)). The critical upper limit of particle size analysis by sedimentation is 63μ when w is the suspending medium. By using suspending media such as dioctyl phthalate the critical diameter may be increased up to about 3500μ

For size analyses of particles larger than $\sim$63μ, the geometric properties of uniformly constructed physical barriers such as sieves are commonly used. Though this technique of finished product size control dates back to at least 2500 BC when the Egyptians constructed woven cloth sieves for preparation of foodstuffs, it is only within the last 100 years that such devices were actually standardized for size analysis

No single method of size analysis is entirely satisfactory for application to the entire range of particle size exhibited by energetic materials. The choice of method from available resources depends largely upon the properties of the material to be analyzed, the basic significance or physical wearing of the measurement, and the purpose for which the information is required. For example, failure to disperse the particles as discrete entities is the biggest single problem in all size analysis methods that depend on individual particulate behavior. With microscopic techniques particles must be dispersed on the slide to permit observation of individual particles, and in sedimentation techniques the material must be suspended in the fluid so that the particles behave as individuals and not as flocs. In sedimentation or in "wet" sieving, the fluid medium chosen must be a dispersant as well as a non-solvent for the particles being analyzed. Most size measurement techniques do not measure size. They usually measure some phenomenon that is markedly, but not solely or uniquely, determined by size. To illustrate, in sedimentation analysis the discriminating property is the terminal settling velocity. In one type of sedimentation analysis particle concn as a function of time is measured (Ref 38). The concn measurement may be made either by gravimetric, or turbidimetric means; in the first case, yielding results on a mass basis while in the second, results are on a surface basis. There is a choice of methods available for particle size analysis (Table 1), and the following details of the methods which have been applied to energetic materials indicate what perticular methods can or cannot achieve, as well as the limitations of the data that are generated

Table 1
PARTICLE SIZING TECHNIQUES AND RANGES

	RANGE (microns)
DIRECT	
1. Microscopy	
a. Visible light	0.2-100
b. Electron beam	0.001-5
2. Coulter Counter	10-1000
INDIRECT	
1. Sieving	44 and up
2. Sedimentation	
a. Liquid	
(1) Pipette	2-50
(2) Hygrometer	2-50
(3) Manometer	2-50
(4) Balance	2-50
(5) Turbidimeter	2-50
(6) Centrifuge	0.05-50
b. Gas or Air	2-150
3. Elutriation	
a. Air	5-50
b. Air and centrifuge	2-50
4. Permeability	1-1000
5. Adsorption	
a. Liquid phase	0.01-5
b. Gas phase	0.01-5
6. Light scattering	0.05-1

DRY SIEVING OR SCREEN ANALYSIS WOVEN WIRE SIEVES

Sieving is probably the easiest and certainly the most popular method of size analysis but is restricted to powders having the greater portion coarser than 75μ. For finer powders the method is limited by the high cost of producing sieves with uniform, small apertures

A sieve is an open container, usually cylindrical, having definitely spaced and uniform openings in the base. The openings are square when wire or filter mesh is used and may be circular or slit shaped when the openings are formed by punching holes in a metal plate

If a series of sieves is stacked in order of increasing mesh size, when a known amount of powder to be analyzed is placed on the topmost sieve and agitated, the powder will then be classified on the individual sieves into fractions in accordance with the size of the particles and the size of the openings. Sieving takes place at the screen if and when: a) a fine particle is located above a vacant mesh; b) the cross section of the particle is smaller than the width of the mesh; and c) a force in terms of time and magnitude is present which moves the particle out of the material-to-be-screened and thru the mesh

A closed pan, a receiver, is placed at the bottom of the stack of sieves to collect the fines, and a lid is placed on top to prevent loss of powder; agitation may be manual or mechanical. Results are usually expressed in the form of a cumulative undersize percentage. The comparatively simple procedure of screening sometimes leads to the assumption that it most probably provides unequivocal results. This is a fallacy attested to by the in-depth investigations by Whitby in the USA (Ref 7) and Batel in Germany (Ref 9). Industrially, most sieving is accomplished by the steady-state approach in which particulate material is fed continuously at a constant rate into a sieving machine and the amount and quality of the material passing and the residue are measured. However, in the laboratory and for test purposes, the far simpler non-steady-state approach is used. In the usual procedure, a known quantity of the particulate material is placed on a screen or a stack of graded series screens and sieved by hand or in a mechanical device such as either a RO-TAP or an End-Shake (Ref 21) and the amount and quality of the particulate passing or retained as a function of time or per impact is measured

Whitby (Ref 7) discovered that in the non-steady-state with mechanical sieve shakers, the percentage passing versus sieving time curve could be divided into two regions with a transition between (Fig 4). Region 1 exists when there are many particles much less than the mesh size still on the sieve, while region 2 exists when the residue on the sieve consists entirely of near-mesh or larger particles

Region 1: It was further discovered that with mechanical sieving the rate at which material passes the sieve in region 1 is very nearly constant and obeys the following relationship:

$$\text{Percent passing} = at^b \qquad (6)$$

where: t = sieving time
b = a constant very nearly equal to 1
a = a sieving rate constant

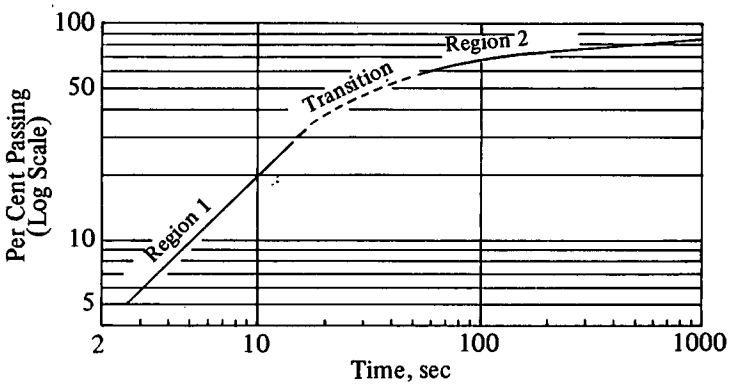


Fig 4 Typical Per Cent Passing - Time Curve

Further investigation revealed that the sieving rate constant was a function of several variables:

$$aW = C_1 \rho N S^3 \left(\frac{S}{k_s d_m}\right)^{1/\ln \sigma gp} \qquad (7)$$

where: W = Total load on sieve
ρ = Particle Density
S = Mesh opening
t = Sieving time
$K_s d_m$ = Geometric mass mean of the particle size distribution
N = Total number of mesh openings in sieve
σgp = Geometric standard deviation at a particular particle size on the size distribution curve
C_1 = Log-Log intercept of $aW / \rho N S^3$ at $S / k_s d_m = 1$

Characteristics of Region 1 (High Load) Sieving: a) Effect of load depth on sieve: Particle interaction influencing sieving rate extends only about 1 mesh opening above sieve; and b) the sieving rate is inversely proportional to the mean particle size for a given ratio of mesh opening to mean size

Effect of Material and Load: The sieving constant, C, increases geometrically with load. In addition there is a shape factor, a roughness factor, and a density factor such that:

$$C = F_s V^{R_s} \qquad (8)$$

where: R_s = a surface roughness factor
F_s = a shape factor
$V = w/\rho$

Rounded particles will have a high-load sieving rate roughly four times that of irregular particles. Rough-surfaced materials drop off in sieving rate, with increasing load at a much higher rate than do the smooth surfaced materials

Effect of Sieve Motion: C for the pure gyratory sifter was found to be about one-half the value for the Rotap sifter

Region 2: It was discovered that region 2 sieving followed a log normal law (Ref 19):

$$P = \frac{dN}{Nd(\log t)} = \frac{\log \sigma gp}{\log \sigma gt} \qquad (9)$$

where: P = probability
N = the number of particles on the sieve
t = time

This important relationship relates the probability of change to σgp (the log geometric standard deviation of the particle size) of the particle size distribution and to the σgt (the log geometric standard deviation of the time-weight curve) of the time-percent passing. It is based on the assumptions that the number of particles passing the sieve is proportional to the number that can pass the sieve at any instant, and that the passage of particles thru the sieve are independent random events. In other words, the relationship of particle size to the size of the mesh opening is of secondary importance, and that chance is the determining factor for passage of near-mesh size particles

In summary, it becomes obvious that sieving should be continued until region 2 is reached. A good procedure might be to plot the time-weight curve on log probability paper and then

Table 2

TYPES OF SIEVES

Country	Designation	Size Range
USA	A.S.T.M. E-11/39 (Fine Series) Tyler	37 to 5660
Netherlands	N480	50 to 850
France	AFNOR NF X11-501-1932	40 to 5000
Germany	DIN 1171 (1934)	60 to 5000
Great Britain	BSS 410 (1962)	76 to 3353

select as an end point a time at the beginning of region 2. Sieving error may be predicted from the relationship:

$$\Delta C(W)_{1\text{-}2} = \frac{100\,P_2}{\log \sigma gp}\,\phi(Z_m)\log\frac{t_2}{t_1} \qquad (10)$$

where: $\Delta C(W)_{1\text{-}2}$ = percent passing the sieve in the time interval t_1 to t_2, log σgp is the particle size distribution standard deviation; $\phi(Z)_m$ is the expected percent passing the sieve from the table of normal areas and ordinates; and P_2 is a constant for a given material and sieving method. Z_m is the mean value of Z (the number of standard deviations above or below the mean of a normal distribution) over a given time interval

A great variety of sieves has been suggested: The common sieves used for particle size determinations are made with woven-wire cloth and have square openings (Table 2). The sizes of screen openings have been standardized, and two standard series are used in the United States. These are the Tyler Standard Scale and the United States Sieve Series. Of these the Tyler series is the most useful. In it the sieve openings progress in the size ratio $1/\sqrt[4]{2}$:1. The designations and dimensions of the Tyler series are given in Table 3. The sieves shown in Table 3 have openings which are in the ratio $1/\sqrt[4]{2}$:1 with the preceding sieve openings. Every fifth sieve, therefore, will have openings in the ratio 1/2

Sieve Frames: Frames for all sieves of the fine series are of the standard 8-inch size, except that frames 3 inches in diameter may be used in case of sieves No. 100 and finer, used primarily in the testing of paint pigments. The standard frames are circular, 8 inches (20.32 cm) in diameter. The height of the sieve from the top of the frame to the cloth is either about 2 inches (5 cm) or 1 inch (2.5 cm). Sieves having a height of 2 inches (5 cm) are designated as full-height sieves; those having a height of 1 inch (2.5 cm) as half-height sieves. The permissible variation on the mean inside diameter, 3/16 inch below the top of the sieve, is plus 1/32 inch. The bottom of the sieve or "sieve skirt" is constructed as to have an easy sliding fit in any sieve conforming to the above permissible variations and in no case is this outside diameter less than 7.970 inches nor more than 8.000 inches. Pans and covers are so made as to be interchangeable with standard sieves

Mechanical Sieve Shakers: a) *"Ro-Tap" apparatus.* The "Ro-Tap" app is a mechanical shaker geared to produce 300 plus or minus 15 gyrations and 150 plus or minus 10 taps of the striker per minute; b) *"End-shake" apparatus.* This is a mechanical shaker with a sieve arrangement for half-height and full-height sieves. In this app, the nest of sieves reciprocates in a direction lengthwise of the gear box. The end-shake testing sieve shaker is a product of the Newark Wire Cloth Company of Newark, NJ

Dry Sieving Particle Size Determination: The number of sieves used for a given determination depends largely upon the reason for making the determination. If a particle size distribution must be obtained, five sieves is often a satisfactory number

The sieving operation starts by mounting the sieves in a nest, the coarsest at the top. The sample is placed on the top screen, and the screens are shaken for several minutes. It is generally impossible to screen a sample completely; the longer one shakes the screens, the more material comes thru, although to a continu-

Table 3

Fine Series[1] — Nominal Dimensions, Permissible Variations, and Limits for Woven Wire Cloth of Standard Sieves

Size or sieve designation	Sieve opening		Permissible variations in average opening	Permissible variations in maximum opening[2]	Nominal wire diameter[3]	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Mm	Inch (approximate equivalents)	Percent, plus or minus	Percent, plus	Mm	Inch (approximate equivalents)
5660 micron (No 3½)	5.66	0.223	3	10	1.68	.0661
4760 micron (No 4)	4.76	.187	3	10	1.54	.0606
4000 micron (No 5)	4.00	.157	3	10	1.37	.0539
3360 micron (No 6)	3.36	.132	3	10	1.23	.0484
2830 micron (No 7)	2.83	.111	3	10	1.10	.0430
2380 micron (No 8)	2.38	.0937	3	10	1.00	.0394
2000 micron (No 10)	2.00	.0787	3	10	.900	.0354
1680 micron (No 12)	1.68	.0661	3	10	.900	.0319
1410 micron (No 14)	1.41	.0555	3	10	.650	.0285
1190 micron (No 16)	1.19	.0469	3	10	.650	.0256
1000 micron (No 18)	1.00	.0394	5	15 [2]	.580	.0228
840 micron (No 20)	0.84	.0331	5	15 [2]	.510	.0201
710 micron (No 25)	.71	.0280	5	15 [2]	.450	.0177
590 micron (No 30)	.59	.0232	5	15 [2]	.390	.0154
500 micron (No 35)	.50	.0197	5	15 [2]	.340	.0134
420 micron (No 40)	.42	.0165	5	25 [2]	.290	.0114
350 micron (No 45)	.35	.0138	5	25 [2]	.247	.0097
297 micron (No 50)	.297	.0117	5	25 [2]	.215	.0085
250 micron (No 60)	.250	.0098	5	25 [2]	.180	.0071
210 micron (No 70)	.210	.0083	5	25 [2]	.152	.0060
177 micron (No 80)	.177	.0070	6	40 [2]	.131	.0052
149 micron (No 100)	.149	.0059	6	40 [2]	.110	.0043
125 micron (No 120)	.125	.0049	6	40 [2]	.091	.0036
105 micron (No 140)	.105	.0041	6	40 [2]	.076	.0030
88 micron (No 170)	.088	.0035	6	40 [2]	.064	.0025
74 micron (No 200)	.074	.0029	7	60 [2]	.053	.0021
63 micron (No 230)	.063	.0025	7	60 [2]	.044	.0017
53 micron (No 270)	.053	.0021	7	60 [2]	.037	.0015
44 micron (No 325)	.044	.0017	7	60 [2]	.030	.0012
37 micron (No 400)	.037	.0015	7	60 [2]	.025	.0010

1 The micron designation of the fine sieve series represents a strong trend among users of precision sieves toward the use of the micron terminology in reporting particle sizes. The openings of successive sieves from the fine series progress in the ratio $\sqrt[4]{2}:1$, and in selecting sieves from this series it is customary to take each sieve in a given range, every alternate sieve, or every fourth sieve

2 For sieves from the 1000 micron (No 18) to the 37 micron (No 400) size inclusive, not more than 5 percent of the openings shall exceed the nominal opening by more than one-half of the permissible variation in maximum opening

3 The average diameter of the warp and of the shoot wires, taken separately of the cloth of any sieve shall not deviate from the nominal value by more than the following:

Sieves coarser than 590 microns – 5 percent
Sieves 590 microns to 125 microns – 10 percent
Sieves finer than 125 microns – 15 percent

provided, however that for sieves finer than 125 microns, for a period not to exceed one year after the adoption of this specification, the wire diameters heretofore permitted in this specification will be in effect

ously diminishing extent. Therefore, if the results of sieve tests are to be compared, the method of shaking and the time of shaking should be standardized as in **MIL-STD-1233** (Ref 21). This involves placing a 100g sample on the wire mesh of the top sieve of a nest of five sieves, shaking on a mechanical shaker for 30 minutes, and weighing the portion of the sample retained on each sieve. The sieves in the nest are of progressively finer mesh, so the weights of the portions retained on the screens constitute a set of classified particle size distribution data

For powders which may be classified dangerous, such as finely divided Ti and Zr and mixts containing these powders, the shaking machine should be grounded and wherever possible the operation carried out behind a suitable barricade by remote control. Operators should observe all safety precautions, including the use of proper clothing, and a liq antistatic agent should be used to coat the screens and frames. A preferable alternative is to use wet sieving (see below) as well as in instances where agglomeration due to static charges may be expected

Finally, the weight percent of the sample retained on each sieve is calcd by dividing the weight of powder on each sieve by the total weight of powder recovered. The percent of powder finer than the corresponding size of the opening on each sieve, in microns, is then plotted on log-probability paper against the size of the opening of the respective sieve, and a straight line of best fit is drawn thru the plotted points. The geometric mean, which represents the average size, is obtained by reading the 50 percent size. The standard deviation, which represents the distribution of the particles is determined by reading the 84.1 percent size and dividing this value by the 50 percent size

Calibration of Sieves: The US National Bureau of Standards recommends measuring the diameter of five to ten wires, making four measurements for each wire. Then the number of wires per centimeter is detd and the average size of the opening calcd (Ref 15). Alternatively, the sieves can be sent to the National Bureau of Standards for checking. It is also ad-

Table 4

Variation in Results for Wet Sieve Tests

(Tests run on a No 325 sieve at 10psi water pressure and nozzle described in ASTM Tentative Method C115-38T; and C430-75)

Material Sample No	Sample, g	Time, min	Screen, inches	Percentage Passing
Silica, D-2	1.0	1	2	78.8
	10.0	1	2	76.7
	10.0	5	2	78.4
	50.0	10	8	77.8
	50.0	5	8	74.4
	10.0	a	8	78.0
Mica, 432	1.0	1	2	82.5
	50.0	10	8	80.7
Slate, 470	1.0	1	2	82.5
	100	10	8	93.8
Coal, C	1.0	1	2	73.4
	50.0	10	8	64.1
Galena, G	1.0	1	2	65.3
	100	10	8	57.6
Silica, W-1	1.0	1	2	70.3
	20.0	5	8	73.5
Cement, 114c	1.0	1	2	90.0 [b]

a = Wet sieving without nozzle but with light brushing

b = Standard cement sample, certified percentage passing 89.2

visable to check sieves with a standard sample to make sure that proper results are being recorded (Ref 15). Carefully sized fractions of glass beads are available from the National Bureau of Standards for calibration purposes (Ref 36)

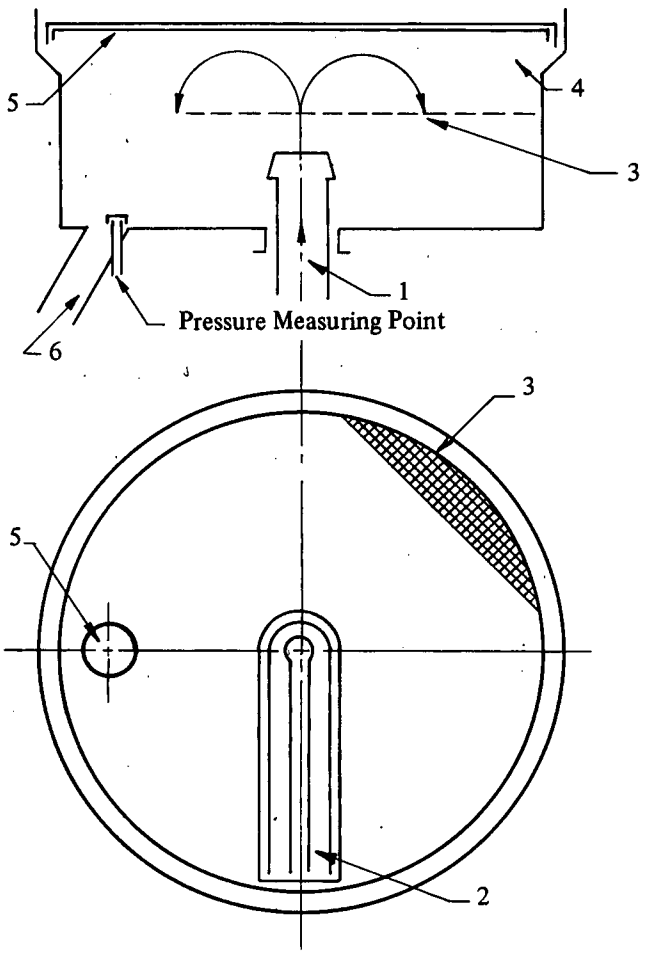
Recent studies with different materials have shown that accurate sieve analyses of fine powders can be assured only when the sieves are precalibrated with samples of the particular material whose size distribution has been determined by an independent method (Refs 8 & 14)

WET SIEVING

Sieving in which a liquid is used to "wash" the material thru the screen. Wet sieving techniques are of value for such substances as the primary explosives Lead Azide and Lead Styphnate (Ref 41) which are not only hazardous in the dry state but which tend to agglomerate from the static charges generated during dry sieving. Water or an organic non-expl nonsolvent is the preferred suspending liq. The ASTM Standard Method of Test for Fineness of Hydraulic Cement using the No 325 (45-micron) sieve is a simple, wet sieving procedure for obtaining results that can be readily duplicated. In this method a 2-inch diameter screen is sprayed with w from a nozzle at a definite pressure for a definite time (Ref 45). A comparison of some sieve data by this method for different materials is shown in Table 4

AIR JET SCREENING

The Alpine Air Jet Sieve test equipment employs a novel vacuum sieving and mixing technique (Ref 9) which has been used to provide rapid and accurate information on the particle size distribution produced in grinding Ammonium Perchlorate (AP) used as an oxidizer raw material in solid rocket proplnts (Ref 17). The principles of vacuum sieving are not new. In conventional vacuum sieving, large particles tend to lodge in the sieve, blocking the sieve opening. However, the Alpine device incorporates a continuous sweeping arm with a narrow aperture along its length, on the underside of the sieve screen, thru which a jet of air passes upward thru the screen. The jet of air dislodges particles from the sieve, thus allowing effective separation as illustrated in Figure 5. The undersized particles are drawn thru the sieve by the air returning, via a suitable filter, to the suction side of a fan. The air jet method apparently overcomes several of the inherent disadvantages of conventional particle size determination. In the Tyler Ro-Tap method, clogging of the material in the sieve is experienced below 60 microns, and the particle size is determined only to approximately 44 microns. On the other hand, the Micromerograph (see below) requires tedious technician effort and lengthy test time.



Air is drawn thru the pipe to the nozzle (1); air passes thru slot in the rotating nozzle (2) to clean the wire mesh (3). The sieve chamber is sealed by a plastic lid (5). The test material is raised and fluidized in the space between the wire mesh and the lid (4). Suction is applied to pipe (6) to draw the particles thru the sieve openings

Fig 5 Schematic Diagram of the Air Jet Sieve

Comparative tests performed on a Ro-Tap unit, a vibrating unit (Sonic Sifter – Allen-Bradley), and the Alpine Air Jet Sieve are shown in Figs 6 and 7. Fig 6 is a powdered cement; Fig 7 is cadmium stearate, a waxlike material which clogs easily. These separations were all made on a 42 micron mesh sieve. These tests showed that the Alpine Jet Sieve effected good separations in a matter of minutes compared with the much longer times required for the other systems

The particle size distribution of AP was determined and compared using the Ro-Tap, the Alpine Air Jet Sieve and the Micromerograph. For this purpose six different samples of ground AP were chosen and separated using sieves calibrated with National Bureau of Standards spherical glass beads. The results were plotted of cumulative percent retained against the respective effective sieve openings. The average relative deviation between Ro-Tap and Alpine in the 44 to 149-micron range was found to be 4.0 percent (Fig 8). In the 25 to 75-micron range, with Alpine and Micromerograph instruments, the average relative deviation between the two methods was found to be 4.6 percent (Fig 9)

It was concluded that approximately three minutes sieving time was adequate with the air-jet sieve even with waxlike materials such as cadmium stearate; whereas, 20 minutes or longer was required for vibrating or shaking screens. The data presented (Refs 19 & 35) for AP by the Alpine, Tyler Ro-Tap, and Micromerograph agree remarkably well

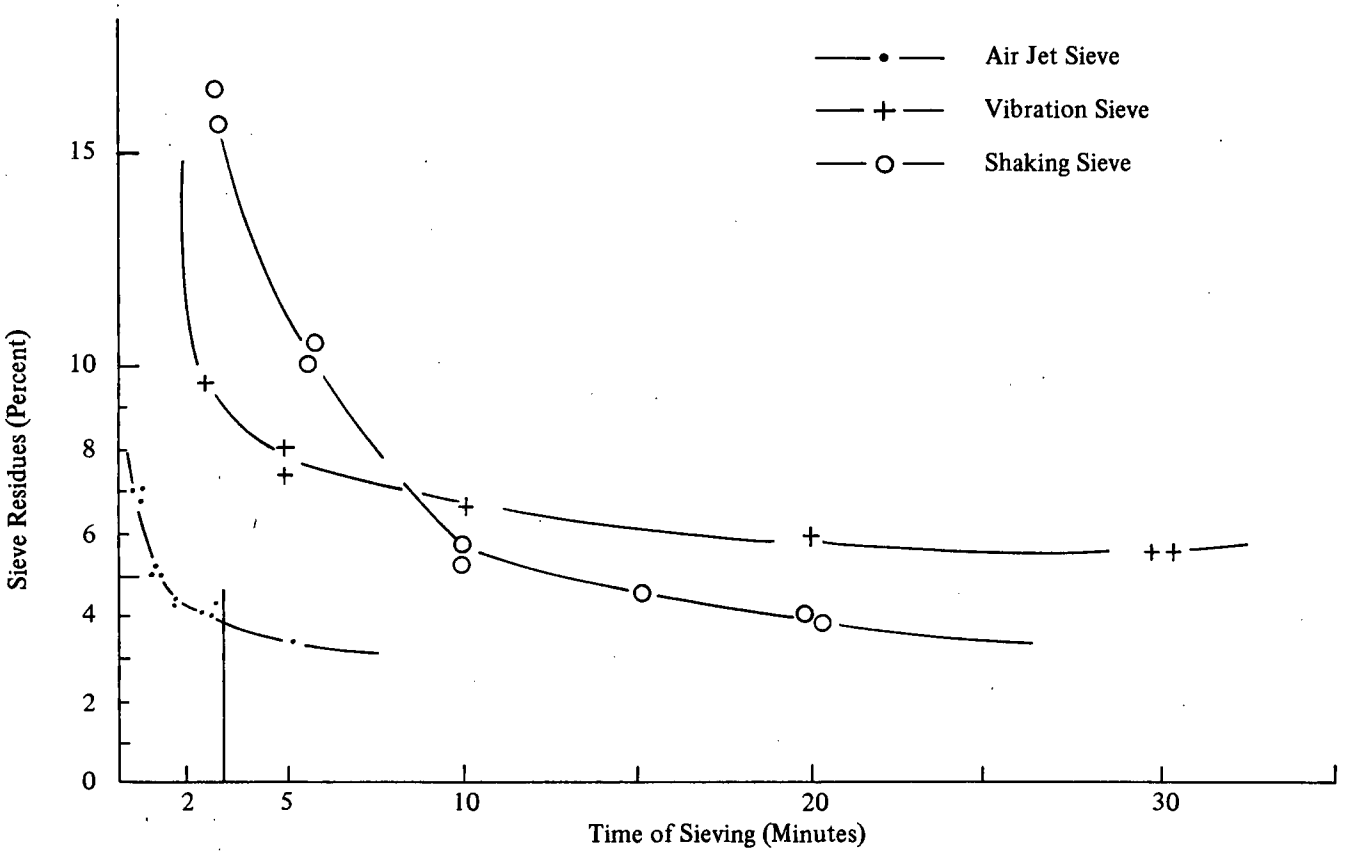


Fig 6 Sieving of Cement (Sieve Opening 42)

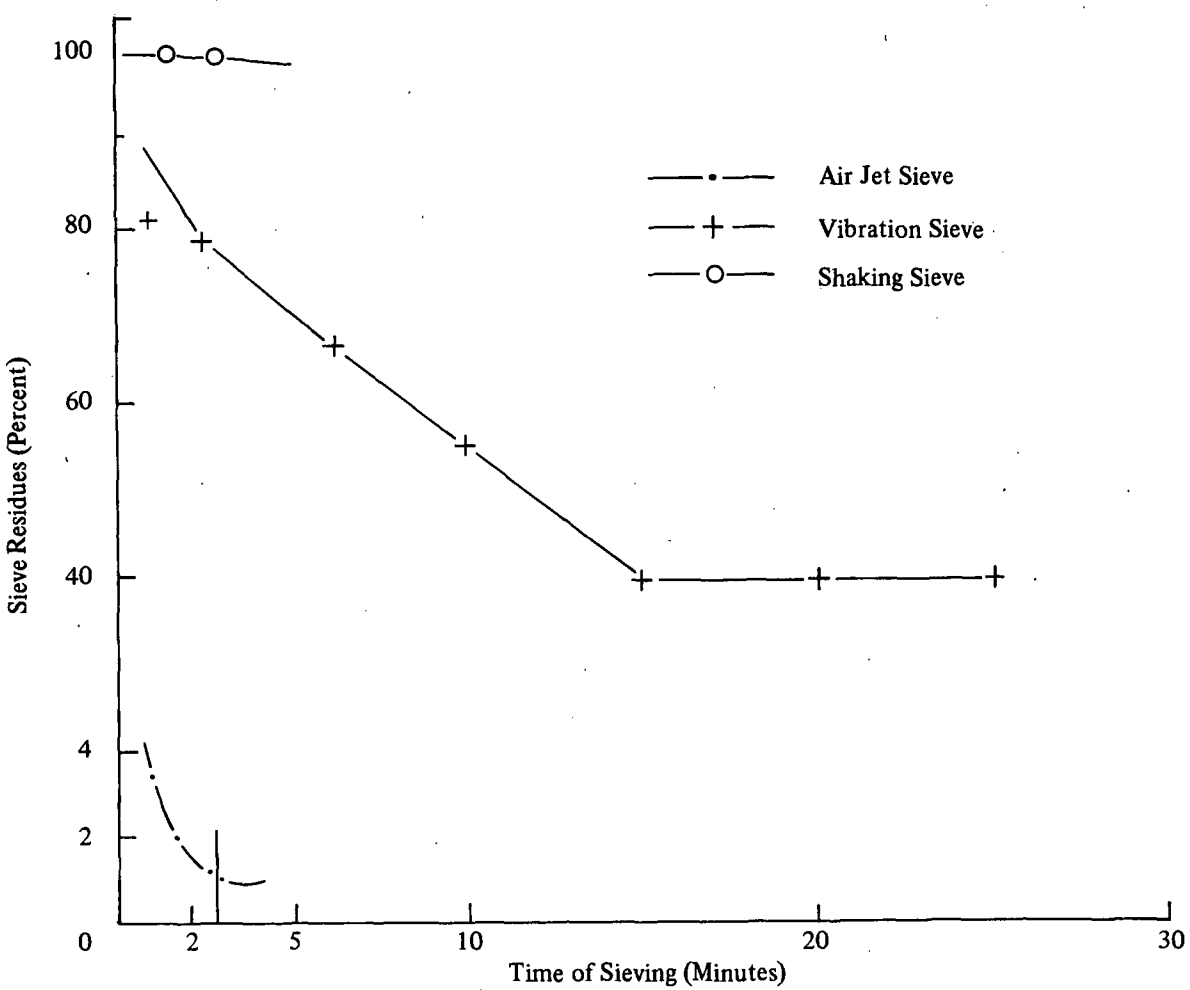


Fig 7 Sieving of Cadmium Stearate (Sieve Opening 42)

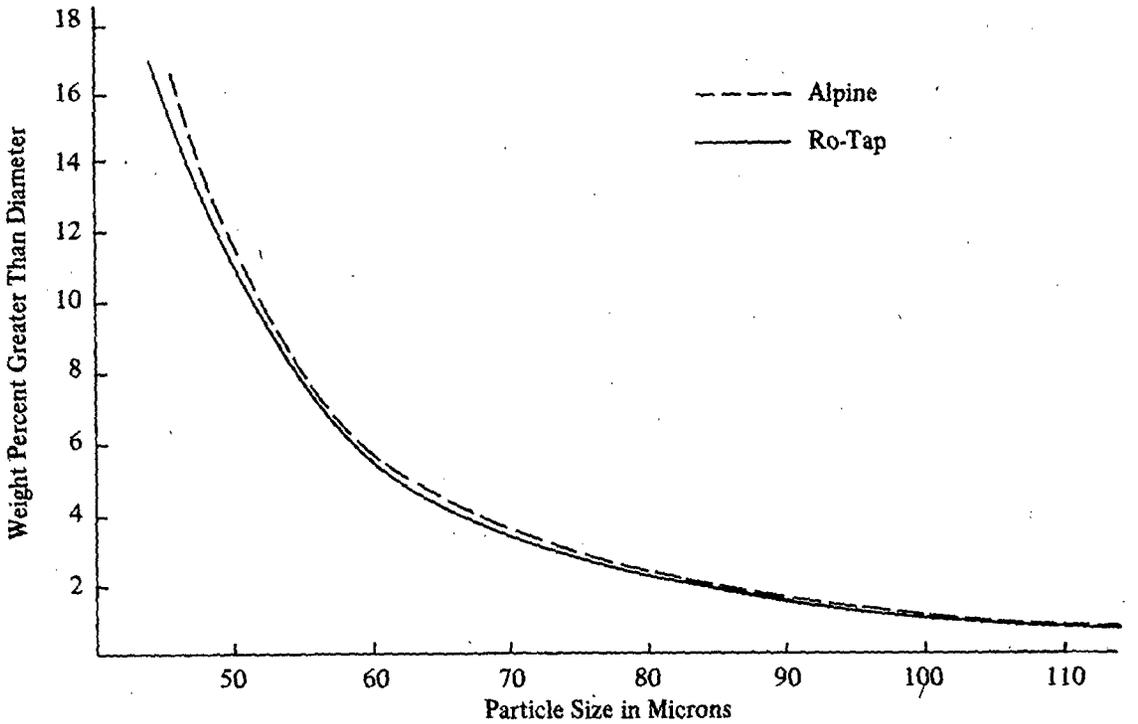


Fig 8 Comparison of Ro-Tap and Alpine Air Jet

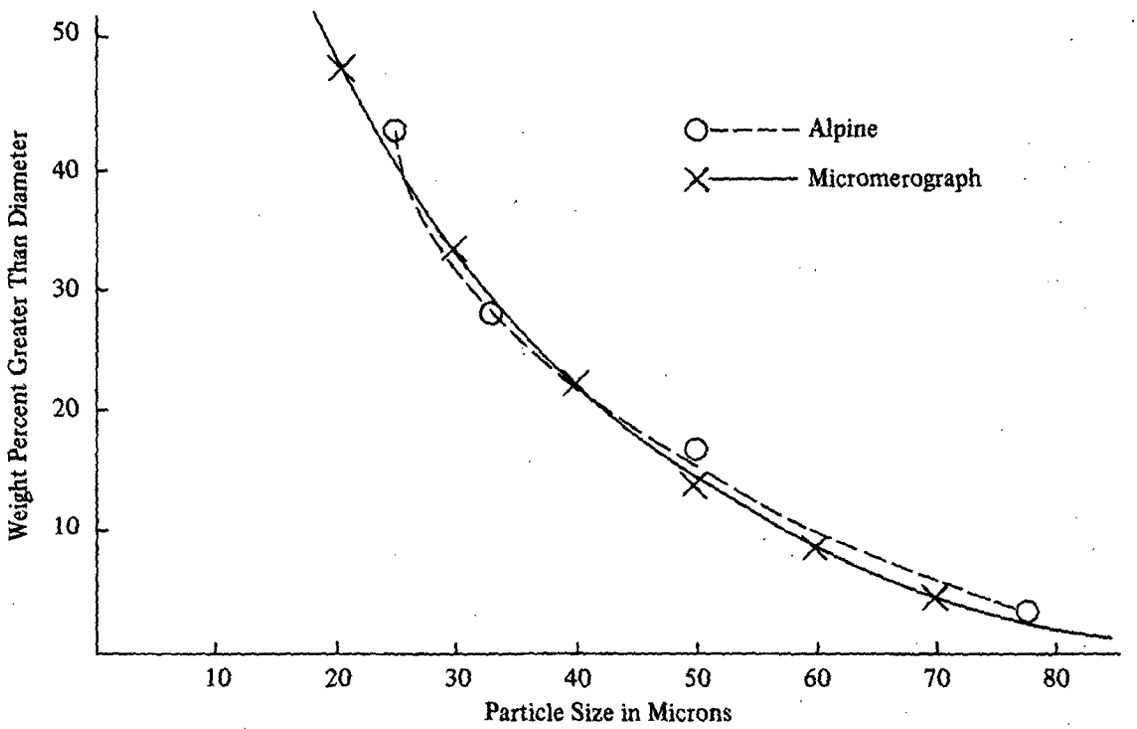


Fig 9 Comparison of Alpine and Micromerograph Tests

ELECTROFORMED SIEVES

The fact that the smaller woven mesh sizes are of little use for precise work has led to the introduction of the so-called micro-mesh sieves formed of nickel by a photoengraving and electroplating technique. The fragile micromesh is bonded to a supporting grid electrolytically and soldered in a 3-inch brass frame. Daeschner et al (Ref 11) first described the application of sieves in the range of 10–20 micron (Buckbee Mears Co, St Paul, Minn) to the particle size distribution of cracking catalysts. The tolerances are much finer than in conventional woven wire sieves, the aperture being guaranteed to within 2μ of the nominal size. Most of the variables associated with the use of woven-wire sieves are present in the use of micromesh sieves. Variables in the sieving procedure may be of two types: (1) those associated with the app, and (2) those pertaining to the particle

Sample Size: It is generally considered that the ideal quantity of sample is one that covers each sieve one particle deep. A more meaningful and more easily calcd estimate is the number of particles per sieve opening. Therefore, with electroformed sieves a sample not greater than 1.5g should be used. This amount corresponds roughly to 15 to 20 particles per 45μ opening and depends in practice upon the particle density and the size distribution. It is recommended that the amount of sample taken for analysis should result in a distribution of not more than 20 particles per opening for any one sieve (Ref 11)

Sieving Motion: The sieve shakers commercially available are designed to handle 8-inch sieves and, therefore, are unnecessarily bulky and powerful for a stack of 3-inch sieves. For this reason they are generally modifieid to permit use of 3-inch sieves by elevating the sieves and adding additional weight to the vibrating platform

Sieving Time: Because sieving time depends upon the type of sieving motion and the provision for continuous movement of the sample over all parts of the sieving surface, the only requirement for sieving time appears to be that shaking be continued until equilibrium conditions are reached

For some time very fine sieve plates have been made in the Netherlands (Ref 32). Unlike the American micro-mesh sieve gauze, the openings of this plate are round and conical, as a result of which the open area percentage is smaller than of the micro-mesh gauze (Table 5)

Table 5
Open Area of Micro-mesh Sieves

Nominal Opening in microns	Open Surface Area, %
Micro-mesh,* square	
5	1.2
10	3.5
20	11
30	25
45	28
90	44
Microplate, # round	
15	2.5
40	15

* American Manufacture
\# Dutch Manufacture

An advantage of this, however, is that the sieve plate is more robust and less liable to be damaged. Owing to the conical shape of the openings, the danger of clogging is at a minimum (provided the sieve is used in the right direction). Figure 10 shows a cross-sectional drawing of this Dutch micro-mesh sieve plate

For substances with particles of 20 microns and coarser, sieving with these sieves is possible in many cases by the normal dry methods. To obtain optimum results, however, it is advisable to use a liq. With sieves of 15 microns and finer,

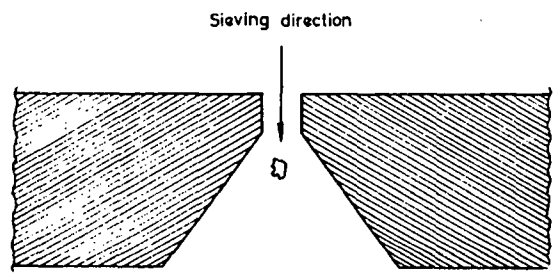


Fig 10 Cross-section of one of the round, conical openings of the Dutch micro-mesh sieve plate

dry sieving is very difficult or even impracticable. The following is the procedure recommended by The Central Technical Institute of the Netherlands (Ref 32): The sieve is dried at 70° to constant weight. After cooling in a desiccator, about one gram of the sample is put on the sieve and weighed accurately to ± 0.2mg. Next, the sieve is very carefully immersed and supported in a beaker of non-solvent, low-viscosity liq. The sieve is then raised and lowered so that the liq flows back and forth thru the openings and the fine particles pass thru. By generating ultrasonic vibrations of 40kc/sec in the bath with a suitable generator, the sieve openings can be prevented from clogging. The liq in the bath is repeatedly replaced at five minute intervals until no further passage of particles can be visually observed. Next, the micro-mesh sieve is dried at 70° together with the retained sample and, after cooling, weighed on an analytical balance, and the percentage retained for the relative sieve opening determined

Micro-mesh sieves have been applied to the determination of solid proplnt ingredients (Refs 17 & 35) and similar materials where sieve analyses are required with great accuracy in the very fine range. They are also applicable to specific problems such as the analysis of magnetic powders, and of powders consisting of mixts of substances of different specific gravities or the preparation of clearly defined particulate fractions in a short time

The particle-size distribution of two test powders, spherical glass beads and crushed quartz was determined with different types of app (Ref 32), and indicate that the micro-mesh sieve data is in good agreement with those of other methods (Table 6):

Table 6

Comparison of Particle-Size Analyses by Various Methods

Percentage greater than limit determined with:

Particle limit in microns	Bahco	Sedimento-meter	Sediment balance	Pipette (Andreasen)	Micro-mesh sieves	Coulter Counter
			Sample: quartz			
2	91	89.5	94	91.5	–	94
3	85	86	91.5	87	–	91.5
4	81	83	88	82	–	88
6	74	78	81.5	74.5	–	81.5
8	67	74	77	70	69	76
10	60	70	71.5	65	–	71.5
15	46	58.5	61	52.5	54	64.5
20	31	49	44	44	43	55
30	25	30	24.5	26	23	40
40	–	19	10	15	12	28.5
			Sample: Spherical glass beads			
2	97.5	96.5	98	–	–	98.5
3	95	95	97	97.5	–	97.5
4	92	93	96	95	–	95.5
6	87	87.5	92	90.5	–	93
8	83	82.5	87	86.5	87	90
10	77	78	84	80	84	86
15	66	67	73	69	73	72
20	54	58	63	56.5	62	63
30	46	44	48.5	42.5	43	51.5
40	–	28	36	–	26	27

Irani and Callis (Ref 14) used two parameters of the distribution of ground monocalcium phosphate (which follows the commonly used log normal distribution law): namely, M_g and σ_g, the geometric mean diameter and the geometric standard deviation, to evaluate the precision and accuracy of electro-formed sieves vs sedimentation as a reference procedure:

Two samples in two size ranges by two operators:

	95% Confidence Precision	
	M_g	σ_g
Replicated five times–Sieves	± 2.6%	± 6.0%
Replicated seven times–Sedimentation	± 7.8%	± 9.6%

Although the screens are more precise than sedimentation, they could not be more accurate because they were calibrated from the sedimentation values

Eleven samples not used for calibration of sieves:

	95% Confidence Accuracy	
	M_g	σ_g
Geometric mean diameter and standard deviation between electro-formed sieves & sedimentation	± 4.7%	± 4.6%

The foregoing close agreement of the geometric mean diameter and geometric standard deviation results indicates that accuracy evaluations were made on an absolute scale, and did not refer to some arbitrary scale

To evaluate the effect of shape factors of particles, the electro-formed sieves were calibrated microscopically with two different materials:

Table 7

Calibration of Sieve Openings – Microns

Sieve	A	B	C
Microscope	44 ±2	28±2	20±2
Ground Monocalcium Phosphate	45±3	23±2	14±1
Spherical Glass Beads	47±1	33±2	18±1

It is evident from the above that micromesh sieves must be calibrated for every material and sieving method for which they will be utilized. When properly calibrated, precision, electro-formed micromesh sieves are useful as reliable primary standards for determining particle size distributions of energetic materials. They are characterized by the following significant features: 1) the uniformity of the openings is such that a precision of 1 to 2 per cent is easily attainable; the accuracy for spheroidal particles, is equal to that by microscopic measurements; 2) the micromesh openings may be reliably measured with a microscope; 3) because of the physical size of the sieves, the sieving rate may be precisely and conveniently followed with an analytical balance and the degree of blinding and agglomeration followed with an ordinary microscope; and 4) compared to the use of woven-wire sieves, the micromesh sieves require less sample and less sieving time, and, because of the uniformity of openings which are in a single plane, the micromesh sieves blind less and give a more accurate separation according to particle diameters

ELUTRIATION PROCESSES
(Fluid Moving)

Elutriation differs from sedimentation in that fluid moves vertically upwards and thereby carries with it all particles whose settling velocity by gravity is less than the fluid velocity. In practice, complications are introduced by such factors as the non-uniformity of the fluid velocity across a section of an elutriating tube, the influence of the walls of the tube, and the effect of eddies in the flow. In consequence, any assumption that the separated particle size corresponds to the mean velocity of fluid flow is only approximately true; it also requires an infinite time to effect complete separation. This method is predicated on the assumption that Stokes' law relating the free-falling velocity of a spherical particle to its density and diameter, and to the density and viscosity of the medium is valid

In this method, the free-falling velocity of particles of selected size, in still air, is counterbalanced by an upward, uniform flow of air or gas at the same (free-falling) velocity. Particles

smaller than the selected size will be carried away and collected, while larger particles will fall. This method is not suitable for fractionation in the 0 to 5 μ range and is, therefore, recommended for those powders whose particle size distribution is such that knowledge of the amount contained in the 0 to 5 μ range (as well as amounts in the coarser ranges) will suffice. The method is strictly accurate for solid, spherical particles of a limited size range and becomes progressively less accurate with increasing particle diameter, with increasing departure from the spherical shape, or with increasing porosity

The rate of air flow may be determined directly from charts supplied by the manufacturers or calculated from Stokes' equation as follows:

$$V = 10^{-8} g\, Pd^2/18N \qquad (11)$$

where: V = velocity of a falling spherical particle in still air or gas, cm/s
g = gravitational constant, 980 cm/s^2
P = absolute density of particle, g/cm^3
N = viscosity of air or other gas
d = diameter of particle, μ

Thus, at 20°C, for air:

$$V = 29.91 \times 10^{-4} \times Pd^2 \qquad (12)$$

The volume rate of air flow, F, in cubic centimeters per minute required to balance the settling velocity of the largest particle which it is desired to float is given by the following equation:

$$F = 47.1 \times V \times D^2 \qquad (13)$$

where: V = free falling velocity, cm/s
D = diameter of the settling chamber, cm

Gravitational Methods

GONELL AIR ELUTRIATOR. This is the prototype of all analytical separators with laminar air flow. It consists of a cylindrical brass tube (or a series of tubes) with a conical base. An air inlet is provided in this base on the axis of the tube. The sample of powder is placed in the inlet cone, and air is blown thru the largest tube until separation is deemed complete, or for specified periods of time. The residue is removed, weighed, and transferred to a smaller diameter tube, and the test is repeated. The tube should have polished internal surfaces and should be periodically tapped or vibrated to disturb settled powder

Batel (Ref 9) pointed out that because the air flow thru the elutriator is streamline, the velocity gradient across the tube diameter is parabolic. The max velocity at the center of the tube is twice the average velocity. It is expected that this velocity distribution has a similar effect upon the analytical results that variations in screen has upon screening analyses, and sharp separations are not possible. He also found that particle sizes in the separation process depend upon the duration of elutriation as shown in Fig 11:

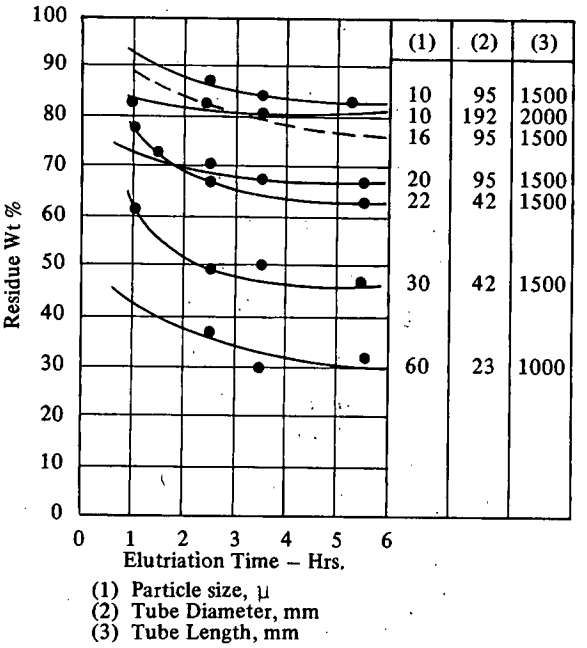


Fig 11 Effect of elutriation time on the amount of residue in the glass attachment of the Gonell Separator for different tubes and air mounts

From several values given above, the characteristic granularity curves were set up as function of the elutriation time:

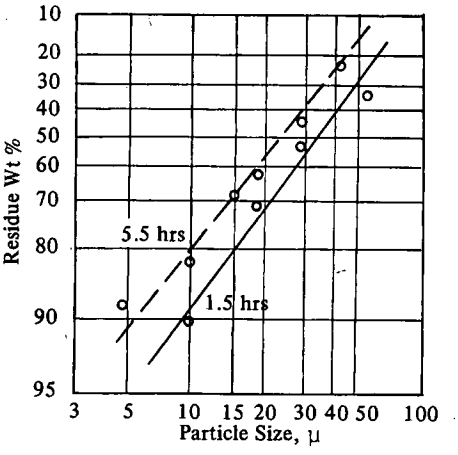


Fig 12 Relation of the granularity characteristic curves to the elutriation times at 5.5 hours and at 1.5 hours in the Gonell Separator

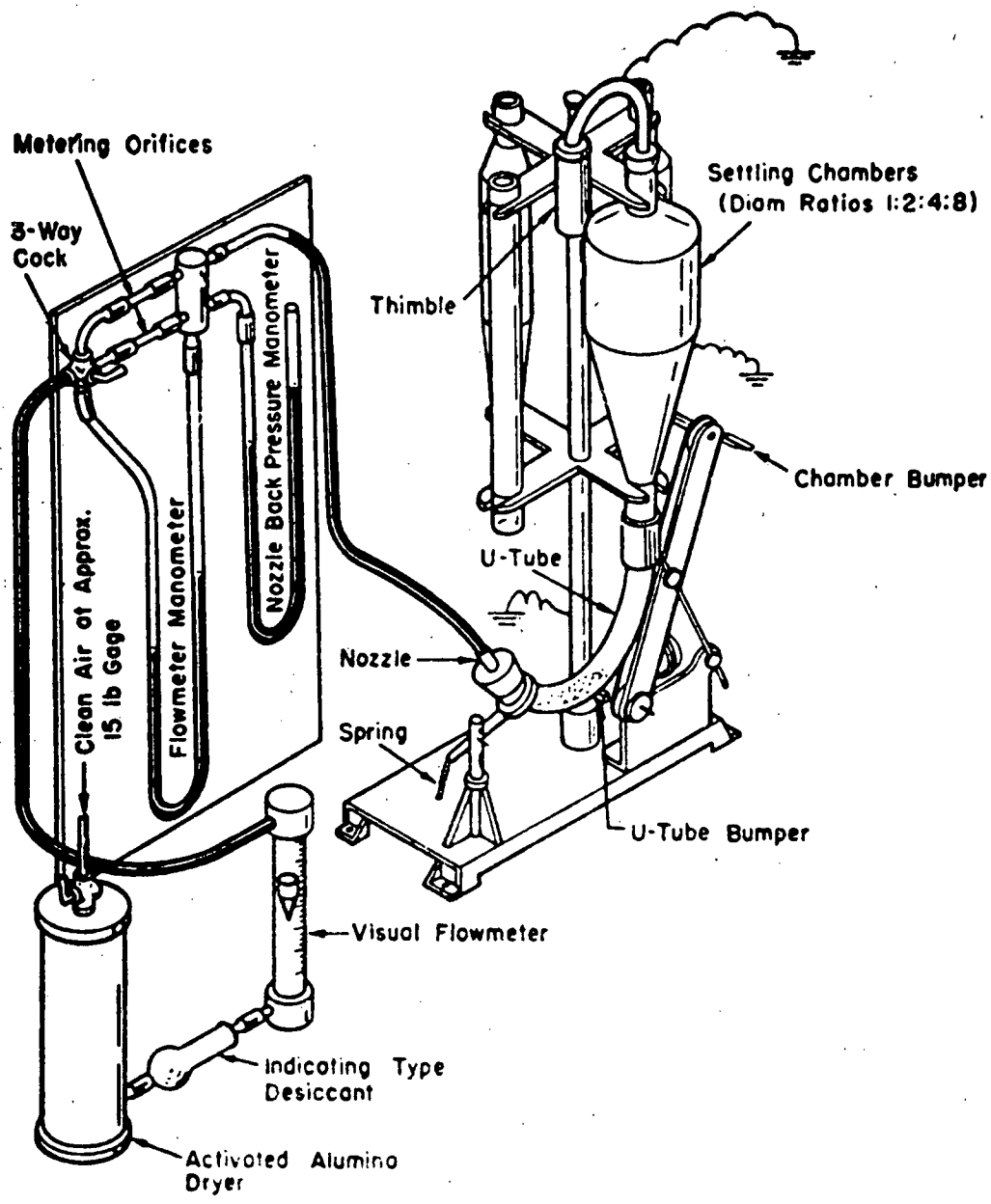


Fig 13. Air Classifier for Subsieve Particle Size Analysis

ROLLER AIR ELUTRIATOR. The app consists essentially of a series of vertical settling chambers of different diameters (in the ratio of 1:2:4:8) in which the uniform upward flow of air is maintained (Ref 42). These are interchangeably connected as shown in Figure 13, at the lower end to a blowing tube (U-tube), in which the sample is dispersed, and at the upper end to a collection system which is usually an Alundum extraction thimble. The app is arranged to provide for the direct impingement of a high-velocity air or gas jet against the powder sample and for the recirculation of the uncollected fraction. Duchesne and Reite (Ref 35) evaluated this instrument for the analysis of castable rocket proplnts. Optimization of particle size distributions was the first objective, with high solids processing and the availability of reliable methods for the determination of this parameter being important. The Alpine Air Jet Siever had been used for those powders coarser than 32 microns; however, the finer particles of Al and of AP were of considerable concern. Even though the Micromerograph failed to sediment the entire sample of castable rocket proplnt it was commonly accepted as the principal app for fine powder analysis. For these reasons the Micromerograph was experimentally compared to the Mine Safety Appliances app (M.S.A.), Whitby Liquid Sedimentation app (Ref 12) and to the Roller Air Analyzer (Ref 42). Results are summarized in Fig 14 for Al powder. Consider-

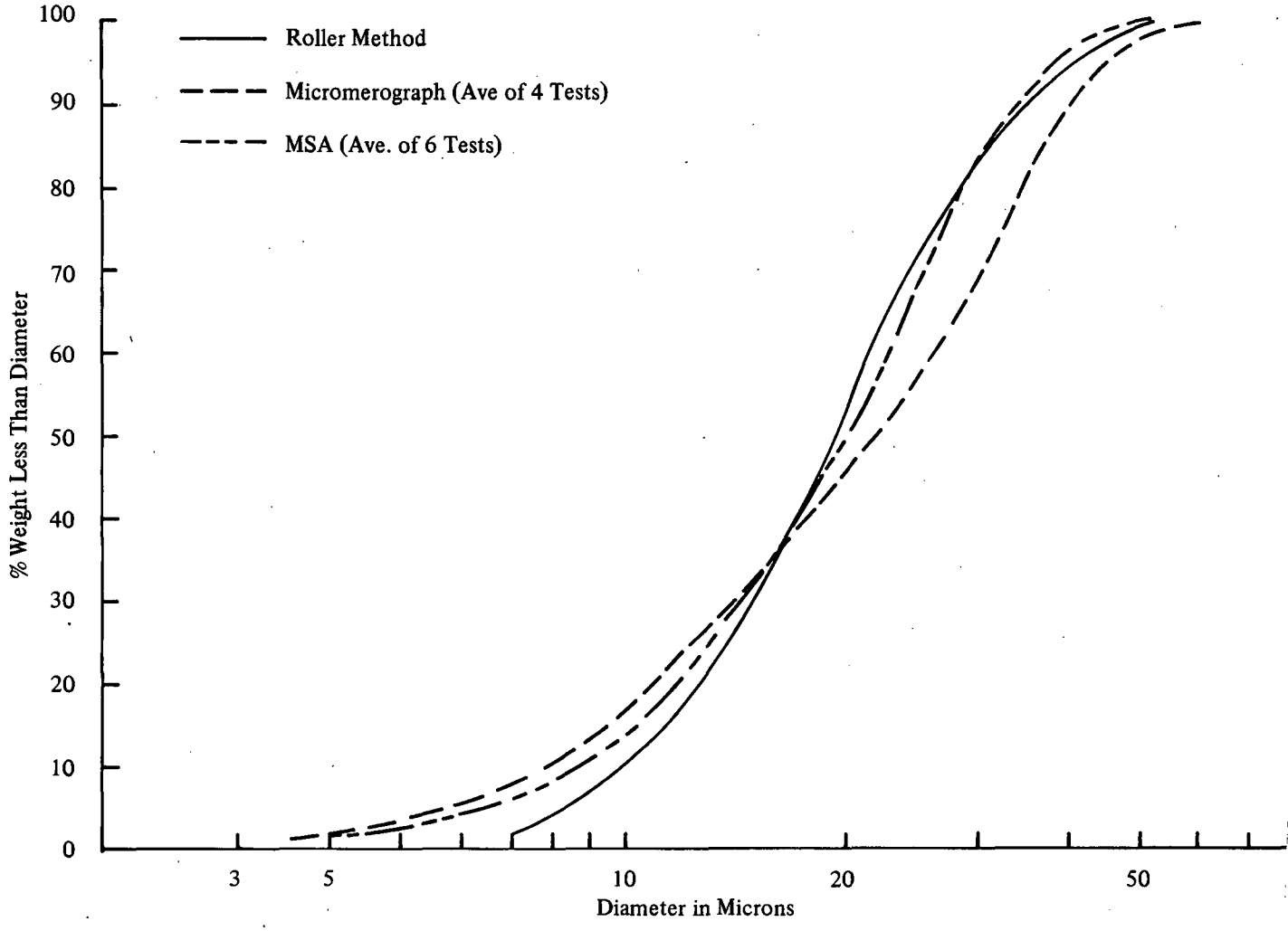


Fig 14 Comparison Between Three Test Methods for Particle Size Distribution of H-15 Al Powder

ing the major differences in techniques, the bias between the three methods was quite acceptable. Earlier, Eigsti and Dwiggins (Ref 16) had found the Roller instrument unsuitable for the particle size determination of chemical delay compns used in solid rocket proplnt systems, because once the sample was separated into fractions by the elutriator, each fraction would need to be analyzed by some other method to determine its actual size distribution. Also, if 10% or more of the particles were less than 5 μ in diameter, a complete fractionation would require about 8 hours, considered to be a prohibitively long time

Centrifugal Methods

Efforts to overcome the problems of long elutriation times of the gravitational separators led to the development of centrifugal separators, since the falling speed of the particles can be increased by using centrifugal fields. Then the law of resistance for the laminar free-falling velocity is replaced by that for the turbulent free-falling velocity. This fact, as well as the difficulty of allowing for the velocity field of the air, precludes a calcn of the particle size for analytical purposes. These analytical separators are, therefore, calibrated with spherical granules. Since the resistance in turbulent air currents also depends upon the particle shape, this calibration is only conditionally valid for technical powders in which particle shapes deviate more or less from the spherical shape.

BAHCO CENTRIFUGAL CLASSIFIER. This is a proprietary instrument that is essentially a centrifugal air elutriator. Air and dispersed powder samples are drawn thru the cavity of a rotating hollow disc in a radially inward direction against centrifugal forces. The powder particles are thus divided into under- and oversize fractions, collected, and weighed. Separation into different size-fractions is made by altering the air velocity. About 20g of sample are required for analysis, and 8 size determinations can be made in 2 hours (Ref 10)

Batel (Ref 9) made a comparison of separation and sedimentation results as shown in Figure 15. The results of separation by Bahco, Gonell, and Air Jet tie in very well with the results of sedimentation (Andreasen and Sartorius)

SEDIMENTATION PROCESSES
(Fluid Static)

Sedimentation processes are those in which the rate of settlement of particles in a static fluid is measured, the analysis being either with the particles uniformly dispersed thruout

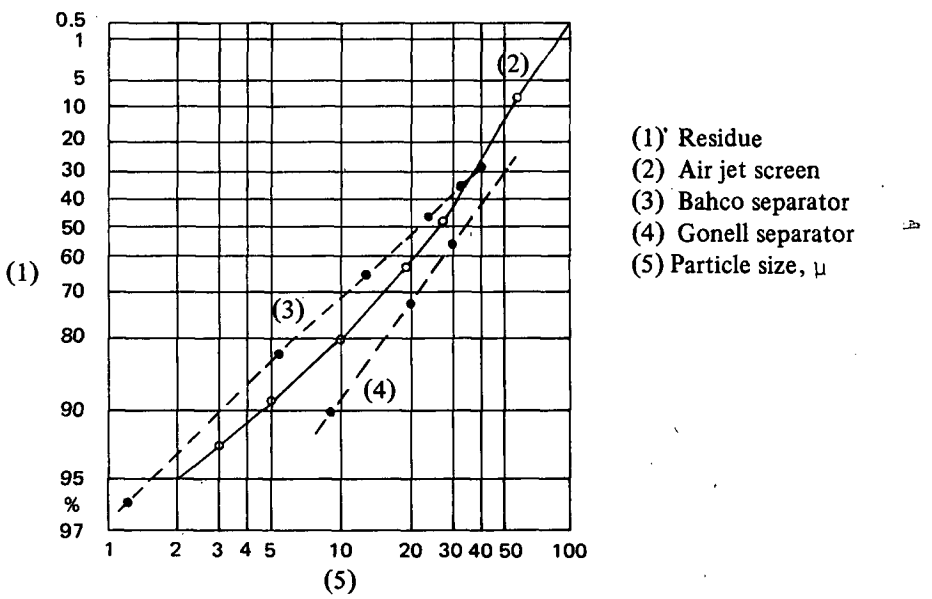


Fig 15 Granularity characteristic curves of an identical quartz dust obtained by different analysis methods

the whole of the fluid, or introduced at the top of a column. The rate of sedimentation usually follows Stokes' law, and settlement may be under conditions of gravitational acceleration, or under centrifugal acceleration, imposed by rotation of the entire system, in order to increase the rate of sedimentation. Stokes' law is valid only in the regime of viscous flow, which sets an upper limit to the size of particle that can be tested by this means in a given fluid. The limit is determined by the magnitude of the Reynolds number, which should not exceed 0.2 if the error when Stokes' law is used is not to exceed 5 percent. The concn of the suspension should always be as low as possible in order to avoid interference between particles, particularly since "clouds" of particles tend to move *en masse* and not individually. The method of measurement, eg, by weighing, may dictate a lower limit of concn beyond which inaccuracies become unacceptably high

Effective dispersion of the particles is an essential prerequisite for all methods of sedimentation analysis. It is often necessary not only to stir the suspension vigorously prior to analysis, but to introduce the powder already mixed with a dispersing agent. A further agent to prevent flocculation may be needed, and it may be necessary to adjust the pH of the suspension to a suitable value determined by experiment

Sedimentation Columns: Liquid

A suspension uniformly dispersed in an upright cylindrical vessel at time t = 0 begins to settle immediately. If two horizontal planes, p_1 and p_2, are taken at depths h_1 and h_2 below the upper surface ($h_1 > h_2$), then, at time t, the mass of suspension remaining between p_1 and p_2 will be determined by $(h_1 - h_2)\sigma$, plus particles that have fallen thru p_2 minus particles that have fallen thru p_1, where σ = mass per unit depth of original suspension

For incremental methods of analysis, the sample is theoretically taken from an extremely thin layer in which h_2 is nearly equal to h_1; for cumulative methods of analysis, the amount settling in a particular plane in a given time, normally at the bottom of the settling vessel, is measured

MSA-WHITBY PARTICLE SIZE ANALYZER. The main features of this method are that it uses gravitational settlement followed by centrifugal sedimentation. A thin layer of the sample suspension is superimposed on a column of clear liq so that all particles begin to settle from the same level. The initial suspending medium is chosen to have a density slightly less than that of the sedimentation liq. The amount of solid sample required for the analysis is a few milligrams

The app consists of a glass centrifuge tube, 14mm internal diameter, ending at the bottom in a graduated capillary tube, 1 mm internal diameter as shown in Fig 16. A feed- or sample

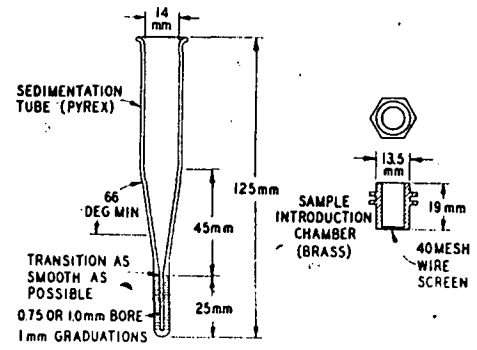


Fig 16 Sedimentation Tube and Sample Introduction Chamber

introduction-tube is provided. This is a short metal tube that fits easily into the mouth of the glass centrifuge tube

In operation, the centrifuge tube is filled with the sedimentation liq to within 10mm of the top. The feed-tube is then filled with the sample suspension and the upper end is closed by the operator's finger. The feed-tube is then placed in the centrifuge tube with the suspension in contact with the column of clear sedimentation liq; this starts the sedimentation. The finger is then removed

Gravitational settlement is allowed to proceed for 4 to 10 minutes, according to the particle-size range of the sample. The sedimentation tube is then centrifuged to reduce the time required for the smaller particles to reach the bottom. By measuring the volume of particles accumulated as a function of time, the equivalent spherical size distribution of the sample may be computed from formulae based upon Stokes' law. In addition to the specially designed sedi-

mentation tubes, the major items of app include two to four constant speed centrifuges (300 rpm to 3600 rpm) driven by hysteresis-type synchronous motors, having stable starting and stopping characteristics, including a max rate of acceleration of five radians per second and the ability to be stopped and started by an interval timer

The principal steps in this method are as follows: 1) select sedimentation and dispersion liqs and determine density of the sample; 2) calculate a particle size-settling time table for gravity settling and for various centrifuge speeds; 3) disperse the sample in dispersing liq; 4) prepare the sedimentation tube and initiate the run by introducing the sample dispersion; 5) record the readings of the sediment height (to the nearest 0.1mm) in the capillary of the sedimentation tube at the times previously calculated for the various particle sizes; and 6) calculate and plot the cumulative size distribution curve from the size-time table

Procedure: (1) In selecting the sedimentation and dispersing liqs to be used, several factors need to be considered. Obviously, the liqs must be inert to the material to be examined and must be miscible with each other. Both must also adequately disperse the sample during sedimentation or suitable surface-active agents must be added. For convenience, the viscosity and density of the sedimentation liq should be such that the largest particles present do not settle out sooner than 10 sec after the start of the run, since it is difficult to obtain the first reading before this time

(2) The time required for a spherical particle to settle under gravity to the bottom of the tube is derived from Stokes' law:

$$t = \frac{18 \times 10^8 \nu h}{(p_1 - p_0) g d^2} \qquad (14)$$

where: ν = viscosity of the sedimentation liquid, poise
h = total settling depth, cm
p_1 = skeletal density of sample, g/cm^3
p_0 = density of sedimentation liquid, g/cm^3
g = gravitational acceleration constant, cm/sec^2
d = Stokes equivalent particle diameter, μ

During the gravity settling period sample particles become classified, all particles larger than or equal to a certain diameter, σ, will have settled to the bottom of the centrifuge tube, while all particles smaller than this diameter will have settled a lesser distance. If the succeeding settling under centrifuging took place at constant speed, the derivation of a table of desired centrifuge times corresponding to various diameter particles would be straightforward. However, the centrifuge is actually started and stopped between readings so that a small correction, α, must be determined and added for each speed and centrifuge. Cartwright and Gregg (Ref 12) in their investigation of the particle size distribution of Ammonium Nitrate described a procedure for calculating α and incorporating it in the derived formula for centrifuge settling time:

$$t' = \frac{18 \times 10^8 \nu}{(p_1 - p_0) w^2 d^2} \ln \frac{r_2}{(r_0 + d^2 h/\sigma^2)} + \alpha \qquad (15)$$

where: t' = Centrifuge settling time
w = angular velocity of centrifuge, radians/sec
r_0 = distance from rotation axis to surface of sedimentation liquid in tube, cm
r_2 = total distance from rotation axis a particle settles = r_0+h, cm
σ = diameter of last particle just sedimented during gravity settling portion of run, μ
α' = centrifuge start-stop correction, sec

As mentioned, the data obtained by this method are expressed as cumulative size distribution curves. Since the computations assume Stokes' law for spherical particles, the plotted curves give the distribution of spherical particles which would behave like the actual sample with respect to this experiment. For this reason, the sizes on the distribution curves should be labelled "Stokes Equivalent Diameter". Because of the underlying assumptions and the above interpretation of the results, it is clear that the repeatability of this method has more meaning than accuracy of comparison with results of other methods

Data given in Table 8 and Fig 17 for a ground Ammonium Nitrate illustrate the degree of re-

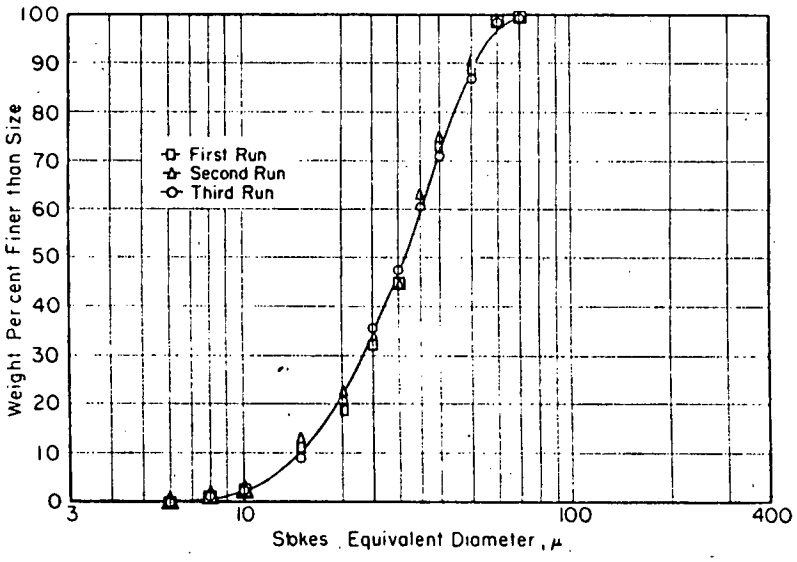


Fig 17 Sedimentation Analysis of Ammonium Nitrate

peatability possible with this technique. The max deviation from the individual mean is 1.2 weight percent and the average deviation is 0.5 weight percent

For the particle size measurements of boron and barium dichromate, components of pyrotechnic delay compns, Freeman (Ref 46) evaluated the M.S.A. Particle Size Analyzer versus microscopy, gravitational liq sedimentation, electrostatic resistivity change, and permeability to fluid flow technique. The conclusion was that the M.S.A. Analyzer was the only available app suitable for the analysis of particle size distribution of substances containing particles as small as 0.1 micron. In initiating the analysis of new materials by this method it was found that evaluation of dispersing agents and methods was the most time-consuming phase.

Table 8

M.S.A.-Whitby Particle Size Analyzer
Data for Ammonium Nitrate

Stokes' Equivalent Diameter, μ	Sediment Height, mm			Weight Finer than Size, percent			
	1st Run	2nd Run	3rd Run	1st Run	2nd Run	3rd Run	Mean
70	0.02	0.02	0.02	99.8	99.8	99.8	99.8
60	0.1	–	0.1	98.9	–	98.8	98.8
50	1.1	1.0	1.2	88.3	89.2	87.8	88.4
40	2.6	2.5	2.8	72.3	73.1	71.4	72.3
35	–	3.5	3.9	–	62.4	60.2	61.3
30	5.1	5.0	5.1	45.8	46.0	47.7	46.5
25	6.2	6.1	6.3	34.0	34.4	35.7	34.7
20	7.5	7.3	7.8	20.2	21.7	20.4	20.8
15	8.4	8.2	8.9	10.6	11.6	9.5	10.6
10	9.2	9.1	9.6	2.1	2.2	2.0	2.1
8	9.3	9.2	9.7	1.0	1.1	1.0	1.0
6	9.4	9.3	9.8	0	0	0	0

The selection of an optimum surfactant, or combination of surfactants, was necessary primarily to prevent re-agglomeration of the dispersed sample while settling. In addition, it was demonstrated that the use of a blender (Waring) was an effective aid in dispersing these two components. The violent action of the blender did not cause a change in the concn of coarse particles in the dispersion with increasing blending times up to 17 minutes

Alley and Dykes (Ref 39), as well as Abbot et al (Ref 37), conducted studies of the M.S.A. method, especially suitability of the method for use as a standard specification procedure for the oxidizer used in double-base proplnts, based on an estimate of its precision. Single analyses of two different Ammonium Perchlorate samples, having weight median diameters in the range of 20–30 microns, were made by each of nine laboratories thru use of the same liq sedimentation technique and calibrated equipment. The precision of analyses was considered to be adequate, and the fact that a number of laboratories are successfully using the procedure supports this conclusion. However, the method was not recommended as a standard specification procedure for the particle size analysis of nominal 20- to 30-micron Ammonium Perchlorate, because of the large systematic error among laboratories in the determination of specific surface area. This could be due to some deficiency in the analytical procedure that permits the introduction of variations by the laboratory personnel. One likely source of inconsistency is in the dispersion of the Ammonium Perchlorate particles. The accuracy of the method was not estimated in this study because a standard Ammonium Perchlorate sample of accurately known particle size was not available. A highly significant correlation was found between the average particle diameter (APD) determined with the Fisher Sub-Sieve Sizer and the mean of the particle diameters derived from the log-normal distributions of 33 samples of Ammonium Perchlorate determined by M.S.A. analysis (Ref 37). Generally the APD is smaller than the mean perticle diameter. This is to be expected since the principles on which the Fisher Sub-Sieve Sizer is based results in a "surface" average rather than the "weight (volume)" average on which the M.S.A. measurement is based

Sedimentation Columns: Gas

SHARPLES MICROMEROGRAPH. A commercially available air sedimentation device introduced in 1953 (Ref 6) that provides rapid particle size distribution determinations for powdered materials by the application of Stokes' law for particles falling thru a static column of gas

As described by Kaye et al (Ref 22), the powder sample is injected downward into the top of the settling column thru a powder feed system and deagglomerator . A small pressure chamber, connected to the powder sample chamber by a solenoid valve, is charged with dry nitrogen to a predetermined pressure. When the solenoid valve is actuated, the nitrogen discharges thru the powder sample chamber and carries the powder at high velocity thru a narrow conical slit in the deagglomerator. The powder is dispersed by the aerodynamic shear forces in the deagglomerator slit. These forces can be varied within wide limits by the choice of pressure in the pressure chamber, and by the choice of the deagglomerator slit width. The pressure is variable from 0 to 400 psi, and the slit width may be adjusted from 10 to 250 microns

The sample then enters the vertical, approximately seven-foot long, insulated aluminum, settling column where the particles reach terminal velocities, and fall until stopped by the pan of the servo-electronic balance at the bottom of the column. As the particles accumulate on the balance pan, a slight rotation of the balance beam on its torsion suspension occurs. A sensing device incorporated in the balance applies a current to a restoring force coil on the balance beam. The current required to balance the accumulating weight of the powder on the balance pan actuates the milliammeter of a moving chart recorder. This accumulated weight-time curve is interpreted by using two templates which are based on experimental calcns and are reported to take into account discrepancies arising due to nonsphericity of the particles and variations in initial velocity

The performance of the Micromerograph has been of interest ever since its introduction because of its potential for a much needed improvement in the analyses of the important sub-sieve sized ingredients of Ordnance. It has been evaluated relative to several other instruments: Coulter Counter

(Refs 16, 28, 29 & 31); Microscope (Refs 20 & 27); Fisher Sub-Sieve Sizer (Refs 16 & 27); Cenco Photelometer (Refs 16 & 28); MSA-Whitby (Ref 25); Cintel Flying Spot Counter (Ref 20); Ro-Tap Siever (Ref 18); and Andreasen Pipette (Ref 31). The advantages most frequently observed were:

(1) Simplicity and ease of operation. (Refs 20 & 25)

(2) Economy of operator time. (Refs 19 & 22)

(3) Reproducibility (especially within a single instrument)(Refs 18 & 19)

The disadvantages observed were:

(1) Low recovery of charged sample. (Refs 16 & 31)

(2) Electrostatic charge on particles. (Ref 16)

(3) Variations between instruments. (Refs 16a & 29c)

(4) Lack of accuracy. (Ref 22)

Probably the most common criticism of the Micromerograph was that of low recovery of the material charged which generally ranged from only 30–50%. The low recovery is in part due to

Table 9
Micromerograph Analysis of Silica Flour (from Ref 16a)

Laboratory		Instrument	Ave ($\bar{X}$) Range (R)	Weight-Percent Greater Than Stated Diameter (micron) 46.1	22.1	9.8	4.9	Specific Surface cm^2/gm
Jet Propulsion Laboratory	(1)	1	$\bar{X}$	27.5	51.0	74.5	88.7	1918
		1	R	4.3	10.1	5.5	3.2	303
Thiokol-Redstone	(2)	1	$\bar{X}$	28.5	57.1	77.5	89.0	1776
		1	R	3.7	2.2	2.7	0.8	129
Rocketdyne	(3)	1	$\bar{X}$	24.7	51.3	76.2	92.3	1737
		1	R	3.6	8.0	3.0	1.8	222
Hercules Powder	(4)	1	$\bar{X}$	24.4	48.4	70.7	87.9	2080
		1	R	5.8	3.4	4.0	2.2	348
Thiokol-Elkton	(5)	1	$\bar{X}$	27.9	48.0	73.3	90.2	1887
		1	R	5.2	3.6	2.2	2.8	210
		2	$\bar{X}$	28.8	53.0	73.3	88.8	1930
		2	R	5.4	4.3	4.5	2.0	327
Aerojet-General	(6)	1	$\bar{X}$	27.6	53.5	75.2	91.2	1758
		1	R	1.3	3.0	1.3	6.2	229
		2	$\bar{X}$	27.0	50.3	71.7	87.6	2021
		2	R	2.9	3.7	4.7	2.7	248
Stanford Research Institute	(7)	1	$\bar{X}$	26.1	51.8	74.1	90.7	1826
		1	R	6.1	3.5	4.2	3.3	307
Rocket Power/Talco	(8)	1	$\bar{X}$	26.5	50.4	74.6	89.5	1939
		1	R	2.1	1.8	3.3	2.2	130
Thiokol-Longhorn	(9)	1	$\bar{X}$	30.3	55.5	77.2	89.7	1861
		1	R	2.0	5.7	2.4	1.9	221
		2	$\bar{X}$	33.0	59.2	78.9	90.8	1725
		2	R	3.3	5.5	4.2	1.4	137

electrostatic charge induced on the particles causing them to be attracted to the walls of the column (Refs 16 & 22)

Long (Ref 16a) has reported on an evaluation of the reproducibility of the instrument conducted by nine laboratories using twelve different instruments to analyze portions of the same ground silica (Table 9). An analysis of variance showed inconsistency among the laboratories and between instruments within the laboratories; this reflected inconsistency among instruments regardless of their location. The testing errors between runs from the same instrument in the same laboratory were, for the most part, fairly comparable. It was concluded that although individual instruments gave reproducible results, a comparison between laboratories of particle size for a given material could not be easily accomplished

Despite shortcomings, the Micromerograph in the early 1960's was the only instrument generally available for determining particle size distribution of sub-sieve proplnt and pyrotechnic ingredients. In general, it appears that the Micromerograph, provided that frequent calibration checks are performed, is a good, reproducible instrument for size measurement. The operator time involved is less than with most other methods, and the calcns are not complicated. As in all sedimentation methods, only when the sample particles are spherical does the "Stokes' diameter" that is measured become a measure of absolute particle size. Microscopic examination should be used to check on particle shape and the effect of deagglomeration

Pipette Methods

In this technique, a sample is extracted from the sedimenting suspension at appropriate intervals by means of a pipette. These methods are incremental, and the sample is taken in one of two ways: (a) at a fixed position in the app, or (b) at a fixed depth below the surface of the suspension. It is assumed in both instances that no disturbance of the suspension takes place by eddies, etc., while the sample is being taken, that the sample is representative of the suspension at the extraction point, and that the sample taken is small. Method (a) must take into account any lowering of the level of the top surface of the suspension

ANDREASEN PIPETTE. This is probably the most frequently used method of sedimentation analysis, the disadvantage being that samples withdrawn must be evaporated to dryness and weighed – a time-consuming procedure (Ref 31)

The glass sedimentation vessel is about 5.5 cm in diameter and has a graduated scale, 0 to 20 cm, engraved on its side. The zero of the scale is positioned about 2.5 cm from the base of the vessel, and the capacity when filled to the 20 cm mark is 550 to 600 ml. The stem of the pipette is fused to a bell-shaped bulb having a ground-glass joint that fits the neck of the sedimentation vessel, the pipette being so positioned that its tip is fixed at the level of the zero mark of the scale; above the bulb is a two-way tap and a side discharge tube. During an analysis, the sedimentation vessel is immersed in a constant-temp bath up to the 20 cm mark

The vessel is filled with suspending liquid and the powder to be analyzed to the 20 cm mark, shaken to disperse the sample, and placed upright in the bath. At time intervals, standing in a 2 to 1 progression, a 10 ml sample is withdrawn from the sedimentation vessel and is discharged into a series of tared dishes. The dishes are reweighed after the samples have been evaporated to dryness, and a deduction is made for the weight of any dispersing agent added; thus, the weight of particles corresponding to each withdrawal time is determined

The size of particles is calculated from the height of fall and time elapsed, according to Stokes' law, but allowance must be made for the decrease in height of sedimentation column after each sample is withdrawn. The initial concn in the suspension is calculated from the weight of powder and the volume of liq in which it has been dispersed. This concn may be up to one percent by volume for easily dispersed powders, but should be reduced if there is any tendency for flocculation to occur. This app is normally applicable to the particle size range 2 to 60 μ, and may be extended to larger sizes if viscous liquids are used, eg, benzyl alc, or to smaller sizes if constant temp is maintained over the longer period required. One operator can perform four analyses simultaneously during a day. The weight of powder required is approximately 5g

Density Variation: Gravimetric

HYDROMETER METHOD. The suspension of a powder is prepd as for other sedimentation

analyses and poured into a 1ℓ glass measuring cylinder. The variation with time of effective density, and hence of particle concn, is determined from readings of a hydrometer immersed in the suspension. The hydrometer should be inserted in the suspension immediately before the reading is taken, and afterwards removed to avoid particle deposit on the bulb. The effective height of the suspension is from the surface level to the center of volume of the bulb, which varies according to the density of the suspension. As the bulb length is an appreciable proportion of the sedimentation height, and not very small, the incremental method of calculating the size analysis is only approximate. Temp and meniscus corrections should be applied. Eigsti and Dwiggins (Ref 16) evaluated this method for particle size measurement of chemical delay compns but found it unsuitable because of the disadvantages mentioned above

DIVER METHOD. This is a modification of the hydrometer method. Variation in effective density, and hence concn, is measured by totally immersed divers. These are small glass vessels of approximately streamline shape, ballasted to be in stable equilibrium, with the axis vertical, and to have a known density slightly greater than that of the sedimentation liq. As the particles settle, the diver moves downwards in hydrodynamic equilibrium at the appropriate density level. The diver indicates the position of a weight concn equal to the density difference between the diver and the sedimentation liq. Several divers of various densities are required, since each gives only one point on the size distribution curve

The advantages claimed for this method over the hydrometer method are that, since the divers are relatively small and surface tension and deposition effects are avoided, the incremental theory is applicable. Smaller divers can be used with centrifuge tubes, so that analysis can be extended down to particles of 0.02μ in size. Eigsti and Dwiggins (Ref 16) pointed out the disadvantages were that a large concn is necessary, thus particle interference and agglomerations may be present. Since the divers are placed directly in the suspension, they may interfere with the settling process. For these reasons and the length of time involved in obtaining the necessary data this method is considered to be generally undesirable for either control or laboratory determinations of chemical delay compns

Density Variation: Absorptiometric

Turbidimetric methods for particle size analysis (Refs 10, 16 & 27) are used in conjunction with sedimentation procedures to determine the concn of particles at given distances below the surface at successive time intervals. From these data, and Stokes' law, particle size distribution can be calculated

When a beam of light is intercepted by a turbid medium, part of the incident light is absorbed, part is directly reflected, and part is scattered. The attentuation produced is a function of the concn, particle size distribution and color of the suspension

If light attentuation is due mainly to scattering, which is usually the case in turbidimetry, the usual light transmission equation may be written:

$$\frac{I_t}{I_0} = e^{-(K\pi r^2 nl)} \qquad (16)$$

where: I_t = Intensity of light transmitted
I_0 = Intensity of incident light
K = total scattering coefficient = the effective scattering cross section divided by the geometric cross section
πr^2 = cross sectional area of particle
n = number of particles per unit volume of dispersion
l = length of light path thru suspension

Values of K have been tabulated for particles of various diameters. For extremely small particles K is nearly zero. Its value increases rapidly to between 3 and 5 for particles in the range of approx 0.3 to 0.7 microns. As the size of the particle increases, K drops to a constant value of 2. When values of K are known, and when either the particle diameter or the number of particles is known, the other may be determined from the ratio I_t/I_0. If both n and r are unknown, they may be determined by making transmission measurements at two different wavelengths and setting up simultaneous equations using equation (16)

Thru a combination of sedimentation and transmission measurements, a particle size distribution can be found. Tranquil settling of a dispersion of non-uniform particles will result in a separation of particles according to size so that transmission measurements at known distances below the surface at selected time intervals, will, with Stokes' law, give the concn of particles of known diameter. Thus, a size frequency distribution can be obtained

EAGLE-PICHER TURBIDIMETER. Based on the research of Harner and Musgrave (Ref 10) is an app which comprises a stable light source, a sedimentation cell, and a photocell and microammeter as illustrated in Fig 19:

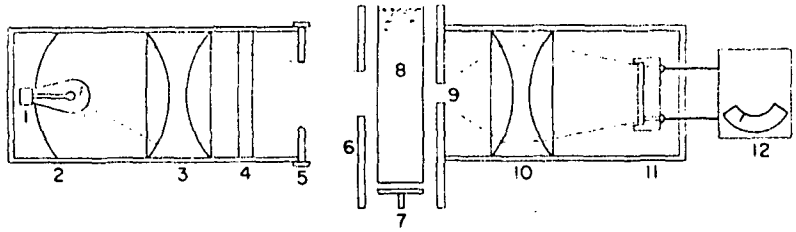


Fig 19 Schematic Diagram of Apparatus Showing the Important Elements of its Construction

1. 6-v spotlight bulb
2. Parabolic reflector
3. Condensing lens system
4. Heat filter glass
5. Adjustable iris diaphragm
6. Cell housing
7. Cell level adjustment
8. Sedimentation cell
9. Light slot
10. Secondary condensing lens system
11. Barrier-layer type photocell
12. Microammeter

The light beam traverses the suspension at a fixed distance below the surface. A plot is made of the percent light attenuated versus time from the microammeter readings. From this, increments of light attenuation for various size ranges are determined. These values are converted to weight percent by the use of "equivalent hiding power" factors

The usual problems encountered with any sedimentation procedure are present. It is necessary to use a dispersing liq compatible with the material being tested. Also, dispersing agents and technique must insure complete dispersion and prevent agglomeration. These factors may vary with materials, and therefore will require special attention when new materials are to be analyzed

In connection with the burning time of chemical delay compns Eigsti and Dwiggins (Ref 16) evaluated the method for the determination of particle size distribution on four lots of tungsten vs four other methods. The results are partially summarized in Table 10:

Table 10

Comparison of Results From Four Particle Size Methods

	Turbimeter		Micromerograph		Coulter Counter		B.E.T.	
Tungsten Sample Lots	Wgt. Ave. Diameter μ	Specific Surface cm^2/gm	Wgt. Ave. Diameter μ	Specific Surface cm^2/gm	Wgt. Ave. Diameter μ	Specific Surface cm^2/gm	Specific Surface cm^2/gm	Burning Time sec/in
M-10*	1.5	1795	2.3	1377	11.8	781	1000	3.41
M-20*	3.1	1107	2.5	1227	11.5	817	1000	4.62
ND 3499**	5.4	688	4.9	709				42.04
ND 3657**	6.5	553	5.0	674				44.96

* Samples obtained from Sylvania Electric Products, Inc

** Samples obtained from Fansteel Corp

Since the foregoing tests were carried out at identical conditions of compn and temp, and in a standard test fixture, the burning times serve as a means of checking the relative fineness of the powdered tungsten fuels. The rapid burning times indicate that both M-10 and M-20 are very fine. Also, the M-10 is definitely finer than M-20, as shown by the difference in burning times

The specific surface being a gauge of the fineness of a powder, comparison of the result for M-10 and M-20 in Table 10 shows that the Turbidimeter yielded analyses which were consistent with the burning time data, that is, M-10 is a finer powder than M-20. The Micromerograph showed a smaller difference between these two lots. The Coulter Counter gave results which were inconsistent with the burning times. It showed both powders to be quite coarse, as indicated by the small surface area, and that of the two, M-20 is finer. The B.E.T. nitrogen adsorption method also indicated coarse powders and failed to show any difference between the two lots

Since the burning times for compns burning in the 40 sec/inch range may vary by as much as 3–5 seconds from batch to batch, the difference in burning times for tungsten samples ND3499 and ND3657 cannot be significantly related to the difference in paticle size. However, the differences in burning time between these coarse powders and the finer M-10 and M-20 is readily apparent

A comparison of the distribution curves given by the Turbidimeter, Micromerograph and Coulter Counter for identical samples of tungsten is shown in Figure 20

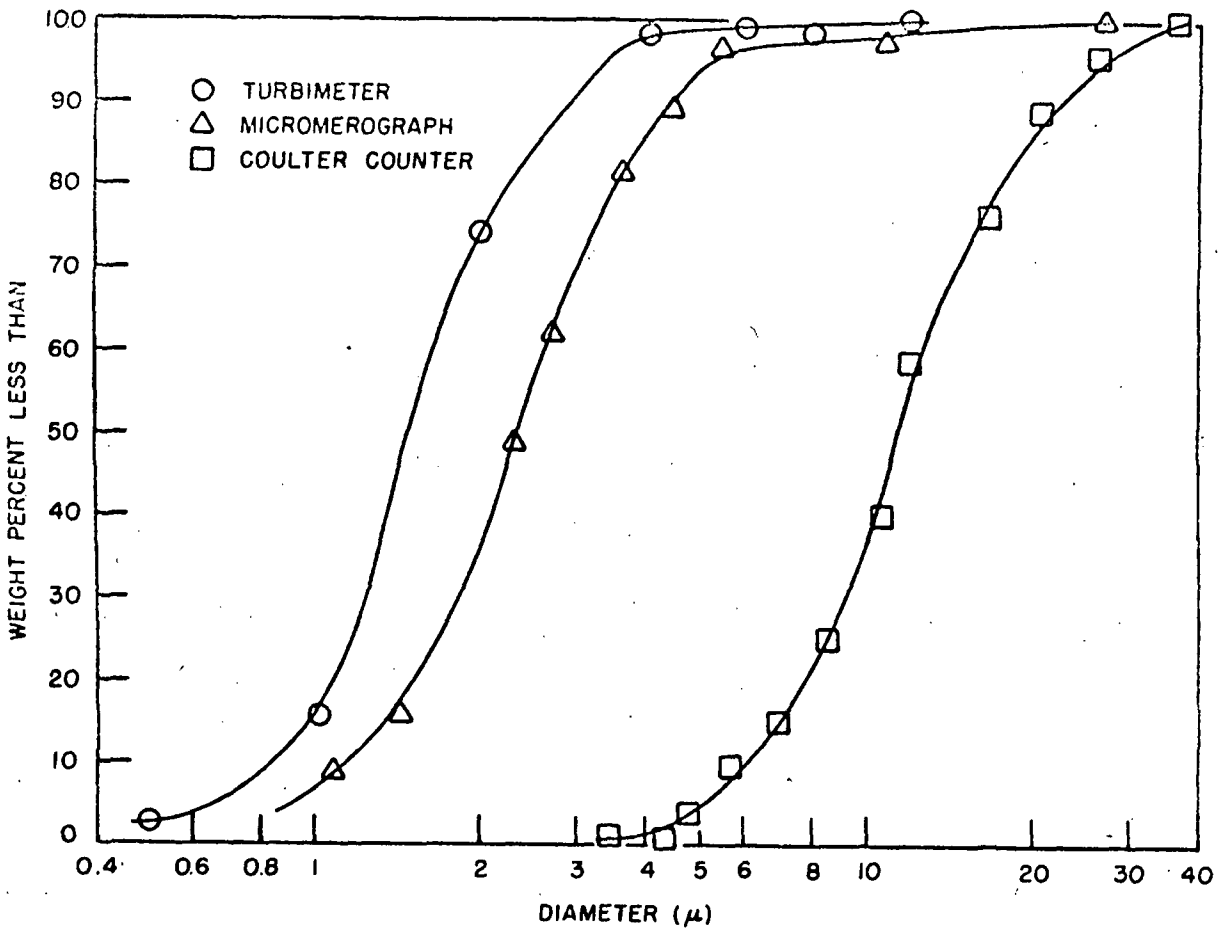


Fig 20 Size Distribution Curves for Three Methods of Particle Size Analysis – Tungsten M-10

Table 11

Precision of Eagle-Picher Turbidimeter Experimental Work

Tungsten Lot	Sample No.	Specific Surface cm^2/gm	Standard Deviation cm^2/gm	Percent of Mean
M-10*	2	1802	13.6	0.76
	3	1789		
M-20*	4	1056		
	5	1171	58.7	5.3
	6	1093		
ND 3499**	13	694	9.2	1.3
	16	681		
ND 3657**	14	558	7.1	1.3
	15	548		

* Samples obtained from Sylvania Products, Inc.
** Samples obtained from Fansteel Corp

The lack of fines shown by the Micromerograph was probably due to the excessive "hang-up" which has been reported. The extreme coarseness of the results given by the Coulter Counter is unexplainable, however, inadequate deagglomeration could produce this effect

The time required to determine a complete size distribution curve on the Turbidimeter and the Micromerograph varies with the fineness of the particulate material. The longest time involved in obtaining a size distribution curve for the finest sample of tungsten was 2½ hours. The time for analyzing a comparable powder on the Micromerograph was 5 hours; however, 4 hours of this was necessary to allow the sample to settle. Since the Micromerograph recorder is automatic, the operator time is reduced accordingly. It is also possible to adapt a recorder to the Turbidimeter, and thus further reduce the operator time for this technique

Table 11 shows the precision obtained with the Eagle-Picher Turbidimeter. Column 4 is the standard deviation of the specific surface values, and column 5 gives these as percentage of the mean specific surface values

An indication of the reproducibility of the Turbidimeter is shown in Fig 21

The results of the microscopic particle size determination are shown in Fig 22

The number-size distribution of the microscopic determination was converted to a weight-size distribution for comparison with the weight-size distributions given by the Turbidimeter and the Micromerograph for the same material. As shown in Fig 22, which is a log-probability plot, there seems to be no correlation; this is probably due to the effect of the extremely small samples which are used in the mciroscopic method. This presents problems of obtaining a representative sample and complete deagglomeration

The turbidimetric method as exemplified by the Eagle-Picher Turbidimeter seems to offer a convenient and fairly rapid method for control or laboratory use, and the precision and reliability seem adequate. A small concn of sample is sufficient so that particle interference and reagglomeration tendencies are negligible, in contrast to other sedimentation methods which require larger samples

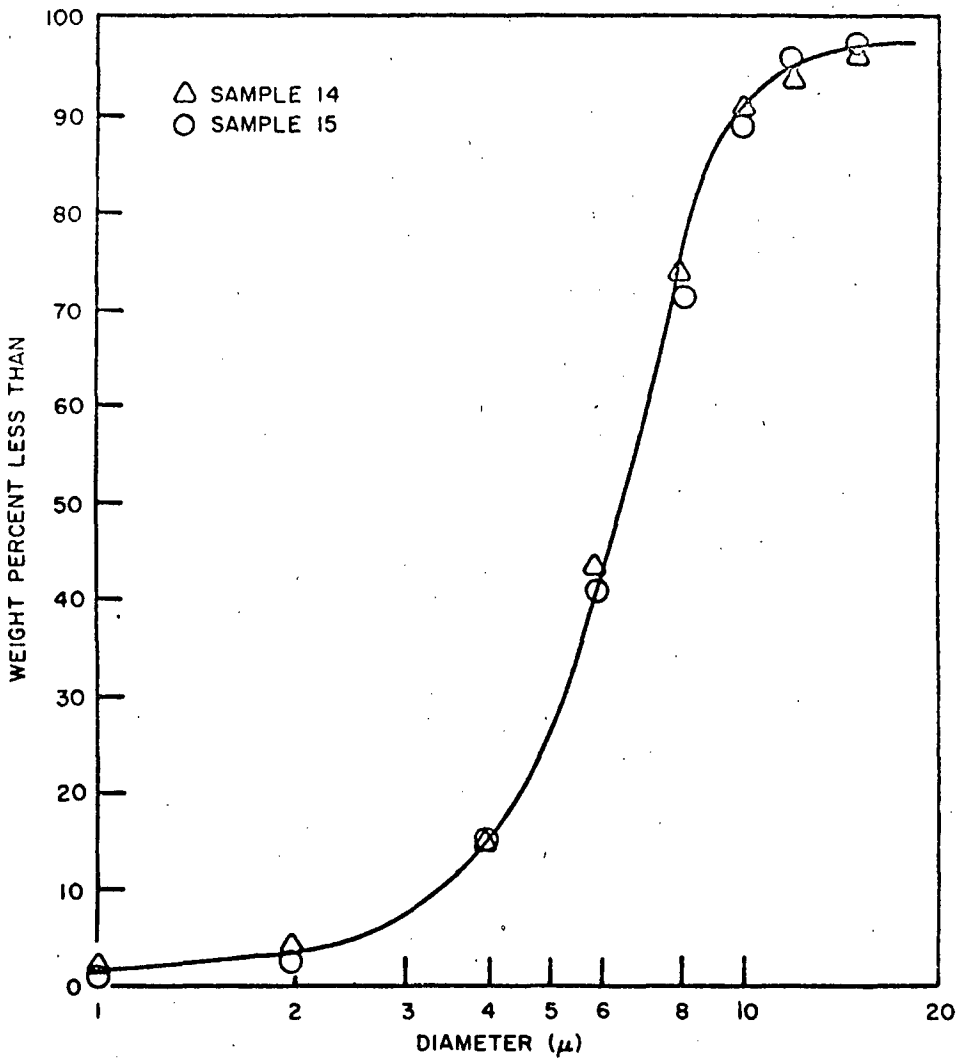


Fig 21 Reproducibility of Turbidimeter – Tungsten ND 3657

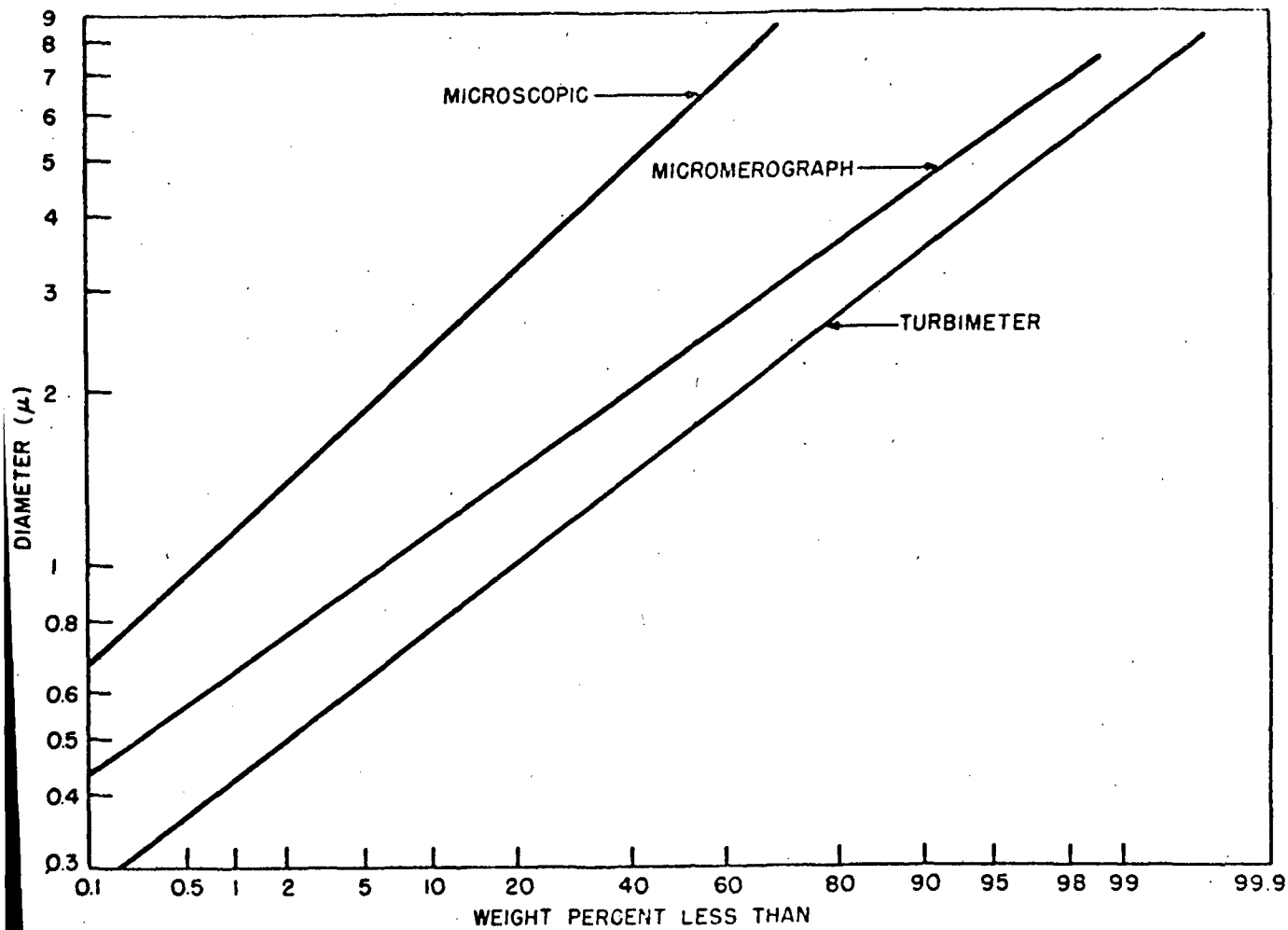


Fig 22 Comparison of Microscopic Method of Particle Size Analysis – Tungsten M-10

Sedimentation Balances

These instruments, sometimes referred to also as sediment accumulation devices, weight the sediment as it accumulates on a weigh-pan at the base of the sedimentation column. The methods are cumulative ones. With the development of sensitive electro balances, the cumulative sedimentation technique is generally easier to perform and more accurate than is the incremental technique. The powder may be dispersed initially in the bulk of the fluid or added instantaneously at the top. An advantage of this type of equipment is the absence of the conical base, needed in sediment extraction devices, upon the walls of which some sediment may adhere. The danger of particles sticking to the vertical walls is however still present

CAHN RG ELECTROBALANCE/SEDIMENTATION ACCESSORY. This app produces a continuous, visible chart record of the sediment weight collected on the balance pan. It has been evaluated for measuring particle size distributions of the primary expls Lead Styphnate, Lead Azide, & Tetracene by Hutchinson (Ref 41). It is difficult to obtain accurate particle size analyses of primary expls because (1) consideration and acceptance of necessary safety precautions make the usually tedious job of particle size analysis even more tedious, and (2) many primary expls used in production contain particles which are non-spherical in shape and are in the subsieve size range. Dry screening Lead Azide, for instance, is hazardous and must be done remotely. Furthermore, static charges

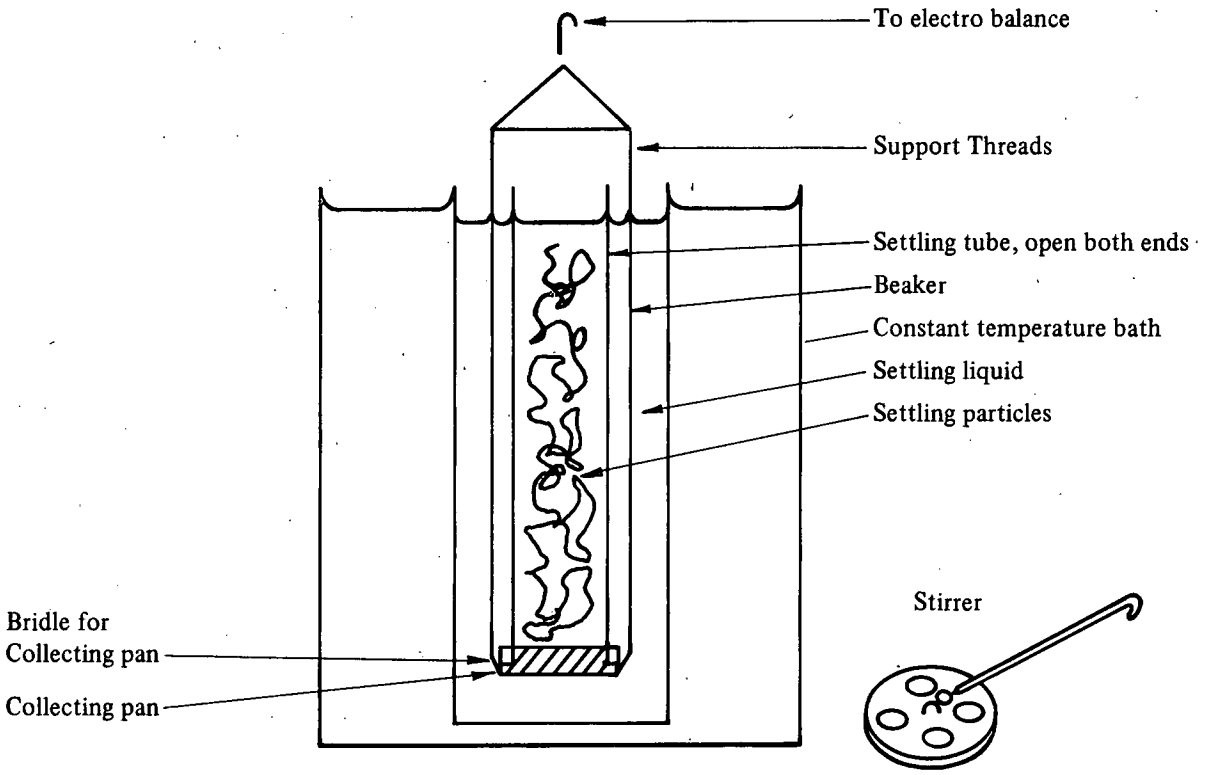


Fig 23 Cahn RG Electrobalance/Sedimentation Accessory

tend to cause the formation of agglomerates, and erroneous results are obtained. Wet screening is tedious, and it is very difficult to remove all the very fine particles from the coarser particles when fine, non-spherically shaped particles are encountered. The apparatus is shown schematically in Fig 23

Four samples of Lead Styphnate were analyzed by dispersing in acet and were found to have average diameters of 15.9μ with a standard deviation of ± 0.4μ. The reproducibility for Tetracene, with average diameter of 35μ, was ± 2μ. Methanol was found to be a satisfactory dispersant for Lead Azide with average particle diameter of 12μ

PERMEABILITY TO FLUID FLOW

The relevance of methods in this section to the measurement of specific surface depends on certain relationships that are assumed to hold between the rate of fluid flow, the pressure head, viscosity of the fluid, density and specific surface of the powder, and porosity of the powder bed. Generally the relationship assumed is the Kozeny equation or some modification of it:

$$u = \frac{Q}{A} = K_1 \cdot \frac{\Delta P}{n L} \qquad (17)$$

where: u = apparent linear rate of flow in cm/sec
Q = rate of flow in ml/sec
A = cross-sectional area in cm^2
K_1 = proportionality constant representing the permeability of the porous medium
ΔP = pressure difference driving the fluid thru the medium, in g/cm^2
n = viscosity of the fluid in poises
L = thickness of the porous medium, cm

Since the permeability of the bed is the property that is measured, the validity of the estimates of specific surface derived therefrom de-

pends on the validity of the relationships assumed. The methods give useful comparisons between different samples of materials of the same type, and hence are frequently used in control of raw materials. Anomalous results may be obtained if materials with widely divergent size or shape distributions are compared; the results of permeability measurements should therefore be interpreted with due caution

Gas Flow

FISHER SUB-SIEVE SIZER. The app consists of a cell, a manometer and a flowmeter. The powder to be measured is compacted into a bed in the cell and dry air is allowed to flow thru it under a constant pressure differential, the rate of flow being measured. A diagram of the mechanics of the system is given in Fig 24 Air flows thru a calcium drying tube and then downward thru the sample tube, in which the powder is supported by a porous plug. The air then passes thru a column of compacted fine sand situated between the upper ends of the two arms of a water-filled manometer. The manometer and the resistance formed by the sand column together constitute a flowmeter, while the manometer, in showing the pressure drop across the sand column, gives by difference, the pressure drop across the other resistance, the powder sample

Since the air passes thru a resistance flowmeter, the pressure on the downstream side of the bed varies with the rate of flow. When the manometer across the flowmeter becomes steady, the reading is taken, and the surface area and "average particle size" (APD) are obtained from a family of curves on a chart incorporated in the instrument. Despite its limitations, the Fisher Sub-Sieve Sizer has been the instrument of choice for measurement of energetic materials in the sub-sieve range (2 to 50 microns) (Refs 13, 21 & 24). It is fast, but provides only a single measurement, the APD. The use of the APD tends to obscure the fact that in practically every case the sample is not a uniform material, but is instead, a mixt of particles whose diameters cover a range of sizes. Because of the principle on which the Subsieve Sizer is based, the APD is a "surface average" and should be distinguished from "number averages" and "weight averages"

The detn of APD's between 100 and 500 microns can be made using a permeability app larger than the Fisher Sub-Sieve Sizer. This app, which was developed at PicArsn, uses a sample size of approx 10 times the sample density (Ref 7a)

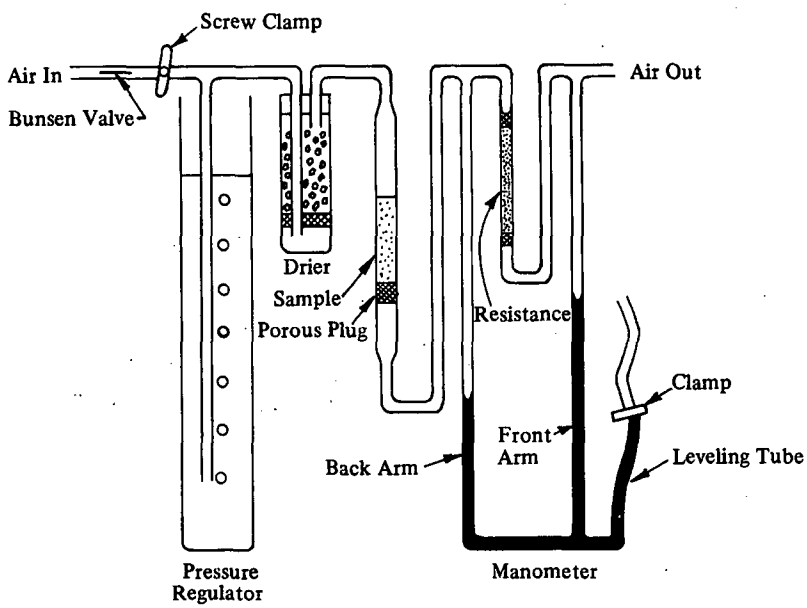


Fig 24 Air Permeability Apparatus

ADSORPTION METHODS

There are various methods for the determination of the surface area of solids based on the adsorption of a mono-, or polymolecular layer on the surface of the solid. These methods do not measure the particle diameter or projected area as such, but measure the available surface per gram or milliliter of powder. The surface measured is usually greater than that determined by permeability methods as the latter are effectively concerned with the fluid taking the path of least resistance thru the bed, whereas the adsorbate will penetrate thru the whole of the bed as well as pores in the powder particles. These methods appear to be more accurate than surface areas calculated from "weight averages" or "number averages" of particle size because cracks, pores, and capillaries of the particles are included and are independent of particle shape and size

Static: Involving Use of Adsorption Isotherms

BRUNAUER, EMMETT, AND TELLER (B.E.T.). In this method the surface area is not measured directly, but the number of molecules of the adsorbed substance required to give a monolayer (N) is determined. If the mean area per molecule (σ) of the adsorbed substance is known by other means, the area of the solid may be calculated as:

$$e = N\sigma$$

The method uses the adsorption isotherm and the expt details of determining this may be summarized as follows: (1) the powder under investigation is thoroughly degassed in a vacuum; (2) a small amount of gas or vapor is added at constant temp; (3) the resultant pressure is noted; with no solid present, the pressure would follow the gas laws; with powder present, the pressure is lower; (4) a curve of volume of gas admitted vs pressure is prepared; and (5) from this isotherm, the surface area may be determined

Harkins and Jura (Ref 5) have described an improved modification of the basic B.E.T. method for the calculation of surface area. Eigsti & Dwiggins(Ref 16) evaluated this method for the determination of the particle size of chemical delay compns vs other methods, as described earlier in this article (see Table 9)

Dynamic

SORPTOMETER (PERKIN-ELMER). This method is essentially a gas-chromatographic technique with the sample powder in place of the normal chromatographic column. A mixt of He and N_2 is passed thru the sample and the concn of N_2 in the exit gas is measured by thermal conductivity or gas-density methods,

Table 12

Aluminum Surface Area

Material	Specific Surface Area Measurements (M^2/gm)			Graphical Surface Area (M^2/gm)*	
	Microscope S_{cal} (1)	Micromerograph S_{vs} (2)	Sorptometer S_s (3)	Microscope S_w (4)	Micromerograph S_w
0-10μ Al	0.444	0.208	0.379	0.606	0.200
10-20μ Al	0.161	0.131	0.250	0.198	0.132
20-30μ Al	0.105	0.097	0.210	0.138	0.100
30-40μ Al	0.094	0.093	0.197	0.120	0.088
40-50μ Al	0.077	0.077	0.178	0.093	0.070
Alco-123 Al	0.299	0.102	0.244	0.405	0.119

(1) S_{cal} = Surface area calculated from microscopic data
(2) S_{vs} = Surface area per unit volume
(3) S_s = Specific surface area
(4) S_w = Specific surface area by the parameters of the weight distribution

* From Log-Probability Plots

and plotted on a recording potentiometer. The change in N_2 content of the exit gas when the sample is cooled in liq N_2 gives a measure of the quantity of N_2 adsorbed on the sample surface. The adsorption measurement is repeated, with three or four different concns of N_2 in the He, and the surface area of the sample is calculated from the B.E.T. equation ($e = N\sigma$)

Johnson, Christian, and Tiedemann (Ref 27) evaluated the Sorptometer vs the Micromerograph and the microscope for particle size and surface area determinations to characterize powdered materials used in solid proplnts. Table 12 compares the surface area of Al powder samples calculated from Micromerograph and microscopic data with that measured using a Sorptometer

Sorptometer measurements ran higher in 8 of the 12 lots of Al tested, apparently reflecting the area measurements of the pores, cracks and capillaries of the material and irregular shapes

Similar comparisons obtained with samples of Ammonium Perchlorate are summarized in Table 13

Both the Al and AP samples appeared to follow very closely the log normal law of particle distribution as evidenced by the straight line plots of the size distribution data obtained microscopically and Micromerographically. This appears to be typical of dispersions obtained by milling, crushing, or grinding

Sulcer and Denson (Ref 19) used the gas chromatographic–B.E.T. procedure for the analysis of Class I Al powder (45 μ max dia) which cannot be tested satisfactorily by sedimentation methods because of the presence of aggregates. A rough statistical evaluation of this procedure was made by running twelve determinations and calculating the standard deviation as shown in Table 14:

Table 14

Specific Surface of Class I Aluminum Powder Lot Number 1457

Specific Surface, cm^2/g (Nitrogen Adsorption)	
6401	
6245	
5220	
5518	
5855	
5842	
6049	
5922	
5744	
6054	
6041	
5421	
5859	Average
670	Standard Deviation
3759	Specific Surface by Micromerograph

Table 13

Ammonium Perchlorate Surface Area

Material	Specific Surface Area Measurements (M^2/gm)			Graphical Surface Area (M^2/gm)*	
	Microscope S_{cal} (1)	Micromerograph S_{vs} (2)	Sorptometer S_s (3)	Microscope S_w (4)	Micromerograph S_w
P-Lot No 13 AP	0.226	0.250	0.462	0.862	0.440
A-28 AP	0.394	0.179	0.284	0.564	0.297
5 AP	0.530	0.404	0.673	0.442	0.502

(1) S_{cal} = Surface area calculated from microscopic data
(2) S_{vs} = Surface area per unit volume
(3) S_s = Specific surface area
(4) S_w = Specific surface area by the parameters of the weight distribution

* From Log-Probability Plots

The Sorptometer appears to offer several advantages for use in determining the surface area of fine powdered proplnt ingredients. By comparing the specific surface determined by N_2 adsorption with the specific surface determined by other methods, an estimate of the deviation of the particles from a sphere can be made. For many very fine powders, N_2 adsorption is one of the few methods available for describing the size of the particles

IMAGE FORMATION

In methods involving image formation there is a common factor. Radiation normally propagated in rectilinear fashion, such as light or an electron beam, is interrupted by the particles under examination, and the pattern of the interruption can be observed in different ways, eg, optically or photo-electrically

Light Beam: Optical Microscope

The image produced may be viewed either directly by the eye or projected on to a screen. The latter method is usually the more convenient and involves less eyestrain; it is less satisfactory than direct observation for fine sizes near the limit of optical resolution. Sizing is commonly achieved by comparison of the particle images with a scale or graticule. Since the process is tedious, sizing is sometimes performed automatically. The smallest resolvable particle size is a function of the wavelength of the light used and varies between 0.5 and 1 μ

The optical microscope has the advantage that it is direct and the analyst examines his material himself, so that he can appreciate changes in shape and size and especially the state of aggregation of his sample, factors not always appreciated in an indirect method of analysis. Nevertheless, judgments are involved and the method is undoubtedly tedious, so that results may vary even in the hands of experienced operators. The method is also very time consuming in the requirements for counting a sufficient number of each sized particle for statistical accuracy. One of the biggest problems is that of obtaining a truly representative sample due to the comparatively small amount of sample capable of being dispersed in the microscopic field of view

Light Beam: Flying-spot Principle

The difference between this principle and that of the optical microscope methods is that the whole field is not illuminated simultaneously, but is scanned by a fine light spot. Interruption of the illumination is measured electronically

RANK CINTEL INSTRUMENT. A moving spot of light, produced on the face of a cathode-ray tube, is focused on the sample by means of a suitable lens system. The amount of light passing thru or reflected from the sample varies according to the optical density and configuration of the individual particles of the sample. These changes in light intensity are detected by a photomultiplier, the signal from which is fed into counting and sizing circuits. A memory device prevents each particle of the sample from being counted more than once, and sizing is accomplished by pulse subtraction

The instrument has been evaluated by Luster, Whitman, and Fauth (Ref 20). They selected atomized Al, AP and NGu as materials for study that would be representative of proplnt ingredients. They found that only 2000 particles could be counted in 2 hours, a time arbitrarily chosen as feasible for control work. This number is not considered sufficient, as 18,000 particles are required for a 95% confidence level. Statistical analysis of results obtained for AP was impossible because of discrepancies in the data resulting from crystal growth and particle agglomeration. The sample of NGu could not be handled by the instrument because it consisted of a mixt of needles and chunky particles. They concluded that for dimensionally stable materials such as Al or carborundum, excellent agreement was found with other methods such as the Micromerograph or visual microscopic count. But because of the properties peculiar to AP and NGu, the Flying Spot Particle Resolver was not believed suitable for process control of these materials

ELECTRON MICROSCOPE. The use of an electron beam in place of light gives the electron microscope a much greater magnifying and resolving power than the optical microscope so that particle diameters of 0.001 to 20μ may be measured when special precautions necessary for preparing the sample and for calibrating the magnification are observed

Suspensions of particles may be examined

after either depositing them on a very thin membrane, or incorporating them into it. For most purposes, the deposition method is preferable, but when it is necessary to draw particle size distribution curves, the incorporation method is more convenient. Membranes are usually made from plastics (collodion, Formvar, polystyrene, etc) or from extremely thin films of light metals (Be or Al) or oxides (SiO_2) formed by deposition. A photomicrograph is produced of the incorporated or deposited particles which can then be treated in just the same way as a photograph produced by the optical instrument. A recent development is Scanning Electron Microscopy (SEM) which is similar in effect to the flying-spot microscope

Kuentzmann (Ref 43) has applied the SEM to the study of the condensed phase of the combustion products of metallized solid proplnts. The aluminum oxide particles in the rocket exhaust were collected on glass plates, metallized under vacuum (the thickness of the metal depositions being negligible when compared to the particle diameter) before being placed on the plates of the SEM. Manual counting using a sliding caliper was found more satisfactory than automatic data reduction

ELECTRICAL PROPERTIES

COULTER COUNTER. This commercially available equipment utilizes the change in resistance of the system caused by the presence of a particle suspended in an electrolyte. The sus-

Table 15

Comparison of the precision of the Sharples Micromerograph with that of the Coulter Counter using standard glass bead sample, type XC-3

	Geometric Means			Standard Deviations of Distributions		
	Micromerograph, microns		Coulter Counter, microns	Micromerograph		Coulter Counter
	By Weight	By Count*		By Weight	By Count	
	13.8	8.9	22.7	0.97	0.98	0.67
	14.3	8.9	23.2	1.04	1.04	0.68
	13.8	9.0	22.3	0.98	0.98	0.77
	14.2	7.6	22.8	1.04	1.05	0.73
	14.2	9.4		0.95	0.96	
	15.0	8.3		0.98	0.98	
Averages	14.2	8.7	22.8	0.99	0.98	0.71
Standard Deviations	±0.4	±0.4	±0.4	±0.04	±0.04	±0.03

Coulter Counter operational conditions:

Gain index	4
Aperture	100 microns
Electrolyte	1% aqueous NaCl solution
Sample weight	25 mgs

Micromerograph operational conditions:

Deagglomerator	250 microns
Pressure	100 psi
Sensitivity	1
Sample weight	40 mg

* By Count – Micron sizes by weight were converted to micron sizes by count using the following equation:

$$\mathrm{Ln}D_n = \mathrm{Ln}D_w - 3\left(\mathrm{Ln}\frac{D_w 50\%}{D_w 16\%}\right)^2$$

where: D_w = particle diameter by weight at percentages shown above

D_n = particle diameter by count at percentages shown above

$D_w 50\%$ and $D_w 16\%$ = particle diameters by weight at 50% and 16% points respectively

pension of particles flows thru a small aperture having an immersed electrode on either side, with particle concn such that the particles traverse the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperture, momentarily changing the resistance between the electrodes and producing a voltage pulse of magnitude proportional to the particle volume. The resulting series of pulses is electronically amplified, scaled and counted

Eigsti and Dwiggins (Ref 16), as reported earlier in this article, compared the Coulter Counter with other methods for the particle size analysis of powdered W (Table 10). Subsequently, Middlebrooks, Kaye, Edelman, and Weingarten (Ref 30) evaluated the instrument with spherical glass beads. They found that in the range of 0–30μ, the Coulter Counter can evaluate spherical glass bead distributions with greater precision than can the Sharples Micromerograph. Geometric means and standard deviations for the Counter were found to be ± 0.4μ and ± 0.03μ, respectively, while the geometric means and standard deviations for the Micromerograph were found to be ± 0.4μ and ± 0.04μ, respectively, as shown in Table 15

The accuracy of the Coulter Counter over the range 0–30μ is poor when compared with microscopic data. The instrument yields geometric mean values which are far coarser than those obtained microscopically. Proportionately smaller size differences are indicated as the distribution curve extends from the geometric mean toward the coarse tail, and proportionately larger particle size differences are apparent as the curve proceeds from the geometric mean toward the fine tail. This effect is shown in the plot comparing Coulter Counter data with microscopic data, Fig 25

H.L. Stalcup (Ref 28) evaluated the instrument for the particle size determination of HMX used in rocket formulations. He found that Coulter Counter distribution was similar to that obtained with the Micromerograph except at the large particle end, where the Micromerograph indicated particles over 100μ compared to 32μ for the Coulter Counter. Median values were 13.5μ by Micromerograph and 16μ for the Coulter Counter. The samples for the Coulter Counter were run on an "as received" basis, ie, while still water-isopropanol wet; whereas, it was necessary to completely dry the samples prior to analysis by Micromerograph. In the latter case the possibility for particle size changes exists due to agglomeration or crystal growth. They found that the instrument is capable of measuring particles from 250 microns down to 0.2 microns by using the proper sized aperture. To prevent plugging, the largest particle diameters in a sample should be no greater than 45% of the diameter of the aperture. It is necessary to find a suitable liq electrolyte for dispersing the sample that is non-dissolving, non-agglomerating, and non-settling. Murphey, Day, and Dillehay (Ref 29) evaluated the instrument for particle size analysis of AP used in solid proplnts. The biggest problem in this case was finding a suitable electrolyte. A 2:3 mixt of benz and n-butanol satd with lithium chloride was found to best satisfy the electrolyte requirements for this material. It was then found that the Coulter Counter was more precise than the Micromerograph in providing data from which to calculate average diameter and specific surface values. Five different samples of AP were chosen to cover a wide range of particle size distributions. Each sample was analyzed five times on both the Micromerograph and the Coulter Counter. The standard deviations found were:

	Specific Surface cm^2/g	Diameter μ
Coulter Counter	48.9	0.34
Micromerograph	129.0	0.95

These data reflect the relative precision of the systems and not the accuracy of either system. It was found essential to maintain cleanliness around the Coulter Counter at all times. Dust and moisture must be avoided or high background counts and instability will result. The Coulter Counter analysis was found to be more rapid than the Micromerograph, requiring approximately 15 minutes per analysis as compared to 90 minutes for high surface material on the Micromerograph. The use of a multichannel Coulter Counter would reduce the time per analysis to less than five minutes

QUADRUPOLE RESONANCE. This concept is based on the theory that the quadrupole resonance frequency of the chlorine nucleus in AP will vary with the particle size. This is because

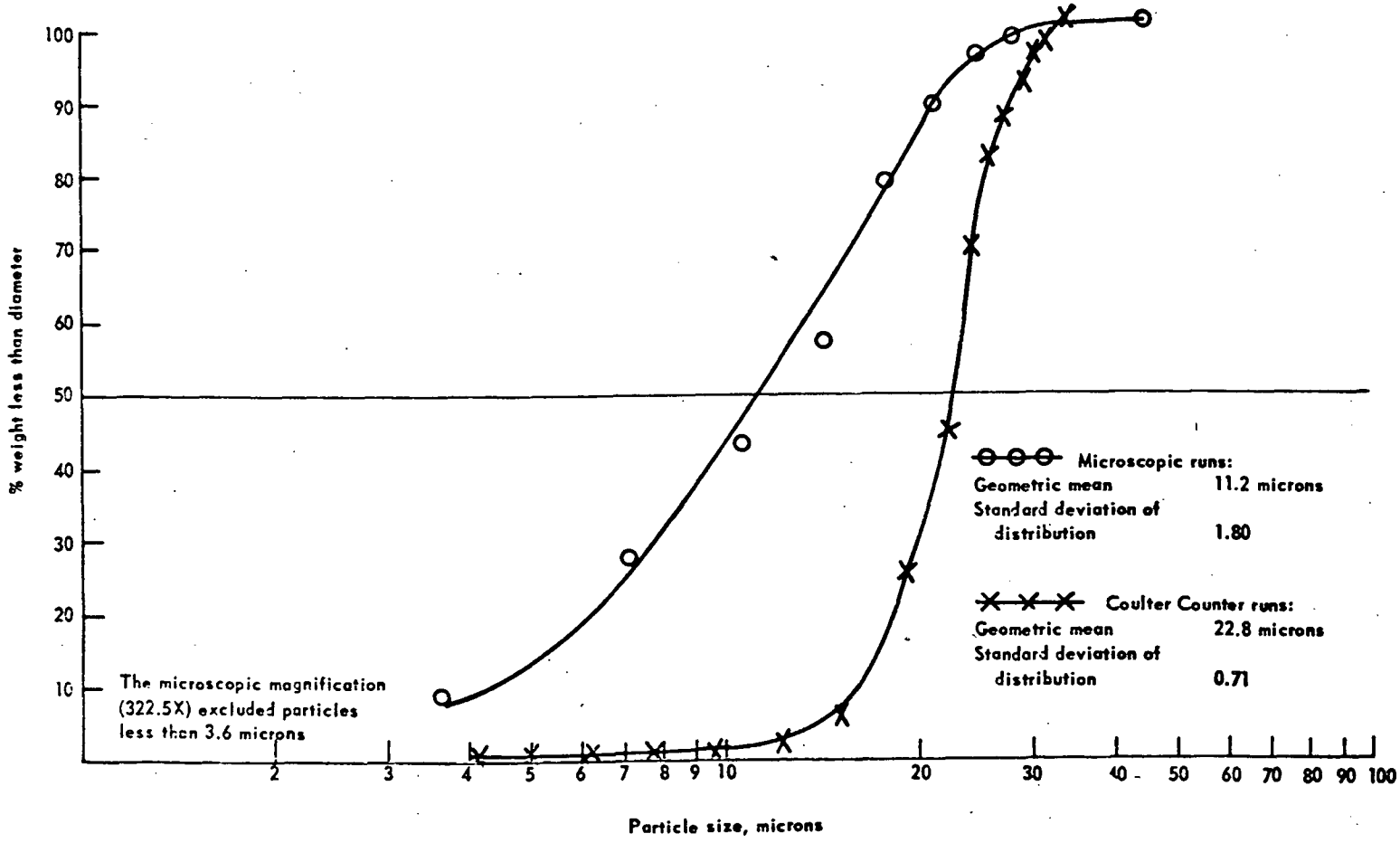


Fig 25 Comparison of microscopic particle size distribution with the average distribution of four identical runs made with the Coulter Counter (Sharples standard glass bead sample, type XC-3)

the internal electric field of a crystal will vary with its particle size, when very small crystal sizes are involved. This variation of internal electric field will cause a shift in the quadrupole resonance frequency. Since extremely small changes in frequency measurements can be made, it is believed that extremely small changes in frequency due to particle size variation can be detected. By determining the amplitude of the quadrupole resonance signal at a range of frequencies, and calibration against known standards, the particle size and distribution could be measured

Wachtell (Ref 23) worked on the application of this principle. However, early in his work a major problem was encountered in finding the quadrupole resonance of the chlorine nucleus which did not exist in the frequency range in which it had been expected (20–40 megacycles). Nuclear Magnetic Resonance studies finally have shown that this quadrupole resonance should exist around 150 kilocycles. Future studies of single crystals of AP should reveal the presence and the exact location of this resonance. If this can be done, then the analysis of particle size, based on the shift of the quadrupole resonance frequency, may be possible

Written by **D. J. VEAL**

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Partridges (Partridge Mortars). Large artillery mortars once used in sieges and in defensive fortifications. They had a central bore for a normal shell, which was ringed by 13 smaller bores for firing grenades
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 340

Pastilles Antilueurs (Fr for Antiflash Pellets). Pellets of a compressed intimate mixt of 4p of K nitrate and 1p of DNT, used during WWI in lieu of *Sachets Antilueurs* (qv) or other flash reducers. For example, pellets used in the 155mm gun weighed 1g each, and were about 2mm thick and 15mm in diameter. Two or three hundred of these were sewn up in a silk bag which was loaded into the gun along with the bag contg the proplnt, such as *Poudre B.* The pellets burned with nearly the same velocity as the proplnt, and had practically no effect on the ballistics. They produced a certain amount of smoke, and the discharge gave a red glow from the muzzle of the gun
Ref: Davis (1943), 326

Patch. A piece of greased cloth or leather which was wrapped around the ball to make it fit the bore more tightly. It was commonly used with muzzle-loading rifles that fired spherical balls, and in some dueling pistols

A second meaning is that of a small piece of cotton cloth used to clean the bore of small arms
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 341

Pâte Explosible. Early Fr Dynamite contg NG 72, Mg carbonate 20, chalk 6 & sawdust 2%
Ref: Daniel (1902), 601

Patent Blasting Powder. Early safety mining expl, consisting of BlkPdr to which ordinary salt was added to lower the deflagration temp
Ref: Daniel (1902), 601

Patent Gunpowder. Smokeless powder based on Nitrolignin, manufd in the 1870's at Clyn-Ceiriog, Wales. The expln of the ship *Great Queensland* in 1876 was attributed to impurities in this proplnt which caused spontaneous combustion
Ref: Daniel (1902), 601

Pattison Explosives. Chlorate expls to which flour or bran was added to diminish the sensitivity. They were patented in Engl in 1880 (BritP 810)
Refs: 1) Daniel (1902), 601 2) Guia, Trattato **6** (1959), 393

Pauli Cartridge. This cartridge was invented by a Swiss gunsmith, Pauli, residing in Paris, and submitted to Napoleon I in 1812. It was the first cartridge in which metal was used; and resembled the present "shotgun" cartridge. It consisted of a brass base in the form of a rosette, to which was attached an envelope of combustible paper contg a charge of BlkPdr. A pellet of primer compn was placed between the base (rosette) and the proplnt charge. The design of the cartridge, very different from anything existing at the time, was not understood by Napoleon and his advisors, and no use was made of it until it was reinvented about 40 years later by other gunsmiths
Refs: M.M. Johnson Jr & C.T. Haven, "Ammunition", W. Morrow & Co, NY (1943), 37

Paulille's Gray Dynamite. Consisted of 20–25% NG mixed with Na nitrate, resin and charcoal
Ref: Daniel (1902), 362

Paulille's White Dynamite. Consisted of 70–75% NG absorbed on 30–25% natural siliceous earth
Ref: Daniel (1902), 73

Paul's Chronograph. A modification of Duda's Ballistograph for detg the velocity of projectiles in flight. See under Ballistograph in Vol **2**, B10-L

Payload. Generally, that part of a load that is expendable, deliverable, or ready for use in direct accomplishment of the mission. The warhead, its container, and activating devices in a military missile. The satellite or research vehicle of a space probe or research missile
Refs: 1) Anon, OrdTechTerm (1962), 220
2) Anon, "Dictionary of United States Military Terms for Joint Usage", **JCS Pub 1** (1964), 108

PBX. An acronym for *Plastic Bonded Explosive.* A term applied to a variety of expl mixts which are characterized by high mechanical strength (above 10,000psi compressive strength), good expl properties (usually > 7800m/sec deton vel), excellent chemical stability, relative insensitivity to handling and shock (to extremes of from 10 to 40% above that detong the basic expl), and high thermal input insensitivity (average autoignition temp > 250°). These expl mixts contain a large percentage of basic expls such as RDX, HMX, HNS or PETN in intimate mixt with a polymeric binder such as polyester, polyurethane, nylon, polystyrene, various types of rubbers, NC, or Teflon. In some instances a plasticizer such as dioctylphthalate (DOP), DPA or butyldinitrophenylamine (BDNPA) is included in the ingredients as well as a fuel such as Al or Fe powd. Available PBX compns and parameter information are shown in Tables 3, 4 and 5

Much of the advantage stemming from the use of PBX compns lies in the simplicity of the technique of end item manuf. About half of the developed PBX compns are used to directly cast end items (see Table 1 for examples). For this proc no elaborate melting equpt or controlled cooling cycles are reqd. All operations may be conducted at ambient temps and, in some instances, can even be carried out in the field (Ref 38). However, where extraordinary mechanical strength is required or where complicated shapes are desired, a pressing or injection technique is applied using a molding powd or slurry of the PBX (see under *Mfg of PBX Type Expls*) (Refs 10, 15, 64 and 73). The final PBX product not only exhibits excellent technical props but also has the economical advantages of low processing costs, the ready availability of all constituents from commercial sources and, (in currently evolved compns) an ease of recycling or disposal because of the use of thermally degradable binders (see under *History*)
History. The first attempts to desensitize RDX were reported by Frankel and Carleton (Refs 1 thru 5) who made use of polymeric materials such as polyurethanes to coat expl crysts by means of emulsion or soln techniques. The first true PB-RDX was developed in 1952 at the Univ of Calif's Los Alamos Lab and consisted of RDX coated with polystyrene plasticized with DOP (Refs 6 & 21). Since then the Lawrence Livermore Lab has evolved a series of PBX formulations, many of which are listed in Tables 3, 4 & 5. These compns are described in Ref 77

(and are so referenced in the Tables) and are identified by their nomenclature code prefixes as to their state of development; viz "PBX- . . ." indicates a prodn expl compn; expls which have reached the stage of being ready for routine mfg are designated "LX- . . ."; while research compns are called "X- . . .", as "XTX-8003". However, much of the work on mil PBX compns has been under the aegis of the US Navy (Refs 10–14, 16, 20–33, 35–38, 40, 43, 44, 50, 53b, 55, 60, 64, 66 & 72). The first formal ordn development program was initiated in Aug of 1954 by the BuOrdn for air-to-air rocket missile (Gimlet) warhead to be developed by the Navy. This program resulted in the development of the PBXN series, also tabulated in Tables 3, 4 & 5. HMX based expls for projects such as the 8" arty fired atomic proj and the Lunar seismic expts were evolved during the 1960's and early 1970's using Teflon as the binder (Refs 51, 55, 60, 67 & 69)

Development work by the US Navy has included attempts to use expls other than RDX and HMX; viz, HNS and TACOT (Tetranitro-1,2,5,6-tetraazadibenzocyclooctatetrene) together with binders such as RTV silicon rubbers. As reported by Stott (Ref 43) such work was not fruitful because of the low deton vel and d of the developed compns

One of the problems arising from the use of PBXs is their disposal or recycling. This problem is, of course, a common one with all munitions. The work of Sitzman et al (Ref 66) provides a technique to recycle or dispose of munitions safely by means of an expl solvent-pump-expl recovery system. A butyrolactone-dimethyl sulfoxide mixt (73/27%) is recommended for PBXs containing a large amt of HMX. However, no solvent was found that disintegrated PBXs (such as PBXN-101 and PBXW-106) containing cast-cured cross-linked polymers. The solution to this problem, as decided upon by the US Navy, was to develop a thermally degradable PBX series. This solution at first glance appears to be almost a complete turn-about in the philosophy of the ultimate PBX being completely heat insensitive. However, this requirement, as expressed in a NavSeaSystCommand Contract to Stanford Research Inst of Calif (Ref 71), was to evolve PBXs (and other expl ordn items) that would undergo *controlled* thermal degradation so as to yield material that could be easily removed from expl casings for the purpose of efficient recycling of the base expl, or for low pollution disposal of the entire item. SRI's Ross et al accomplished a portion of this goal by using a polypropylene-glycol-urethane polymer to prepare an HMX-based PBX. Upon heating the developed PBX at 160° for 10 hrs, the binder decompd to a readily sol material, and the HMX was quanty recovered. It is predicted that by 1979 this nonpolluting recycling technique will not only supplement expl solvation procedures, but will also displace both burning and sea disposal of ordnance to a great degree

Available data on mil in-house or contractor developed compns are presented below using USA mil specs as well as tabular format (Tables 3, 4 & 5)

There are more than several PBX compns developed outside of the USA or by USA non-military organizations which are of interest and are presented here. The PBX developed by Wright (Ref 41) is a molding powd prepd by mixing a w dispersion of a binder such as a polyacrylate, a plasticizer such as paraffin oil, with w slurry of an expl such as RDX and a coagulant such as ethanol. Hard, well-formed granules are produced which contain 90–98% expl. Subsequent pressing at 25000psig and 120° yields pellets with a compressive strength of 10000psi. In another expl patented by Wright (Ref 44a) much the same procedure is followed using, in this instance, poly (hexamethyleneadipamide) as the binder and Diaminotrinitrobenzene as the expl. The prod contains 90–98% expl with a bulk d of 0.6–0.7g/cc

Sato (Ref 44b) reported the development of a PBX series using PETN and a combination of Epikote 871 (an epoxy resin) copolymerized with diethylenetriamine in percent ratios of 70/30, 65/35 and 60/40 (expl/binder). The compression strength of this expl series avgs 60kg/sq cm. Vacek and Skrivanek (Ref 52) invented a series of PBXs using an aq dispersion of poly- (vinyl acetate) binder, PETN as the expl, with dibutylphthalate as the plasticizer in a typical wt % ratio of 36/60/4. A typical deton rate is 5200m/sec using a 28mm charge diam with a d of 0.92g/cc. A self-supporting PBX

series has been developed by Minekaura et al (Ref 58) which can be fabricated in plate, strand or tape form for use in metal forming by impulsive loading. The compn can include polyethylene as binder, a paraffinic hydrocarbon as plasticizer, and an expl-oxidizer combination. The development of PBX compns using a polyester as the binder and RDX as the expl has been reported by Reichel in Ref 76. Evans (Ref 70) invented a PBX series with compns using, for example, PETN as the expl, a polyethacrylate rubber as the binder, and dibutylphthalate as the plasticizer in wt % ratios of 60-85/10-40/0-10. A typical product detond with a No 6 elec blasting cap at a rate of 8180m/sec. In another PBX series, that of Butler et al (Ref 68), β-hydroxyethyl acrylate is the binder, ethylene glycol is a copolymer, benzoyl peroxide is the catalyst, while $LiClO_4$ is the oxidant, and RDX or HMX is the base expl. A typical wt % ratio is 20/13/1/9/57. An invention of Kegler et al (Ref 84) has increased the pot life (before molding) of PBX compns contg 5–15% polyester binder by several days thru use of gelatin microcapsules to inclose the benzoyl peroxide. The catalyst is released during the pressure-molding operation. Frankel et al of Rockwell Intl Corp (Refs 80 & 81) developed a series of nitrofluoroalkyl epoxides (epoxy ether expls) which are heat and impact stable and are used as binders with RDX (80%) as the expl. For available parameter data see Tables 3 & 4. A flexible, self-supporting PBX was patented by Rothenstein (Ref 83) which uses fine-particulate expl in admixt with low d prepolymers. For example, using hydroxy-terminated polybutadiene as the binder, RDX as the expl, toluenediisocyanate as a co-polymer, sym-di-(2-naphthyl)-p-phenylenediamine as an antioxidant, and polybutene as the plasticizer in a wt % ratio of 12.1/42.7/5/0.2/40, a castable expl is produced.

Manufacture of PBX Type Explosives. Several mfg procedures are currently used to produce PBXs. One of these techniques is that of *casting.* (Fig 1 illustrates a process for PBXN-101). This procedure, at first glance, merely involves combining a dried expl, such as HMX, with binder constituents and curing initiators in a mixing vessel, blending to desired homogeneity, then casting into a given warhead or other ordnance item. Unfortunately, there are hazards associated with the drying of large quantities of expls such as HMX or RDX. Hence, a desensitizing procedure must be added for production-scale operations. This procedure involves coating the HMX (or RDX), w-wet as normally stored and shipped, with the alkyd or polyester portion of the binder. The resulting lacquer is added slowly to an aq slurry of the HMX (or RDX). Agitation at approx 250rpm in the presence of w causes the resin to ppt onto the surface of the HMX (or RDX), producing an insensitive powd which may be safely dried, handled, shipped, and stored until ready for use in the final PBX compn. Precoating techniques and equipment are adequately covered in Refs 1 thru 7, 9, 17, 18, 22, 25, 31a, 41, 44a, 50 & 53a. The precoated expl is then combined in a mixing kettle with sufficient copolymer to constitute the final binder compn. An accelerator (such as Co naphthenate) is added at this point. The mixt is then stirred until homogeneous, at first under ambient press, and finally in a partial vacuum to remove entrapped air. The curing agent (such as methyl ethyl ketone peroxide) is then added. After another short mixing period ($\sim$ 15 min) the expl compn is poured into the desired molds. Vacuum casting has not been found necessary to obtain good density, provided that the mold design is not too intricate or the height-to- diam ratio not too great (Ref 38)

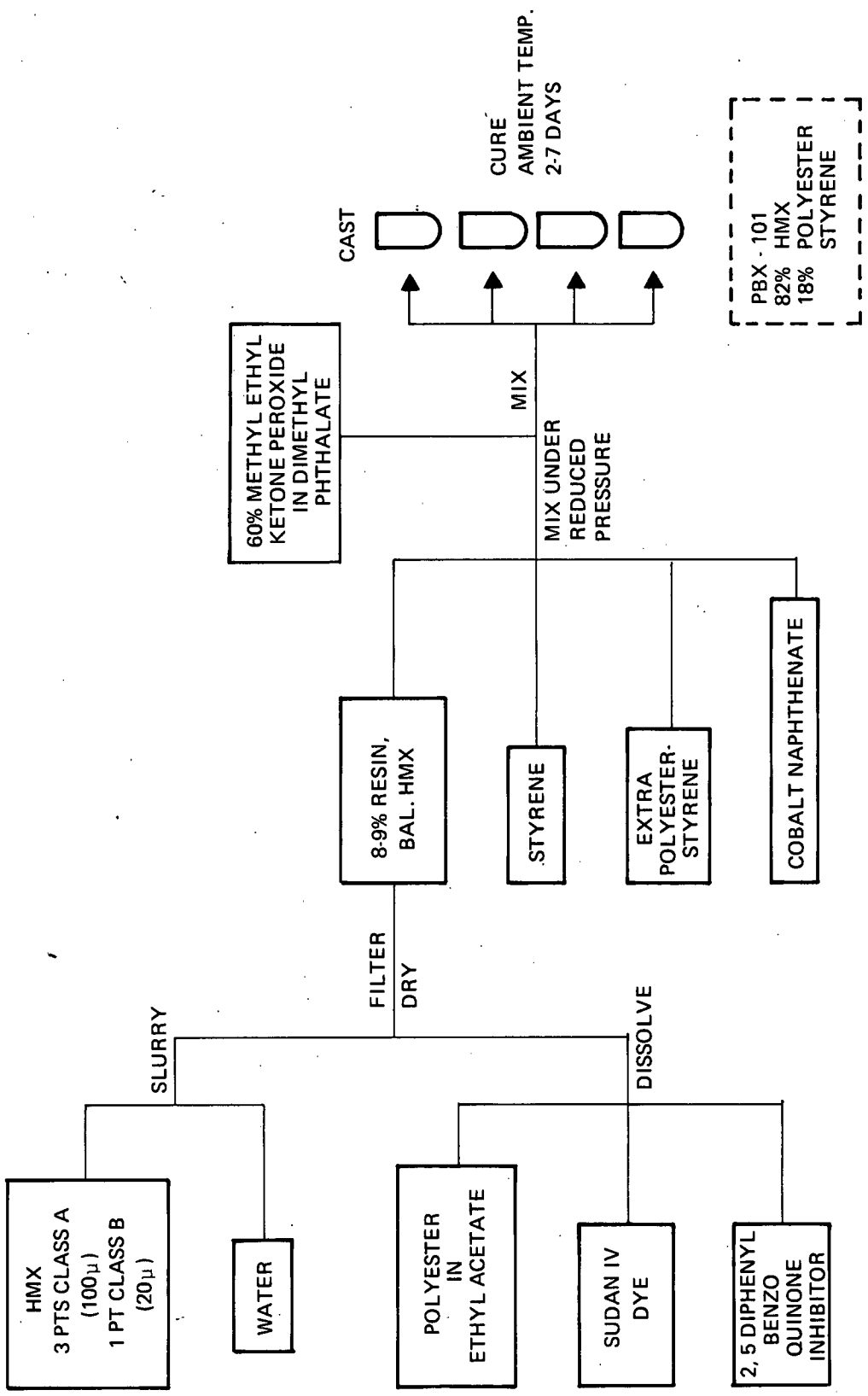


FIG 1. Flow Diagram Showing Processing Steps for PBXN – 101 Preparation

In another casting technique, that of *injection molding,* used for intricate shapes or small diam dimensions, the complete item is produced in place by relatively low press-forcing of an expl-plastic mixt which is then allowed to cure (Fig 2).

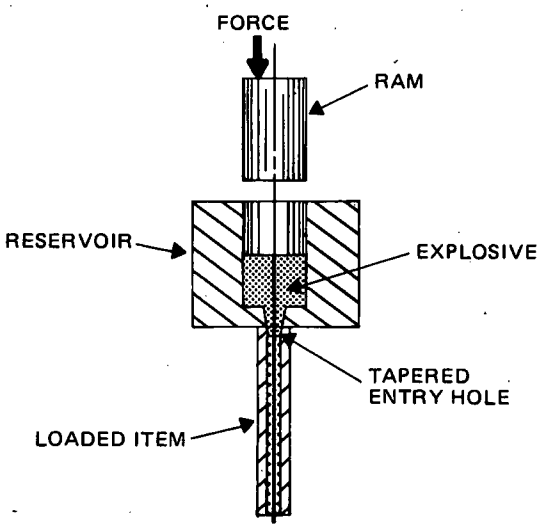


Fig 2 Injection Loading Operation Schematic

The PBX usually employed contains a high solids content expl such as PETN (PBXC-303(1), see in Tables 3, 4 & 5) which provides for steady-state deton in small cross-sectional channel or tubes (Fig 3). Indeed, this technique was developed by the US Navy to provide expl logic links of less than 0.1" in diam. As reported by Lind et al (Ref 73) the technique of injection molding involves the movement of expl material at RT into a cavity or tubing from a reservoir. This is accomplished by applying piston press (at about 12000psig) to the expl compn in the reservoir, which forces it into a cavity or tubing. When the accepting device is full, press on the piston is relaxed and flow stops. The device is then removed and set aside to allow the expl to polymerize into an elastic rubber-like solid

A second mfg technique produces a molding powd which is *pressed* into the desired end item shape under pressures in excess of 30000psi

Two methods have been reported for the prepn of PB-RDX for subsequent pressing. The earlier method employed a Baker-Perkins type mixer to blend the components. This procedure gave a product with good pressing characteristics. However, the molding compn was nonuniform in granulation and tended to be dusty. The slurry method of PB-RDX prepn gave a product which was uniform, free-flowing and dustless. In addition, PB-RDX granulated by the slurry method exhibited satisfactory drying, handling and pressing characteristics. The final procedure incorporating the better features found from the study of such variables as solvents, solvent/plastic ratios, lacquer addition and temp, agitation, RDX particle size distribution, dispersants and rosin additive, was as follows (Ref 7):

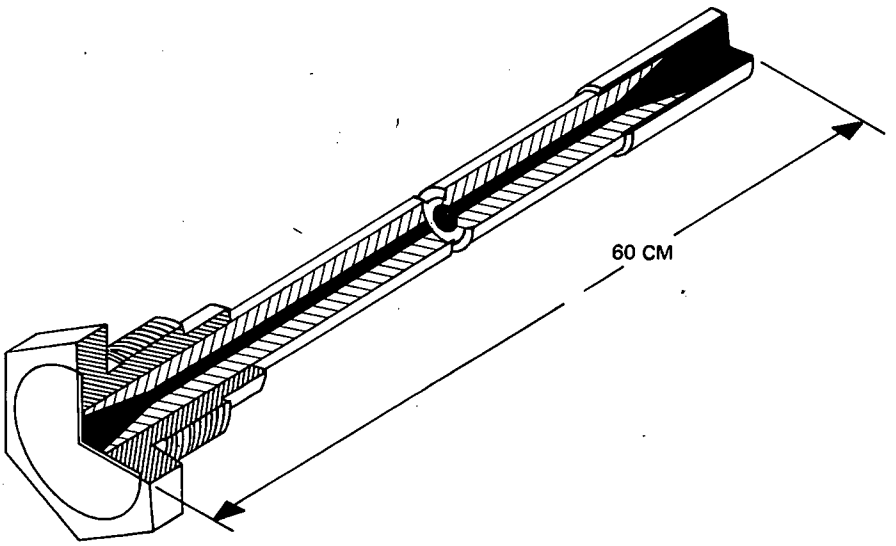


Fig 3 Continuous Explosive Column for use With Zuni Weapon

Testing Procedures for PBX's. These are covered by either the US Mil Specs presented below or individual specs developed for such compns as the PBXNs as reported by Mason (Ref 30) and Pennington (Ref 37). Chem analysis of individual materials unique to PBXs such as the binder stabilizers hydroquinone and/or p-tert butylcatechol are reported by Smith in Ref 36, who used Fe-o-phenanthroline in a spectrophotometric procedure at 500 millimicrons and Stott et al in Ref 38, who also used a spectrophotometric technique employing NaOH at 480 millimicrons. More current research has led to a potentiometric titration technique for RDX or HMX (Ref 78), while Werwerka et al (Ref 79) have reported on the use of gel-permeation chromatography to detect binder degradation by ascertaining the molecular size distribution

Mechanical properties such as viscosity, plasticity and stress under load conditions affecting various PBXs have been investigated by Armendt (Ref 15), Stott (Ref 31a), Hoge (Refs 47 & 48), Garrison (Ref 49), Springer (Ref 54) and Lindman (Ref 72)

The thermal, vacuum thermal and storage stability performance of the PBXs has been reported on by Gordon in Ref 12 and also in Refs 26, 38, 51, 56 and 77. Most of the **NAVORD** Refs (see under Refs) have some information on these subjects relative to the subject PBX compn of each report

There are four PBX compns for which US Mil Specs exist, viz:

PBHMX. The requirements of the USA armed forces are covered by a Mil Spec (Ref 53a) which contains the following criteria: (1) the material shall be Grade II, Class B HMX **(MIL-H-45444A)** coated with plastic binder by a wet slurry method; (2) plastic binder gravimetrically by wt difference after extrn with toluene satd with HMX, 5.0 ± 1.0%; (3) HMX, by subtraction of the percent plastic binder from 100%, 95.0 ± 1.0%; (4) bulk density, by wt and vol measurement, 0.90g/cc min; (5) moisture by the Karl Fischer method, 0.10% max; (6) granulation, gravimetrically, for information purposes only, using a mechanically shaken nest of US Standard Sieves Nos 20 (850 microns), 60 (250 microns), 80 (180 microns), and 100 (150 microns)

PBX. The requirements of the USA armed forces are covered by a Mil Spec (Ref 85) which contains the following criteria: (1) type I, the molding powder shall be a mixt of RDX, coated and surrounded by a homogeneous mixt of polystyrene and dioctylphthalate; (2) type II, the molding powder shall be a mixt of RDX and plastic plasticizer; (3) composition, as shown below:

PBX Composition

Constituent	Type I, %	Type II, %
RDX[a]	90.0 ± 0.5	90.0 ± 0.5
Polystyrene[b]	8.5 ± 0.3	–
Dioctylphthalate[c]	1.5 ± 0.3	–
Plastic-plasticizer[d]	–	10.0 ± 0.5[e]

a - By chromous chloride-ferric alum titration to a phenosafronin end point (green to red)
b - By calculation
c - By wt difference after extrn with isopropanol satd with RDX
d - By calculation
e - A mixt of 91 ± 1% polystyrene, 5.0 ± 1% dioctylphthalate and 4.0 ± 1% gum rosin;

(4) foreign matter, by visual inspection of the molding powder, no inclusions or particles; (5) color, pink; (6) moisture content, by wt difference after vacuum heating, 0.3% max; (7) granulation, by use of a mechanical shaker and weighing the residue retained by each sieve as shown below:

Granulation of PBX

US Standard Sieve No	Type I %, min	Type II %, min
18 (1000 microns)	thru 100	thru 100
30 (600 microns)	thru 95	thru 95
60 (250 microns)	retained 90	retained 90
80 (180 microns)	retained 98	retained 98
100 (150 microns)	retained 99.9	retained 99.5

PBXN-1. The requirements of the USA armed forces are covered by a **NAVORD** Spec (Ref 50) which contains the following criteria: (1) a preproduction sample which meets specs is required; (2) a homogeneous mixt of RDX and treated Al, each coated and surrounded by nylon; (3) RDX, acet recryst fines of 25 ± 10 microns, by wt difference following extrn with hot acet, 66.0 ± 1.5%; (4) Al, Type A, Class A **(JAN-A-289)**, by wt difference after extrn with hot methanol, 25.0 ± 1.0%; (5) Nylon, "Zytel" 61, by subtracting the percentages of RDX plus

Forty-two and five-tenths gms of polystyrene and 8cc dioctylphthalate were dissolved in 200cc toluene in a lacquer dissolver. Steam was introduced into the jacket until the temp reached 65°. The lacquer was agitated constantly until it was ready to be added to the granulator. This lacquer contained a 1:4 ratio of plastic-plasticizer to toluene

Four hundred and fifty gms of RDX and 4500gms of water (ratio 1:10) were added to the granulator. The agitator was set for 400rpm and the temp was raised to 75° by introducing steam into the jacket. The temp differential between the lacquer soln and the RDX/water slurry was 5–10°

The lacquer soln was poured thru the charging funnel into the granulator. As soon as the lacquer was added, a soln of gelatin in water was added, and the mixt was agitated until the lacquer was well dispersed in the RDX slurry (approx 5 mins). Granulation took place at this point. Steam was introduced again into the jacket to distill the solvent until the temp reached 98°. Cooling water was then run into the jacket to cool the batch to 40°. The coated material from the granulator was collected on a Buchner funnel and dried in a tray at 70° for 24 hours. Temps below 70° did not furnish enough heat, but a temp of 80° produced stickiness and caking of PB-RDX

Another (similar) procedure for preparing up to 50 lbs of molding powd is reported in Ref 32, pp 29–31

In a typical molding procedure the molding powd is heated in a steam oven at 112° for 2–4 hrs, then pressed to shape at 120° using 30000psi with 5mins dwell time under a vac of at least 4mm. A billet of PBX is thus produced with a compressive strength of at least 10000psi (Refs 23 & 64). Heinemann et al (Ref 34) have reported the application of expl metal forming techniques to expl pressing of PB-RDX so as to increase the d of this expl. Other advantages are economy and ease of operation. To produce an end-item the press-formed billet is usually machined using w as a coolant (Ref 61). If further assembly of the expl end-item is required the machined components are usually fastened together with a phenolic type adhesive such as Plaskon 9600 (Ref 20)

Table 1 lists examples of PBX mfg techniques and applications

Table 1

Examples of PBX Manufacturing Techniques and Applications

PBX Nomenclature	Refs	Mfg Techniques	Applications
PBXN-101	38	Slurry – Casting	Fragmentation Type Warheads
PBXN-2	23, 32	Slurry – Molding Powd – Pressing – Machining	Gimlet Rocket Warhead
HNS-II/Teflon	55, 60, 65, 67	Slurry – Molding Powd – Pressing – Machining	Lunar Seismic Expts
PBXN-102	40	Slurry – Casting	Mk 80 Series Low Drag Bombs
PBXC-105	35	Slurry – Casting	Sidewinder
PBXN-3	33	Slurry – Molding Powd – Pressing – Machining	Continuous – Rod Warhead
TSE-1002	62	Slurry – Casting	High Expl Simulant
LX-10-1	74	Slurry – Molding Powd – Pressing – Machining	8" Arty Fired Atomic Proj
PBXW-106	53b	Slurry – Casting	5"/54 Hi-Frag Proj
PBXC-303(1)	73	Injection Molding at 12000psi and RT	Booster Expl or Communication Link in FAE, Zuni, Expl Logic Elements, etc

Al from 100%, 9.0 ± 0.5%; (6) moisture content by the Karl Fischer method, 0.5% max; (7) compressive strength, by pressing to 30000psi with subsequent measurement of pellet diam and height to 0.001 inch, 10000psi min; (8) density, by wt and vol measurement, 1.814g/cc min; (9) granulation, gravimetrically after w/aerosol OT washing, 100% shall pass thru US Standard Sieve No 4 (4.76 mm), and 2% thru sieve No 200 (74 microns); (10) impact sensitivity, using a 2kg wt with type 12 tools (NOTS), 50% pt, 16 inches min (≥ HBX-1); (11) vacuum thermal stability, at 120° in 48 hrs using a 5g sample, 1.0ml/g max; (12) thermal stability, after exposure for 5 hrs at 135° using methyl violet indicator paper, same color as RDX; (13) moisture stability, by gasometric measurement during a 24-hr exposure to w at 77°, 1.0ml/g max

PBXN-5. The requirements of the USA armed forces are covered by a Mil Spec (Ref 61) which contains the following criteria for Types I and II compns: (1) a preproduction sample which meets specs is required; (2) copolymer consisting of vinylidene fluoride and hexafluoropropylene, by wt difference after digestion with hot 1% NaOH soln and w washing, 5.0 ± 0.5%; (3) HMX (MIL-H-45444A[a]) by subtracting the binder percent from 100%, 95.0 ± 0.5%; (4) moisture content by the Karl Fischer method, 0.15% max; (5) granulation, both Type I and II compns, gravimetrically after w/aerosol OT washing – Type I, 99 ± 1% shall pass thru US Standard Sieve No 4 (4.75mm), Type II, 100%; 60 ± 10% of Type II shall pass thru sieve No 20 (850 microns); 2.5 ± 2.5% of Type I shall pass thru sieve No 40 (420 microns), 1.0 ± 1.0% of Type II; (6) density, by wt and vol measurements, 1.831 g/cc min; (7) impact sensitivity, ERL-Bruceton machine using No 12 tools, 50% pt, 2kg wt, ≥ Tetryl; (8) vacuum thermal stability at 120° in 48 hrs using a 5g sample, 0.5ml/g max; (9) wet bulk density, by wt and vol measurement, 0.80g/ml min; (10) autoignition temp, by controlled heating of a thermocouple monitored 1 g sample, ≥ 225°; (11) machineability, using a lathe at 158rpm with w as the coolant, sample shall not crumble or fracture during operation; (12) abrasion resistance, by tumbling 5 pellets in a cardboard box at 20rpm for 60 min and weighing, wt loss of 2.0% max; (13) workmanship, uniform quality, mfg by standard industrial techniques, and free of foreign materials

a -HMX used for type I shall be grade II, class E; HMX used for type II shall be grade II and consist of 75.0 ± 3.0 parts by wt of class A and 25.0 ± 3.0 parts by wt of class E.

Toxicity. PBXs, per se, are *not* highly toxic, but careless handling of the expls or their constituents (see Table 2) can cause systemic poisoning by inhalation of dust or vapor, by ingestion, or by contact with the skin

Table 2

Toxicity of Selected PBX Constituents

Constituent	Toxicity	Refs
HNS	Slight	77
PETN	High, causes headaches, weakness, and a fall in blood pressure; decompn fumes NO_x are toxic	86
RDX	Exposure causes epileptiform convulsions; acute oral LD_{50} for mice is 500mgs/kg	63, 86
DOP	Low	77, 86
Polystyrene	Suspected carcinogen	86
Teflon	None, except by exposure to pyrolysis or decompn products	86

Uses. PBX compns are used wherever high mech strength, high energy and excellent heat insensitivity are reqd. These requirements encompass such applications as a booster (Refs 8 & 51), a means of connective initiation and logic linkage (Ref 73), a filler in rocket warheads (Gimlet, Sidewinder, Shrike, Zuni, etc; Refs 10, 11, 16, 21, 29, 33, 35 & 38), a bomb filler (Mk 80-GPLDB; Ref 40), a seismic shock generator for the Apollo lunar surface expt package (Refs 55, 60, 65 & 67), a means of metal processing and working (Refs 58 & 69), an expl gas shock wave generator (Ref 59), a simulant for larger amts of expls at great distances (Ref 62), a grenade filler (Ref 53a), the shaped charge in a device for foxhole digging (Ref 45), the filler in the 5″/54 Hi-Frag Proj (Ref 72), and as a filler for the 8″ arty fired atomic proj (Ref 74). Additional possible uses are for mil pyrot systs (Ref 75), and as expl fillers for end items such as HEP shells or linear shaped charges which can be used to breach walls in urban warfare (Refs 9 & 87)

Listed below in tabular form are the available parameters found for over 43 selected PBX formulations, supported by unclassified refs. Table 3 presents the nomenclature and formulation of each compn; Table 4, sensitivity and stability data; and Table 5, performance parameters

Table 3
Selected PBX Type Explosives – Composition

Nomenclature	Density, g/cc	RDX, %	Al, %	HMX, %	Plasticizer, %	Binder, %	Refs
Desensitized RDX	–	90	–	–	–	Polydinitro Butyl-Acrylate – 10	4
EL-506A	–	PETN – 85	–	–	–	Not Named – 15	77
EL-506C	–	PETN – 63	–	–	–	Not Named – 37	77
Epoxy Ether Expls	–	80	–	–	–	Glycidyl-2-Fluoro-2,2-Dinitro-Ethoxide – 20	80,81
Flexible Expls	–	PETN – 52	–	–	Bis-(2-Ethyl-Hexyl) Adipate – 12	Latex – 36	70
HMX/Laminac-Styrene	–	–	–	83	–	Polyester Resin-Styrene – 17	39
HMX/Butvar B72A	–	–	–	86	–	Butvar B72A[a] – 14	39
HMX-Viton	–	–	–	88.0	Benzoyl Peroxide – 2.0	Hexafluoropropylene – 10.0	31
LX-02-1	1.44	PETN – 73.5	Cab-O-Sil 2.0	–	Acetyl Tributylcitrate 6.9	Butyl Rubber – 17.6	77
LX-04-1	1.865	–	–	85	–	Viton A[b] – 15	77
LX-07	1.860-.870	–	–	90	–	Viton A[b] – 10	77
LX-08-0	≥ 1.42	PETN – 63.7	Cab-O-Sil 2.0	–	–	Silicone Resin – 34.3	77
LX-09-0	1.837-.845	–	–	93	Bis(2-Fluoro-2,2-Dinitro-ethyl) Formal (FEFO) – 2.4	2,2-Dinitro Poly-Acrylate (PDNPA) – 4.6	77
LX-09-1	1.837-.845	–	–	93.3	FEFO – 2.3	PDNPA – 4.4	77
LX-10-0	1.858-.868	–	–	95	–	Viton A[b] – 5	77
LX-10-1	1.870	–	–	94.5	–	Viton A[b] – 5.5	74,77
LX-11-0	1.870-.876	–	–	80	–	Viton A[b] – 20	77
LX-14	1.833	–	–	95.5	–	Estane 5702-F1 (Polyurethane)[c] – 4.5	77

Table 3 – Selected PBX Type Explosives – Composition (continued)

Nomenclature	Density, g/cc	RDX, %	Al, %	HMX, %	Plasticizer, %	Binder, %	Refs
Nylon Bonded RDX-1	–	90	–	–	–	Nylon – 10	12
Nylon Bonded (Zytel 69) RDX-1	–	69.5	–	–	–	Nylon – 30.5	12
Nylon/Al PBX	–	66	25	–	–	Nylon – 9	24
Nylon/HMX PBX	1.8(?)	–	–	93.6	–	Nylon – 6.4	23
PBX Compns	1.67	90	–	–	DOP – 2.0	Polystyrene (PS) – 8.0	6, 11
	1.66	89.41	–	–	–	Nylon – 10.59	6, 11
	1.68	89.89	–	–	–	Ethyl Cellulose (EC) – 10.11	6, 11
	1.79	92.09	–	–	–	Teflon – 7.91	6, 11
	1.66	89.89	–	–	–	EC – 10.11	6, 11
	1.67	88.34	–	–	DOP – 1.81	PS – 9.85	6,11
	1.79	92.09	–	–	DOP – 1.9	Rubber – 6.01	6, 11
	1.78	89.89	–	–	–	Rubber – 10.11	6, 11
	1.67	92.26	–	–	–	Nylon – 7.74	6, 11
PBX	1.655	90	–	–	–	Nylon – 10	14
PBX	1.798	70	20	–	–	Nylon – 10	14
PBX	1.83	65	26	–	–	Nylon – 9	14
PBX-HNS-Teflon	1.69	HNS-II – 90	–	–	–	Teflon – 10	55, 60
PBX-Mil Spec Type A	–	90	–	–	DOP – 1.5	PS – 8.5	39, 85
PBX-1	1.80	69.50	21.00	–	–	Nylon – 9.50	13
PBX-1	1.83	65	26	–	–	Nylon – 9	13
PBX-9007	1.66	90.0	–	–	Di-2-ethyl-phthalate – 0.5, Rosin – 0.4	PS – 9.1	77
PBX-9010	1.789	90	–	–	–	KelF – 10[d]	77
PBX-9011	1.770	–	–	90	–	Estane[c] – 10	77
PBX-9205	1.68	92	–	–	Di-2-ethyl-phthalate – 2.0	PS – 6	77
PBX-9404	1.829-.844	–	–	93.73	Tris(β-Chloroethyl) phosphate – 3.09, DPA – .09	NC – 3.05	56, 57
PBX-9404-03	1.831-.844	–	–	94	Tris(β-Chloroethyl) phosphate – 3.0	NC – 3	26, 77

Table 3 – Selected PBX Type Explosives – Composition (continued)

Nomenclature	Density, g/cc	RDX, %	Al, %	HMX, %	Plasticizer, %	Binder, %	Refs
PBX-9407	1.60-.62	94	–	–	–	Exon 461[e] – 6	77
PBX-9501	1.843	–	–	95.00	Bis(2,2-Dinitropropyl) Acetal – 1.25 Bis(2,2-Dinitropropyl) Formal – 1.25	Estane[c] – 2.50	77
PBXC-105	1.80	–	23.0	59.0	–	Polyester-Styrene	35
PBXC-303(1)	1.40	PETN – 80	–	–	–	Silicone Resin – 20	73
PBXN-1 (A)	1.80-.84	66	25	–	–	Nylon – 9	21
PBXN-1 (B)	–	69.3	20.5	–	–	Nylon – 10.2	27
PBXN-2	1.803	–	–	94.7	–	Nylon – 5.3	27, 32
PBXN-3	1.734	–	–	86	–	Nylon – 14	33
PBXN-4	–	DATB – 95.0	–	–	–	Nylon – 5	37
PBXN-5	1.897	–	–	95	–	Viton A[b]	37, 61
PBXN-101	1.66-.69	–	–	82	–	Styrene-Polyester – 18	38
PBXN-102	1.798	–	23	59	–	Styrene-Polyester – 18	40
Polystyrene Bonded RDX (Type A)	1.600	90.0	–	–	DOP – 1.5	PS – 8.5	28, 39, 53
RDX-Nylon-A	1.579	78.2	–	–	–	Nylon – 21.8	27
RDX-Nylon-B	1.627	83.2	–	–	–	Nylon – 16.8	27
Self-Supporting Expl	0.92	PETN – 80.0	–	–	diButyl Phthalate – 2.0	p-Vinyl Acetate – 18.0	52
TSE-1002	0.92	PETN – 35.9	Fe Powd– 28.0	–	Peroxide Catalyst – 0.2	Polyester & Styrene – 35.9	62
X-0242	1.855	–	–	95	n-Propanol – 2.2	Polyurethane – 2.5	57
XTX-8003	1.53	PETN – 80	–	–	–	Silicone Rubber – 20	77

Footnotes to Table 3

Binder Nomenclature Identification:
a – Polyvinyl butyral resin – Monsanto Co
b – Hexafluoropropylene/vinylidine fluoride 1:2
c – Polyurethane soln system – B.F. Goodrich Co
d – Polytrifluorochloroethylene – 3M Co
e – Trifluorochloroethylene/vinylidine chloride copolymer – Firestone Plastics Co

Table 4
PBX Type Explosives – Sensitivity and Stability Data

Nomenclature	Autoignition Temp, °C	Gap Test, 50%, Inches	Impact Sensitivity	Rifle Bullet Impact Test	Vacuum Stability Test (ml/g/48hrs @ 120°)	Refs
Desentized RDX	–	–	50-60cm/2kg	–	–	4
HMX-Viton	256	–	35cm/50%pt/NOTS	–	0.03	31
LX-02-1	–	–	80cm/50%pt/12 Tool	–	0.3-0.6ml/.25g/22hrs @ 120°	77
LX-04-1	> 250	0.040-0.060[a]	41cm/50%pt/12 Tool	–	0.01-0.04ml/.25g/22hrs @ 120°	77
LX-07	> 250	0.070-0.090[a]	38cm/50%pt/12 Tool	–	0.01-0.04ml/.25g/22hrs @ 120°	77
LX-08-0	129-35	–	–	–	–	77
LX-09-0 & -1	> 280	0.075-0.105[a]	32cm/50%pt/12 Tool	–	0.03-0.07ml/.25g/22hrs @ 120°	77
LX-10-0	> 250	0.080-0.100[a]	35cm/50%pt/5kg-12 Tool	–	0.02ml/.25g/22hrs @ 120°	77
LX-10-1	250-270	0.080-0.100[a]	35cm/50%pt/2.5kg-12B Tool	–	0.04-0.06ml/.25g/22hrs @ 120°	74,77
LX-11-0	> 250	0.045-0.065[a]	59cm/50%pt/12 Tool	–	0.01-0.04ml/.25g/22hrs @ 120°	77
LX-14	> 270	0.060-0.080[a]	51cm/50%pt/2.5kg-12B Tool	–	0.025	77
Nylon Bonded RDX-1	–	–	–	–	0.30-0.41	12
(Zitel 69)/ RDX-1	–	–	–	–	1.2	12
Nylon/HMX PBX	–	–	54cm/50%pt/2kg	–	0.15	23
PBX	209	–	–	–	–	14
PBX-HNS/Teflon	–	< 0.200	–	–	0.15ml/g/hr/2hrs @ 230°	60
PBX-1	–	–	72cm/2kg (RDX=17)	–	1.655	13
PBX-2	–	–	49cm/2kg (RDX=17)	–	2.220	13
PBX-9007	> 200	0.045-0.055[a]	35cm/50%pt/12 Tool	–	0.03-0.07ml/.25g/22hr @120°	77
PBX-9010	> 200	0.075-0.095[a]	30cm/50%pt/12 Tool	–	0.2-0.3	77
PBX-9011	> 250	0.055-0.070[a]	44cm/50%pt/12 Tool	–	0.024ml/.25g/22hrs @ 120°	77
PBX-9205	> 200	0.025-0.035[a]	42cm/50%pt/12 Tool	–	0.025ml/.25g/22hrs @ 120°	77
PBX-9404	–	1.00 (P_{CJ})	42.4cm/50%pt/2.5kg Type 12 Machine	–	3.5	26,56,57

Table 4 — PBX Type Explosives — Sensitivity and Stability Data (continued)

Nomenclature	Autoignition Temp, °C	Gap Test, 50%, Inches	Impact Sensitivity	Rifle Bullet Impact Test	Vacuum Stability Test (ml/g/48hrs @ 120°)	Refs
PBX-9404-03	> 250	0.085-0.105[a]	34cm/50%pt/12 Tool	–	3.2-4.9	77
PBX-9407	> 200	0.090-0.120[a]	33cm/50%pt/12 Tool	–	0.06ml/.25g/22hrs @ 120°	77
PBX-9501	> 240	0.050-0.070[a]	44cm/50%pt/5kg/12 Tool	–	0.8	77
PBXC-105	245-50	–	≥28cm/50%pt/ERL-Bruceton 12 Tool	–	0.5	35
PBXC-303(1)	179	0.10mm	18cm/50%pt/2.5kg	–	0.12ml/g/48hrs @ 100°	73
PBXN-1 (A)	180-82	–	35-190cm/50%pt/2kg	0/4 shots	0.5-1.0	21
PBXN-1 (B)	188	–	40cm/50%pt/NOTS	–	–	27
PBXN-2	215-21	0.295	35-44cm/50%pt/NOTS	–	1.1	27,32
PBXN-3	202-16	0.290	55-67cm/50%pt/NOTS	–	0.05-0.13	33
PBXN-5	> 225	–	52cm/50%pt/NOTS	–	0.15	37,61
PBXN-101	237	–	48cm/50%pt/NOTS	–	0.17	38
PBXN-102	242	–	28cm/50%pt/BM	10% expln/ 90% partial	0.41	40
Polystyrene Bonded RDX (Type A)	275 (expln temp)	–	28cm/BM/2kg(TNT=95)	1 expln/ 9 partial	0.08ml/g/40hrs @ 120°	28,39,53
RDX-Nylon-A	–	0.280	65cm/50%pt/NOTS	–	–	27
RDX-Nylon-B	–	0.272	51cm/50%pt/NOTS	–	–	27
TSE-1002	165 (expln temp)	–	–	0/5 shots	–	62
XTX-8003	–	0.130-0.160[a]	21cm/50%pt/12 Tool	–	>0.02ml/.25g/22hrs @ 100°	77

Footnote to Table 4

a – Small scale test using brass shim spacers

Table 5
PBX Type Explosives – Performance Data

Nomenclature	Peak Overpressure, PSI	Impulse, PSI-Msec	Detonation Rate, M/Sec	Q_e, cal/g (H_2O Liq at 25°)	Refs
Flexible Expls	–	–	7700-8200	–	70
HMX/Butvar 2A	30.4 at 10 ft (7 lbs charge)	18.0 at 10 ft (7 lbs charge)	–	–	39
HMX/Laminac-Styrene[a]	31.9 at 10 ft (7 lbs charge)	24.8 at 10 ft (7 lbs charge)	–	–	39
HMX-Viton	–	–	8510	–	31
LX-02-1	–	–	7370	1420	77
LX-04-1	–	–	8460	1420	77
LX-07	–	–	8640	1490	77
LX-08-0	–	–	6560	1980	77
LX-09-0 & -1	–	–	8810	1600	77
LX-10-0	–	–	8820	1550	77
LX-10-1	–	–	8820	1550	74, 77
LX-11-0	–	–	8320	1380	77
LX-14	–	–	8837	1576	77
Nylon/Al PBX	30.55 at 5.7 ft (7 lbs charge)	19.07 at 7.7 ft (7 lbs charge)	–	3480 (detond in air)	24
Nylon/HMX PBX	–	–	8700	–	23
PBX	–	–	8127, 8227 (indvdl detns)	–	14
PBX	–	–	7970	–	14
PBX	–	–	7850	–	14
PBX-1	–	–	–	974	13
PBX-2	–	–	–	998	13
PBX-9007	–	–	8090	1560	77
PBX-9010	32.6 at 10 ft (7 lbs charge)	19.6 at 10 ft (7 lbs charge)	8370	1470	39,77
PBX-9011	–	–	8500	1530	77

Table 5 — PBX Type Explosives — Performance Data (continued)

Nomenclature	Peak Overpressure, PSI	Impulse, PSI-Msec	Detonation Rate, M/Sec	Q_e, cal/g (H_2O Liq at 25°)	Refs
PBX-9205	–	–	8170	1460	77
PBX-9404	–	–	8782	–	57
PBX-9404-03	–	–	8800	1560	77
PBX-9407	–	–	7910	1600	77
PBX-9501	–	–	8830	1590	77
PBXC-105	20.0 at 20 ft (11 lbs charge)	27.0 at 20 ft (11 lbs charge)	7512	–	35
PBXC-303(1)	–	–	7200	–	73
PBXN-1 (B)	30.8 at 10 ft (7 lbs charge)	21.5 at 10 ft (7 lbs charge)	–	–	39
PBXN-2	–	–	8670	–	32
PBXN-3	25.8 at 10 ft (7 lbs charge)	25.0 at 10 ft (7 lbs charge)	8390	–	33, 39
PBXN-101	–	–	7980	–	38
PBXN-102	18(avg) at 26.75 ft (250 lbs charge)	38(avg) at 26.75 ft (250 lbs charge)	7550	–	40
Polystyrene-RDX (Type A)	33.3 at 10 ft (8 lbs charge)	19.7 at 10 ft (7 lbs charge)	–	983	28, 39, 53
Polystyrene-RDX (Type B)	31.5 at 10 ft (7 lbs charge)	18.2 at 10 ft (7 lbs charge)	–	–	28, 39, 53
RDX-Nylon-A	–	–	7876	–	27
RDX-Nylon-B	–	–	8038	–	27
Self-Supporting Expl	–	–	5200	–	52
TSE-1002	–	–	2550	–	62
X-0242	–	–	8826	–	57
XTX-8003	–	–	7300	1880	77

Footnote to Table 5

a — Polyester resin — American Cyanamid Corp

Written by **H. L. HERMAN**

Refs: 1) M.B. Frankel et al, "Explosives Research", Aerojet Engrg Corp, Azusa, Calif, **Rept No 538**, Contract N7onr-46208 (1951) 2) Ibid, **Report No 562** (1951) 3) L.T. Carleton & M.B. Frankel, Ibid, **Report No 621** (1952) 4) Ibid, **Rept No 637** (1952) 5) Ibid, **Rept No 660** (1952) 6) E. James & L.C. Smith, "Plastic Bonded RDX", Univ of Calif, **LA 1448** (1952) 7) J.L. Vermillion & R.C. Dubberly, "Plastic-Bonded RDX, Its Preparation By the Slurry Method", Holston Defense Corp, Tenn, Control **No 20-T-16 Series A (PAC 1081)** (1953) 8) A.J. Pascazio, "The Suitability of a Bare PBX Booster Pellet In The 2.75-Inch HEAT M1 Rocket Head", PATR **2271** (1955) 9) H.W. Voigt et al, "Development of Plastic Explosives For HEP Shell Filler", PATR **2176** (1955) 10) K.G. Clemens, "Penetration Tests With PBX-Filled Reinforced Plastic Gimlet Warhead", **NOTS 1110, NAVORD 3487** (1955) 11) K.S. Skaar et al, "Development of Plastic-Fiberglas Cased Plastic-Bonded-Explosive Warhead For the 2.0-inch Gimlet Rocket", **NOTS 1114, NAVORD 3491** (1955) 12) W. Gordon, "Vacuum Thermal Stability of Nylon-Bonded RDX", **NOTS 1271, NAVORD 4949** (1955) 13) K.S. Skaar et al, "Technical Progress Report – 1 November to 30 November 1955", NOTS (1955) 14) Ibid, "Minutes of Meeting On Plastic-Bonded Explosives At China Lake, California – 14 February 1956", **NOTS 1512, NAVORD 5287**, (1956) 15) B.F. Armendt, "Qualitative Test of Dynamic Strength of Various Plastic-Bonded And Fiber-Reinforced Explosives", BRL, APG, **MR 977** (1956) 16) K.G. Clemens, "A Study of the Penetration Characteristics of PBX-FRP 2.0-inch Warheads", **NOTS 1334, NAVORD 5001** (1956) 17) F.C. Anderson et al, "Explosives Research", Aerojet-General Corp, Azusa, Calif, **Rept No 1200**, Contract N7onr-46208 (1956) 18) J.R. Fischer et al, Ibid, **Rept No 1224** (1956) 19) C.B. Frost & C.H. Tieman, Ibid, **Rept No 1239** (1957) 20) B. Stott, "Adhesives For Use With PBX", NOTS MR (23 April 1956) 21) K.S. Skaar et al, "Plastic-Bonded Explosive (PBXN-1) And Its Use In A Fiberglas-Plastic Warhead", **NOTS 1341, NAVORD 5007** (1957) 22) E.E. Mason & G. Svadeba, "Preparation of PBXN-1 Using Immiscible Liquids in the Slurry Process", NAVORD 5795 **(1957)** 23) C.W. Falterman et al, "Investigation of Nylon-HMX Plastic-Bonded Explosive", **NOTS 1790, NAVORD 5586** (1957) 24) E.M. Fisher et al, "The Blast Performance of Aluminized Nylon PBX", **NAVORD 6067** (1957) 25) G.S. Rogers, "Pilot Plant Preparation of PBXN-1 By The Stoddard Solvent Slurry Process", **NAVORD 5799** (1958) 26) Anon, "Thermal And Stability Properties of LASL PBX 9404", Mason & Hanger – Silas Mason Co, Inc, Iowa, Progress **Rept 5** (1958) 27) K.S. Skaar et al, "PBX Progress For Quarter Ending 30 June 1958", **NOTS 2072, Tech Progress Rept 216** (1958) 28) B.J. Zlotucha et al, "Characteristics of Polystyrene-Bonded RDX (PB-RDX)", PATR **2497** (1957) 29) C.W. Falterman et al, "A Nylon-Bonded Explosive And Simulant For Penetration Testing", **NOTS 1936, NAVORD 5841** (1958) 30) E.E. Mason, "A Rapid Method of Analysis For PBXN-1", **NAVORD 5797** (1958) 31) M.H. Kaufman, "PBX Based on HMX-Viton", **NOTS TP 2151, NAVORD 6443** (1959) 31a) B.A. Stott, "Effect of Slurry Additives and Aluminum Treatments On Coagulation of PBXN-1 Molding Powder", **NOTS TP 2224, NAVORD 6531** (1959) 32) B.A. Stott, "An Evaluation of PBXN-2, A High-Energy, High-Strength, Nylon-Bonded Explosive", **NOTS TP 2456, NAVWEPS 7057** (1960) 33) P.E. Shea & C.W. Falterman, "PBXN-3: Its Development For Use In The Continuous-Rod Warhead", **NOTS TP 2451, NAVWEPS 7054** (1960) 34) R.W. Heinemann et al, "Explosive Forming of Explosives", PATR **2685** (1960) 35) C.W. Falterman, "Qualification Tests For The PBX Loaded Warhead For Sidewinder 1A", **NOTS TP 3075, NAVWEPS 8069** (1963) 36) S.E. Smith, "Analytical Procedure For Determining Hydroquinone and/or p-Tert-Butyl Catechol In Castable PBX Raw Materials", **NAVWEPS 8236** (1964) 37) O.K. Pennington, "Composition Analysis Procedures For PBXN-1, PBXN-2, PBXN-3, PBXN-4 and PBXN-5", **NOTS TP 3337, NAVWEPS 8409** (1964) 38) B.A. Stott et al, "PBXN-101, A Heat Resistant, Castable Explosive For Fragmentation Type Warheads", **NOTS TP 3612, NAVWEPS 8597** (1964) 39) H.L. Herman, "Comparative Blast Measurements of Various High Explosive Compositions In A Standard

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PCX. Code name for 1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate

PD. The US military designation for the war gas Phenyldichloroarsine, which is both a blistering agent and a vomiting agent, and has a delayed-action casualty effect (Ref 2). $C_6H_5AsCl_2$, mw 222.91, colorl liq, bp 252°, fr p −16°, liq d 1.65g/cc at 20°, vap d (compared to air) 7.7

Vapor pressure. 0.021mm Hg at 20°, 0.113mm Hg at 40°

Volatility. 404mg/m^3 at 20°. The vaporizing tendency of PD is too low to give it any value as a blister agent in the field. If dispersed as an aerosol, it would be effective against unprotected troops, although only as an agent with a short duration of effectiveness

Flash point. High enough not to interfere with the mil use of the agent

Decompn temp. Stable to bp

Latent heat of vaporization. 67 cal/g

Rate of hydrolysis. Rapid to HCl and phenylarsenious oxide

Stability in storage. Very stable

Action on metals or other materials. None

Odor. None

Median concn detectable (by nasal and throat irritation). 0.9mg/m^3

Median lethal dosage (by inhalation). 2600mg-min/m^3

Median incapacitating dosage. 16mg-min/m^3 as a vomiting agent; 1800mg-min/m^3 as a blistering agent

Skin and eye toxicity. 633mg-min/m^3 will produce casualties by eye injury. On bare skin PD is about 90% as blistering as HD (distilled mustard), but it is decompd immediately by wet clothing

Rate of action. Immediate effect on eyes, effects on skin delayed ½ to 1 hr (Ref 1)

Refs: 1) Anon, "Military Chemistry and Chemical Agents", **TM3-215** (1963), 28–9 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 347

PDNA. Abbr for Propylenedinitramine

PE. Abbr for Pentaerythritol (See in this Vol)

PE-1, -2, -3, -3A, -4 Explosives. Brit plastic expls contg RDX, similar in compn to the US Composition C-4 (See Vol **3**, C485)

Refs: 1) Anon, "Summary Report", **NDRC Rept VI**, Div 8 (1946), 29 2) L. Jablansky, "Examination of British Plastic Explosive, PE-3A", PATR **2095** (1955) (Conf) 3) J. Cogan, "Comparative Testing of United Kingdom Explosive PE-4 and Composition C-4", TechRept **1650-TR**, Engineer Res & Dev Labs, Ft Belvoir, Va (1960) (For Official Use Only)

Peak Pressure in Detonation and Explosion. See Vol **2**, B181–2 and Vol **4**, D484-R to D485-L

PEAP. Acronym for Pentaerythritol Acetate Proprionate. See under Pentaerythritol Diacetate Dipropionate in this Vol

Peat, Nitrated (Nitrotourbe in Fr). When partially dried peat (preferably approaching the lignite stage) is nitrated with nitric-sulfuric acid, tarry expl substances (resembling nitrated tars in appearance) are obtained. If the peat is of recent formation, the nitration reaction proceeds too violently (Ref 1)

Peat has also been used as an ingredient of AN-based blasting expls (Refs 2 & 3)

Refs: 1) Daniel (1902), 572 2) H.W. Clapham, CanP 350872 (1935) & CA **29**, 5658 (1935) 3) E. Whitworth & J. Hornell, BritP 595443 (1947) & CA **48**, 6699 (1948)

Pebble Powder (P Powder). See under "P" (Pebble Powder) in this Vol

Pectin Nitrates (Nitropectins). Pectin is a high mw substance (polyuromide) related to carbohydrates and found in varying quantities in fruits and plants. It consists chiefly of partially methoxylated galacturonic acids joined in long chains. Pectic acid is derived from pectin by treating it with NaOH soln, washing with isopropyl alc, adding alc HCl, and finally washing again with isopropyl alc and drying (Ref 6)

Prior to WWII, attempts were made in Germany to nitrate pectins prepd by extracting sugar beet shavings (Refs 1, 3 & 4). However, the properties of the nitropectins were of no great interest, and they have not found any practical application

Schneider and Ziervogel (Ref 2) obtained nitric esters of pectin as intermediate products which were then esterified by means of acet anhydr to the corresponding acetates. In 1949, Rogovin, Treyvas and Shorygina (Ref 5) prepd pectin nitric esters by nitrating pectic acid for 4 hrs at 20° in a mixt composed of 48% HNO_3, 50% H_3PO_4 and 2% P_2O_5 to yield a product contg 9.2% N and 7.5% carboxylic groups

Refs: 1) F.A. Henglein & G. Schneider, Ber **67B**, 309–24 (1936) & CA **30**, 3780–2 (1936) 2) G. Schneider & M. Ziervogel, Ber **69**, 2530 (1936) & CA **31**, 1369 (1937) 3) G. Schneider & V. Fritschi, Ber **70B**, 1611–17 (1937) & CA **31**, 7397–7400 (1937) 4) W. Obst, NC **9**, 221 (1938), not found in CA 5) Z.A. Rogovin, M.G. Treyvas & N.N. Skorygina, ZhPriklKhim **22**, 1244 (1949); not found in CA 6) CondChemDict (1971), 661–2

Pedersen Device. An invention of the US arms designer J.D. Pedersen, this was a noteworthy ordnance secret of WWI. It consisted of a receiver unit that could be locked into the receiver of a Springfield or Enfield rifle. Installed, it converted the rifle into a semiautomatic weapon that fired .30 cal pistol-type cartridges from a 40-round box magazine. To hide its identity, the mechanism was officially listed as the US .30 cal automatic pistol Model 1918. The system was dropped after the war

Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 342

Pelargonic Acid Esters. Esters of pelargonic acid or of other open-chain carboxylic acids with 7 to 10 carbon atoms, were claimed by Barsky to be excellent plasticizers in proplnts, good muzzle flash reducers without excessive smoke formation, as well as acting to render the proplnt compn practically non-hygroscopic. The following are examples of proplnt compns containing such esters: 1) NC 86, DNT 10, triethyleneglycol dipelargonate 4%; 2) NC 96, mixed di- and triethyleneglycol pelargonate and caprylate 4%; and 3) NC 82, TNT 15, diethyleneglycol

diheptaoate 3%

In order to prepare the esters mentioned above, eg, triethyleneglycol dipelargonate, 2 moles of pelargonic acid were heated with 1 mole of triethyleneglycol while bubbling thru a gentle stream of CO_2. During the first 2-3 hours of heating, the temp was raised gradually to 270–275°, and maintained for several hours until esterification was complete. The crude product was purified by washing with alkali and w, followed by vacuum drying at 90°. It was then subjected to a bleaching operation with activated C at about 110°, and filtered

The same procedure was used in the prepn of esters of other acids, such as caprylic and heptylic

Barsky also used as a plasticizer, a compn prepd by heating a mixt of pelargonic acid 80, caprylic acid 15, and heptoic acid 5%, with a mixt of diethyleneglycol and triethyleneglycol in equal proportions

Ref: G. Barsky, USP 2396074 (1946) & CA **40**, 3607 (1946)

Peley Explosive Paper (Papier explosible in Fr). See under Explosive Papers or Pyropapers in Vol **6**, E424

Pellet Loading. See under Loading and Fabrication of Explosives in Vol **7**, L46 to L57

Pellet Powder (Poudre Balle in Fr). BlkPdr compressed into grains of cylindrical shape. It was used by the Brit in large cal cannon before the introduction of "Pebble Powder" (see in this Vol)

Ref: Daniel (1902), 603

Pellet Powder. A special grade of BlkPdr, of approx the same compn as Blasting Powder B (contains $NaNO_3$ instead of KNO_3), but slightly modified by the addition of various ingredients to control the physical and expl properties. The powder is pressed into cylindrical pellets of approx 2″ in length, from 1-1/8 to 2-1/2″ in diameter, with perforations 3/8″ in diameter. Two to four of these cylinders are wrapped in paraffined paper to form cartridges 4, 6 or 8″ in length. They are safer to handle than granular powder, and can be used for various types of blasting, particularly in mining coal, where permissible expls are not required

Refs: 1) Bebie (1943), 113–114 2) Davis (1943), 49

Pellets, Antiflash. See under Pastilles Antilueurs in this Vol

Pellier Explosive. A Fr expl invented in 1884 contg K perchlorate 67.1, K nitrate 8.4, sulfur 8.4, fine sawdust 6.0, and extract of campeachy weed 10.1%

Ref: Daniel (1902), 603

Pellier Résine Explosible. A Fr expl invented in 1886, with a brownish color, resembling a resin in appearance. It was prepd by the nitration of sugar with mixed nitric-sulfuric acids

Ref: Daniel (1902), 603

Pelouze, Théophile-Jules (1807–1867). Fr scientist who made many important contributions to organic and inorganic chemistry. He nitrated paper in 1838, and was thus probably the first to prepare NC. Pelouze did not recognize the importance of his work, and thought that his product was identical with nitrated starch (which he called "xyloidine"), prepd in 1833 by Braconnot (see Vol **2**, B259-R). Much better grade NC was prepd in 1846, independently by Schönbein and Bottger, by the nitration of cotton

Ref: Davis (1943), 245–8

Pembrite. A Brit mining expl contg AN 93–96, vegetable oil 3–6, sulfur 1–2 and Ba nitrate 1%

Ref: Daniel (1902), 604

Pendulum, Ballistic, Test. See under Physical Tests in Vol **1**, VII to VIII (Also see A. Schmidt, Explosivst **1962**, 23-34)

Pendulum Chronographs. (Pendelchronographe in Ger). A mechanical-electrical device to measure the velocity of a projectile in flight. Cranz (Ref, p79) describes the Navez-Leurs chronograph used in Fr for several years beginning in 1853, until replaced by the LeBoulengé Chronograph in 1866 (see Vol **3**, C307-R to C308-R). Another pendulum chronograph was invented by Casperson (Ref, p129)
Note: Pendulum chronographs are not the same as ballistic pendulum chronographs (see Vol **2**, B6-R)
Ref: Cranz **3** (1927), 79 & 129

Pendulum, Friction, Apparatus. See under Friction Sensitivity Tests in Vol **6**, F204-L to F206-L

Penetration Aids (Pen Aid). Generic name for devices and tactics intended to assist the penetration of aircraft and missiles against defense systems. Six main classes of *Pen Aid* have been prospected: 1) use of chaff, jamming or nuclear blackout to hide the delivery vehicles or warheads from defense radars; 2) the saturation of defense radars by the use of multiple warheads (including MIRV payloads), and target simulations such as decoys, balloons or false radar echoes; 3) the shielding of missile warheads against weapon effects, and the use of maneuverable re-entry vehicles; 4) active defense against interceptors by means of anti-ABM missiles or anti-SAM missiles in strategic bombers; and 5) salvage fusing – this is intended to detonate the offensive weapons, and especially ICBM warheads when interception appears probable, or, more practically, upon sensing the first effects of interceptor weapon effects. This reduces the effectiveness of the offense since its weapon is still not on target, but it may achieve a partial kill

A further evasion measure specifically intended against ballistic-missile defenses is a low trajectory flight pattern for strategic missiles. This reduces the height and therefore the radar visibility of incoming warheads, thus complicating the defense's mission
Ref: E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 151–2

Penryhn Antifrost Powder (or Antifrost Penryhn Powder). A Brit expl which passed the Buxton Test (see Vol **2**, B394-R). It contained a nitrated mixt of glycerin and ethylene glycol 9, AN 60, woodmeal 9, and Na chloride 22%. Power by BalPend 2.42″ (vs 3.27″ for standard Brit Gelignite contg 60% NG)
Ref: Marshall **3** (1932), 120

Penta. One of the names for Pentaerythritol Tetranitrate (PETN) (See in this Vol)

Pentaborane. See Vol **2**, B254-L to B256-R
Addnl Ref: Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 396–7

3-Pentadecylphenol. $HO.C_6H_4.(CH_2)_{14}CH_3$ mw 304.52. Can be prepd by a series of reactions from cardanol, $HO.C_6H_4.C_{14}H_{27}$, obtained by distg cashew-nutshell liq at reduced press, or by steam distn at atm press (Ref 1)
Trinitro-3-pentadecylphenol. $(O_2N)_3(HO)C_6H.C_{15}H_{31}$, mw 439.57, N 3.19%, mp 89–90° (impure 82–86°). Can be prepd by nitration of 3-pentadecylphenol, as described in BritP 627928 (Ref 2). It is an expl compd
Refs: 1) S. Kaplan, USP 2181119 (1939) & CA **34**, 1992 (1940) (Derivatives of a phenol obtained from cashew-nutshell) 2) Harvel Corp, BritP 627918: 627927; 627928 (1949) & CA **44**, 4502–3 (1950) (Nitrogen-contg derivatives of 3-pentadecylphenol)

PENTAERYTHRITOL AND ITS DERIVATIVES

Pentaerythritol [Pentaerythrite, Tetrakis-(hydroxymethyl)methane, Tetramethylolmethane, Methanetetramethylol, 2,2-Bis-(hydroxymethyl)-1,3-propanediol (name

currently preferred by CA), **Pentek, Penetek, Pentaerythrit** (Ger), **Pentaeritrit** (Russ), **PE**]. $C(CH_2OH)_4$, $C_5H_{12}O_{14}$, mw 136.15, white tetragonal crysts (frequently twinned), mp 262–3° (coml grades mp 180–250°) (Refs 1 & 18). By using resublimed PE a mp of 265.5° was obtained from the mp curve (Ref 10). A phase change at 187.7° from the tetragonal to the cubic system was also found. The Q of transition and fusion were found to be 10.5 and 1.7-kcal/mole resp (Ref 10). Its bp is 276° at 30mm with sublm (Refs 5 & 12); d by flotation of a single cryst is 1.39g/cc (Ref 6); RI 1.548 (Ref 18); CA Registry No 115-77-5

Historical. PE was first isolated by Tollens who was examining the effect of heat and reagents on formaldehyde. Apparently the crude formaldehyde he was working with contained a small % of acetaldehyde, which accounts for the PE formed. Although Tollens isolated it in 1882, it was not identified as PE until 1888 (Ref 2). Further details of the prepn and props of PE appeared in 1891 (Ref 3). The prepn is essentially a condensation betw 3 moles of formaldehyde and 1 of acetaldehyde to give an intermediate tris(hydroxymethyl)-acetaldehyde which is not isolated. An intermolecular oxidn/redn then takes place betw this intermediate, and a 4th mole of formaldehyde, giving PE and formic ac (Ref 13, p 2). This type reaction is discussed under Cannizzaro Reaction in the Encycl (Vol **2**, C25)

Preparation. Its prepn on a lab scale is given in Ref 7. A detailed exptl proc for its prepn on a coml (1000 lb) scale is given in Ref 4 as follows: In the reactor is placed 3175 lb of 37% formaldehyde and ca 700 lb of w. To this is added with stirring 1050 lbs of 50% NaOH at a rate so as to keep the temp at 15–20° (with cooling if necessary). Then is added 385 lbs of 99% acetaldehyde under the surface of the soln with vigorous stirring and cooling so as to keep the temp at 20–5°. The mixt is held at 25–30° for several hours and then held at 60° until the acetaldehyde concn falls to 0.1%. The mixt is transferred to a neutralizing tank where formic ac is added until the pH is 7.8–8.0. The soln is transferred to an evaporator, evapd to a d of 1.27g/cc, chilled, and the crude PE filtered off using a wringer or a Nutsch filter. The crude PE, yield 85–90% based on acetaldehyde, conts poly(pentaerythritols) (see Encycl Vol **5**, D1407) plus small amts of pentaerythritol ethers and cyclic formals. It is suitable for mfg resins, plastics, and drying oils; but can be further purified as follows: the crude cake is dissolved in dil aq HCl, activated C added, the soln filtered hot, chilled, and the crysts filtered. By evapn of the filtrate and chilling 2nd and 3rd crops may be obtained. The mother liquors and filtrates may be recycled to recover Na formate and poly(pentaerythritols). A variation of the process uses lime as the condensing agent instead of NaOH. In this case the soln is neutralized with sulfuric ac instead of formic ac, the pptd Ca sulfate filtered, the filtrate treated with oxalic ac to ppt the remaining Ca ions, and the PE isolated as above (Ref 4). A flow sheet of this process is in Ref 16. PE can be sepd from the last traces of the dimer and higher polymers by prepn of the cyclic dibenzylidene deriv which is recrystd from hot acet, mp 164.5° (Ref 13, p 154). The latter is hydrolyzed with aq HCl in a continuous app which can be scaled up to the kg scale (Ref 8)

Analysis. Quant detn with Ce(IV), proc: a sample contg 3–16mg of PE is mixed with a 50–100% excess of the Ce(IV) reagent, 1 ml of catalyst B and 8.5ml 72% perchloric ac added, the mixt heated on a hot plate at 95° until a pink color develops, the mixt quenched by chilling, 10–15ml of 6M sulfuric ac added, and the excess Ce(IV) back titrated with std Fe(II) soln. For prepn of reagents and calcns see Ref 15

Reactions. PE readily forms esters with organic and inorganic acids (Refs 9, p 157 & 13, pp 54, 212 & 246); and cyclic as well as open chain acetals and ketals (Refs 9, p 195 & 13, p 141). Some of these prods are used in expls, while others

give valuable expls on nitration. For info on individual compds of interest see below under Derivatives of PE

Solubility (g/100g solv) w 6.5 at 25°, 90 at 100°; EtOH 0.5 at 25°; glycerol 10.3 at 100°; diethylene glycol 7.7 at 100°; formamide 21.3 at 100°; sl sol in dioxane, pyridine, and liq ammonia; insol acet, bz, C tetrachloride, eth, oils, fats, & petr eth (Ref 12)

Specification. US Armed Forces requirements for PE intended for mfg of PETN are given in US Army Mil Spec **MIL-P-20304** (1951) as follows: *Color*–white; *Moisture*–max 0.5%; *Melting Point*–min 250°; *Hydroxyl Value*–min 49.0%; *Water Insoluble*–max 0.25%; *Chloride*–max 0.01%; *Ash*–max 0.10%; and *Granulation*–through US No 18 sieve, min 100%; through US No 20 sieve, min 99%; and retained on US No 100 sieve, min 90%

Thermal Decomposition. In the presence of Al oxide PE at 270–80° was found to give Me alc, CO_2, w, & 2-methylacrolein. In the presence of powd Cu bronze less Me alc and more 2-methylacrolein were formed (Ref 10)

Toxicity. Low, the finely divided dust is a nuisance hazard (Ref 19)

Uses. Its primary use in peacetime is for the prepn of esters, ethers, ketals, etc, which have widespread use in the paint, plastic, and resin inds (Ref 9). In WWII, PE esters of long chain unsatd fatty acids were developed as a substitute for tung oil, whose supply from China was cut off (Ref 13, p 231). In wartime large quants are consumed in the mfg of PETN, Petrin, and other nitrate esters (see below). A castable expl has been patented contg 12.66% of a 49/51% Na nitrate/Mg dinitrate eutectic, 50.65% AN, 11.68% PE, and 25% Hexogen (Ref 14). Mixts of PE with powd metals (Al, Mg, and alloys of these) react to form metal oxides, C, and H. The reaction is very exothermic ($Q_{reaction}$ 1.49–1.55kcal/g) and the mixts are readily ignited. Other props: crit diam for complete comb 21mm, burning rate 31 x 10^3g/cm^{2}sec (Ref 17)

Written by **C. H. Mc DONNELL**

Refs: 1) Beil **1**, 528, (280), [601], {2361} & ⟨2812⟩ 2) B. Tollens, ChemZtg **12**, 141 (1888) 3) B. Tollens & P. Wigand, Ann **265**, 319 (1891) 4) A. Stettbacher, SS **11**, 112 & 182 (1916) & CA **11**, 2543 (1917) 5) L. Ebert, Ber **64**, 114 (1931) 6) F.J. Llewellyn et al, JCS **1937**, 883 7) H.B.J. Schurink, "Pentaerythritol" in OrgSyn Coll, Vol **1** (1941), 425 8) S.D. Brewer, "Studies on the Stability of PETN and Pentolite", OSRD **3983** (Aug 1944), 47 9) S.F. Marrian, ChemRevs **43**, 149 (1948) 10) R.W. Brown & G. Dougherty, JOC **13**, 173 (1948) 11) I. Nitta et al, ProcJapanAcad **26**(9), 25(Eng) & CA **45**, 4545 (1951) 12) Faith, Keyes & Clark (1957), 473 13) E. Berlow et al, "The Pentaerythritols", ACS Monograph **136**, Reinhold, NY (1958) 14) A. Rost & G. Knöffner, GerP 1057514 (1959) & CA **55**, 6868 (1961) 15) G.G. Guilbault & W.H. McCurdy, Jr, AnalChem **33**, 580 (1961) 16) M. Sittig, "Organic Chemical Process Encyclopedia", Noyes Development Corp, Park Ridge, NJ (1967), 421 17) V.V. Borbunov et al, FizGoreniya-Vzryvz **4**, 182 (1968) & CA **70**, 39425 (1969) 18) ChemRubHdb (1974–75), C-407, 74 19) Sax (1975), 998

Pentaerythritol Mononitrate [2,2-Bis(hydroxymethyl)-1,3-propanediol 1-mononitrate (name preferred by CA), *PEMN].* $C_5H_{11}NO_6$, mw 181.15, N 7.73%, crysts from chlf, mp 79° (Ref 2), CA Registry No 1607-00-7

Best prepn is by melting together a mixt of PE tetrakis(trifluoroacetate), PE, and K carbonate for 1 hour, extn of the cooled and powd melt with methyl chloride, treatment of the ext with 99% nitric ac, and working up to give a PE nitrate/trifluoroacetate mixt. The mixt is hydrolyzed with MeOH/K carbonate and the hydrolysate sepd by fractionation betw eth & w to give a 40% yield of the pure mononitrate (Ref 3)

Refs: 1) Beil, not found 2) J. Simecek, CollCzechChemCommun **27**, 362 (1962)

& CA **57**, 647 (1962) 3) M. Goldstein & R.P. Pews, Chem&Ind **1966**, 1943 & CA **66**, 10517 (1967)

Pentaerythritol Mononitrate (Tris[tris(di-fluoramino)methyl ether], FA-PEMON). $C_8H_8F_{18}N_{10}O_6$, mw 682.19, N 20.52%, OB to CO_2 +2.35%; a shock sens liq.

$$O_2NOCH_2C(CH_2OC(NF_2)_2)_3$$

Prepd by the addn of perfluoroguanidine to PEMN followed by fluorination of the adduct. Procedures for the prepn of this type compd are described in Refs 3, 4 & 5 *Explosive Properties.* Q_f −158kcal/mole, Q_e 1599cal/g; impact sensy PA app 5.1cm (PETN 30cm); fricn sensy measured as grit hardness for expln 4 (PETN above 9) (Ref 2)

Written by **C. H. McDONNELL**

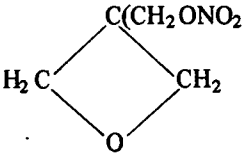
Refs: 1) Beil, not found 2) J.A. Brown et al, "Desensitization of Available High-Energy NF Compounds", Esso Research & Engrg Co Report **ED-8** (Dec 1966), AD 379575, 59 3) A.V. Fokin et al, IzvestAkadN,SerKhim **1970**, 199 & CA **72**, 110701 (1970) 4) L. J. Engel et al, USP 3692837 (1972) & CA **77**, 151449 (1972) 5) J.L. Zollinger et al, JOC **38**, 1065 (1973)

Pentaerythritol Dinitrate [2,2-Bis(hydroxymethyl)-1,3-propanediol 1,3-dinitrate (name preferred by CA), **PEDN].** $C_5H_{10}N_2O_8$, mw 226.15, N 12.39%, OB to CO_2 −49.6%; a liq, bp 150° at 10mm; d 1.476g/cc at 20/4°, RI 1.4928 at 20° (Ref 4), CA Registry No 1607-01-8

It has been prepd by the action of Ag nitrate on PE dibromide, yield 92% (Ref 2); by the same procedure as used for the prepn of the mononitrate (see above) (Ref 4); and by the nitration of the mono-benzylidene deriv of PE followed by hydrolysis of the benzylidene group (Ref 5). It is one prod which has been isolated by thin layer chromatography from the hydrolysis of PETN (Ref 3). The IR spectrum is in Ref 2, p 11; and the impact sensy by the BM app is 100cm (PETN 17cm) (Ref 2). It has been patented as a plasticizer for NC (Ref 5)

Refs: 1) Beil, not found 2) D.J. Cragle & F. Pristera, "Preparation and Analysis of the Di-, Tri-, and Tetranitrates of Pentaerythritol", PATR **2684** (Apr 1960), AD 490782 3) F.J. DiCarlo et al, Anal-Chem **36**, 2301 (1964) 4) M. Goldstein & R.G. Pews, Chem&Ind **1966**, 1843 & CA **66**, 10517 (1967) 5) R. Nec & F. Krampera, CzechP 130911 (1969) & CA **72**, 66380 (1970)

Pentaerythritol Cyclic Ether Dinitrate [Oxypentaerythritol Dinitrate, 3,3-Bis-(nitratomethyl)oxetane (name preferred by CA)]. $C_5H_8N_2O_7$, mw 208.13, N 13.46%,



OB to CO_2 −49.6%; a solid, mp 89–91° (Ref 4); cryst d 1.76g/cc (Ref 3). It is prepd by the action of Na ethoxide on Petrin (Ref 4), or by the action of di-N pentoxide in chlf on oxetane-3,3-dimethanol (Ref 6); Q_e 851cal/g (Ref 2). There is a differential thermal analysis exotherm at 160° (Ref 5). The impact sensy is similar to RDX and Tetryl and the ign temp is 233° (Ref 3)

Refs: 1) Beil **17**, {2011} 2) Anon, ABL Monthly Progress Report No 8 (June 1952), AD 031913, 11 3) J.M. Rosen & H.T. Simmons, "Preliminary Examination of Compounds Prepared in the New High Explosives Program", NOL **NAVORD 2782** (Feb 1953), AD 13408, 19 4) D.E. Elrick et al, JACS **76**, 1374 (1954) 5) J.M. Pakulak & G.W. Leonard, "A Thermistorized Apparatus for Differential Thermal Analysis", **NOTS 1920** (June 1958), 14 6) A. Schrage, USP 3058994 (1962) & CA **58**, 5638 (1963)

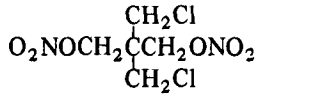
Pentaerythritol Diacetate Dinitrate. $C_9H_{14}N_2O_{10}$, mw 310.22, N 9.03%, OB to CO_2 −77.4%; a solid, mp 47° (Ref 4). It is prepd by acetylation of Pentaerythritol Dinitrate (Ref 4). Its impact sensy with a 2kg wt is 175cm for no explns (PA 35cm) (Ref 3). It has been patented as an ingredient in expls, proplnts, and ign devices (Ref 2)

Refs: 1) Beil, not found 2) Westfälische-Anhaltische Sprengstoff A-G, GerP 638432-3 (1936) & CA **31**, 1212 (1937) 3) Blatt, OSRD **2014** (1944) (found on Class of Compounds page "Nitrates") 4) J. Simecek, CollectCzechChemCommun **27**, 362 (1962) & CA **57**, 647 (1962)

Pentaerythritol Diallyl Ether Dinitrate. $C_{11}H_{18}N_2O_8$, mw 306.27, N 9.15%, OB to CO_2 −120.3%; a liq, d 1.191g/cc at 20°, RI 1.4688 at 20°. Other physical and expl props are given in Ref 2

Refs: 1) Beil **1**, ⟨2816⟩ 2) Anon, "Propellant Powders Ingredients Manual", **SPIA M3b** (Oct 1949), Unit 128 (Conf) 3) R. Evans & J.A. Gallaghan, JACS **75**, 1248 (1953)

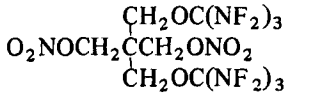
Pentaerythritol Dichloride Dinitrate [2,2-Bis(chloromethyl)-1,3-propanediol Dinitrate (name preferred by CA)]. $C_5H_8Cl_2N_2O_6$, mw 263.04, N 10.65%.



A mixt with PE monochlorohydrin trinitrate (see below), mp 43–50°, gives a Pb block expansion of 107% of TNT and is less shock sens than TNT

Refs: 1) Beil, not found 2) Urbański **2** (1965), 192

Pentaerythritol Bis[tris(difluoramino)methyl Ether] Dinitrate, FA-PEDIN). $C_7H_8F_{12}N_8O_8$, mw 560.17, N 20.0%, OB to CO_2 −11.4%; a shock sens liq. Prepd



by the addn of perfluoroguanidine to PEDN followed by fluorination of the adduct (for refs to the prepn of this type compd see under Pentaerythritol Mononitrate, **FA-PEMON**)

Explosive Properties. Q_f −147kcal/mole; Q_e 1582cal/g; impact sensy on PA app is 5cm (NG 10cm), on Bruceton app 2.3cm (NG 10cm)

Refs: 1) Beil, not found 2) J.A. Brown et al, "Desensitization of Available High Energy NF Compounds", Esso Research & Engrg Co Report **ED-8** (Dec 1966), AD 379575, 59

Pentaerythritol Diformate Dinitrate. $C_7H_{10}N_2O_{10}$, mw 282.17, N 9.93%, OB to CO_2 −85.1%. Its impact sensy with a 2kg wt is 175cm for no explns (PA 35cm) (Ref 3). It has been patented as an ingredient in expls, proplnts, and ign devices (Ref 2)

Refs: 1) Beil, not found 2) Westfälische-Anhaltische Sprengstoff A-G, GerP 638432-3 (1936) & CA **31**, 1212(1937) 3) Blatt, OSRD **2014** (found on Class of Compounds page "Nitrates")

Pentaerythritol Dimethyl Ether Dinitrate. $C_7H_{14}N_2O_8$, mw 254.20, N 11.02%, OB to CO_2 −81.9%; a solid, mp 53–4° (Ref 3); impact sensy with 2kg wt, no explns at limit of machine (Ref 3); power by Pb block expansion 97% of PA, 106% of TNT (Ref 3). It has been patented for use in expls, proplnts, and ign devices (Ref 2)

Written by **C. H. McDONNELL**

Refs: 1) Beil, not found 2) Westfälische-Anhaltische Sprengstoff A-G, GerP 638432-3 (1936) & CA **31**, 1212 (1937) 3) Blatt, OSRD **2014** (1944)

Pentaerythritol Trinitrate (Petrin). $HOCH_2C(CH_2ONO_2)_3$, mw 271.1, N 15.48%, OB to CO_2 −26.6%. Production grade material is a viscous liq (mp <20°). Purified Petrin melts at 26–28°. It decomps (without boiling) at 130° and 4mm Hg. At 20° its d is 1.54g/cc.

The viscosity of production grade material is as follows:

temp (°C)	viscosity (poises)
17	14.8
23	4.8
28	3.0
38	1.2

(Ref 15). The vapor press of Petrin at 60° is 4.5×10^4mm Hg (Ref 13). The dipole moment of Petrin is 5.06D (Ref 5a)

Petrin is used in the preparation of *Petrin-acrylate* which is a monoproplnt that can also be used as a high energy polymerizable binder (Ref 15). Petrin is also an intermediate in the prepn of many mixed nitrate esters (Refs 3 & 7). Dallet claims Petrin as a constituent of proplnt binder compns (Ref 8), and Crescenzo et al (Ref 9) claim it as a plasticizer for slow-burning proplnt compns. Its use in a binder for cloud-seeding pyrotechnic compns is claimed by Finnegan & Burkardt (Ref 11). Foltyn et al state that it is an excellent gelling agent for NC (Ref 13). Such gels are claimed to be stable between −20 and +50°. Petrin is used in medicine as a vasodilator (Ref 7)

An analytical method based on its IR absorption at 5.82 microns has been developed by Rohm & Haas (Ref 4). A thin-layer chromatographic sepn and identification of Petrin (as well as other impurities) in PETN was recently developed by Yasuda (Ref 14). He used Na-sulfanilate-impreganted Zn dust-silica gel G plates which he developed with an acet-benz solvent. The spots thus produced were diazotized and identified photometrically

Preparation. A number of prepn methods for Petrin have been reported in the open literature. The first of these (at least the first that is well-documented) is that of Marans et al (Ref 2) in which pentaerythritol (PE) monoacetate is reacted with 100% nitric acid at 0° to give PE acetate trinitrate. After recrystallizing the latter from hot ethanol it is treated with a 10% NaOH-water soln to produce a viscous oil which is recrystd from water to give Petrin. A more economical method was then also developed by ABL (Ref 3). This improved method utilized direct nitration of PE, at 0°, by a mixed acid consisting of 80% nitric acid and 20% sulfuric acid. The product, prepresenting a mixt of PETN with trinitrate, is pptd by adding water. To separate the components the acet soln, neutralized by means of ammonium carbonate, is treated with aq alc so as to form a mixt of 7 parts of acet, 3 parts of water, and 2 parts of ethanol. PETN ppts from this soln, while Petrin remains in the liquor to be completely sepd as a ppt by further treatment with hot water. The yield of trinitrate amounts to about 50%

A further improvement involves the essentially simultaneous synthesis and extrn of Petrin from the reaction mixt. Methylene chloride solvent is added to the PE/nitric acid mixt before the addition of sulfuric acid. After adding the sulfuric acid the solvent is removed, and fresh solvent is added and removed several times. The combined solvent extracts are neutralized and concd. Yields of 60 to 65% are claimed (Ref 15)

A somewhat similar technique was patented by Brown (Ref 6) who removed Petrin or nitric acid from the equilibrium reaction mixt. Petrin was removed by reacting it with a carboxylic acid, and nitric acid was removed by reacting it with benz or phenol

A method which appears to be essentially equivalent to the best ABL method was patented by Brennecke (Ref 10) who claims better utilization of the spent acid and solvent and better yield in a repetitive, step-wise procedure. Another modification patented by Rolewicz et al (Ref 12) utilizes mixed acid and methylene chloride extrn and appears to be little different from the above methods, except that the nitric acid is made oxide-free. A method of obtaining 98.4% pure Petrin from its mixts with PETN and PE dinitrate is claimed by Brennecke (Ref 16)

Chemical properties. As already stated, Petrin is an intermediate in the prepn of numerous mixed esters. Marans et al (Ref 2) prepd a series of Petrin-nitrobenzoate esters by reacting Petrin with the appropriate nitrobenzoyl chloride. They also prepd Petrin-formate, acetate, propionate, oxalate, glutarate, succinate, adipate, and phthalate. An especially important Petrin derivative is Petrin-acrylate. It is prepared by reacting Petrin with a mixt of acrylyl chloride and dimethylaniline (Ref 4)

Explosive Properties. Relatively little information has been published on the expl props of

Petrin. The earliest reference to its prepn and use appears to be in German patents (Ref 1). Ref 15 gives its heat of explosion as 1204cal/g, and its impact sensitivity as 5 to 10 inches on the PicArsn impact machine (or roughly equivalent to Tetryl)

The writer (Ref 8a) detd explosion times of Petrin rapidly heated in small stainless steel tubes (Wenograd test). The measurement scatter was too large to obtain reliable kinetic data. It was possible, however, to establish an approx minimum explosion temp of about 280° under these test conditions. For comparison, the Wenograd test results gave minimum explosion temps of about 420° and about 280° for TNT and NG respectively

Written by **J. ROTH**

Refs: 1) Anon, GerPats 638432 & 638433 (1937) & CA **31**, 1212 (1937) 2) N.S. Marans et al, JACS **76**, 1304 (1954) 3) A.T. Camp et al, Ibid **77**, 751 (1955) 4) Anon, "Process for the Manufacture of Pentaerythritol Trinitrate Monoacrylate and Petrin Acrylate Propellants", Rohm & Haas Co, Redstone Arsenal (12 March 1956) 5) R.H. Pierson, "An Infrared Spectrophotometric Method for Determination of Acetone Content of Pentaerythritol trinitrate", **NOTS 1877, NAVORD 5649** (1958) 5a) A.R. Lawrence & A.J. Matuszko, JPhysChem **65**, 1903 (1961) & CA **56**, 5483 (1962) 6) F.W. Brown, USP 3116320 (1963) & CA **60**, 6748 (1964) 7) Urbański **2** (1965), 194–5 8) L.R. Dallet, USP 3276379 (1966) & CA **66**, 11519 (1967) 8a) J. Roth, Final Rept Contr NOwr 65-0283-d (1966) 9) F. Crescenzo et al, USP 3306790 (1967) & CA **66**, 117555 (1967) 10) H.M. Brennecke, USP 3309397 (1967) & CA **67**, 21449 (1967) 11) W.F. Finnegan & A. Burkardt, USP 3337148 (1968) & CA **68**, 97228 (1968) 12) H.A. Rolewicz et al, USP 3408383 (1968) & CA **70**, 19564 (1969) 13) J. Foltyn et al, CzechPat 132327 (1969) & CA **73**, 27156 (1970) 14) S.K. Yasuda, JChromatogr **51**, 253 (1970) & CA **73**, 116133 (1970) 15) Anon, "Explosives Series, Properties of Explosives of Military Interest", EngrDes Hndb, **AMCP 706-177** (1971) 16) H. Brennecke, USP 3806578 (1974) & CA **81**, 3380 (1974)

Pentaerythritol Tetranitrate (PETN; listed as 1,3-Propanediol, 2,2-[bis-(nitroxy)methyl]-dinitrate in CA since 1972, Penta; Penthrite in Fr; Pentrit, Niperyth, Nitropenta (NP) in Ger; TEN in Russ). $C(CH_2ONO_2)_4$, mw 316.15, N 17.71%, OB to CO_2 −10.1%. Colorl tetragonal crysts of 1.77g/cc d, melting at 141–42° (pure), and having a RI=1.558. An orthorhombic cryst modification has a d of 1.72g/cc (Ref 92)

An enormous amount of material has been published on PETN. There are some 360 CA references since 1961! The older literature is also very voluminous (see Additional Refs). Consequently, the writer has chosen to emphasize modern work in this article, of course including important older studies. The article is divided into the following sections: I. Physical Properties; II. Solubility; III. Chemical Properties; IV. Specifications and Analytical; V. Uses; VI. Preparation; VII. Detonation Characteristics; VIII. Thermal Decomposition; IX. Combustion & DDT (deflagration-to-detonation transition); X. References. The major emphasis will be placed on Sections VII, VIII and IX

I. Physical Properties

Vapor Pressure. The vapor pressure, p (in cm Hg) of solid PETN is given by Edwards (Ref 14) as log p = 16.73 − 7750/T where T is the absolute temp. The vapor press of liq PETN, according to Crimmins (Ref 73), is log p = 14.44 − 6352/T where p is in mm Hg. Earlier vapor press measurements by Belyaev (Ref 10) appear to be too high because of PETN decompn. Crimmins' data give a heat of vaporization of 29.0kcal/mole as compared to 23kcal/mole obtained by Belyaev. Edward's heat of sublimation is 36.3-kcal/mole. Then, by difference with the Crimmins heat of vaporization, the heat of fusion of PETN is about 7kcal/mole. However, recent studies by Rogers & Dinegar (Ref 90) show that the heat of fusion of single crystals of PETN is 11.8kcal/mole and may be as low as 9.8kcal/mole due to surface imperfections

Thermochemical and thermal characteristics. Standard heat of formation: 128.7kcal/mole (Ref 74a); Specific heat: 0.272cal/deg g at 115° (Ref 8); 0.24cal/deg g at 25° (quoted in Ref 94). Coefficient of heat conduction: 6 x 10^{-4} cgs units (Ref 19). Linear coefficient of thermal

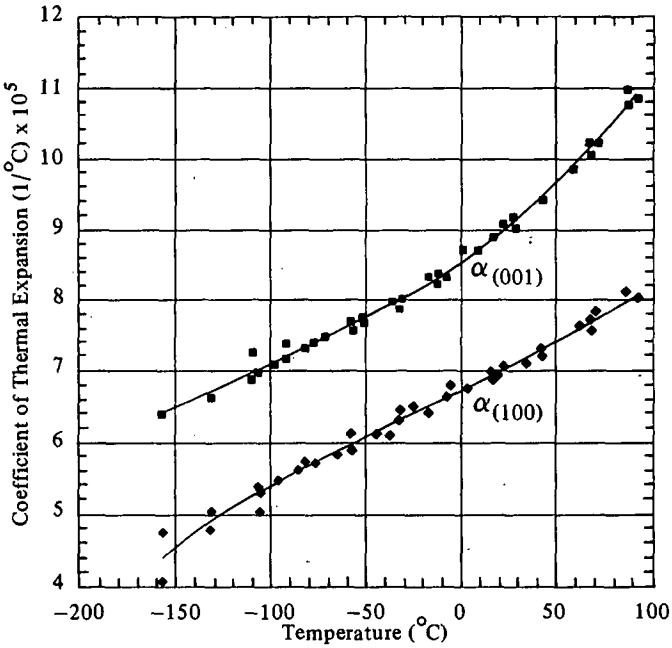


Fig 1 Linear coefficients of PETN (Ref 91)

expansion: average over 88°C (above room temp) 11 x 10^{-5} cm/cm°C for 1.6g/cc PETN aggregates (Ref 60). See Fig 1 for Cady's data (Ref 91) for single crystal PETN

Electrical Properties.

Packing density (g/cc)	Dielectric Constant (at 30GHz, Ref 92)
1.4	2.45
1.5	2.58
1.6	2.73
1.7	2.89
1.75	2.95 at 25GHz

Dipole moment: 4.74D (Ref 27)

Optical & Spectral Properties. Mullen & Orloff (Ref 100) give the uv absorption spectra of PETN in MeCN soln from 1825 to 3900Å. Bands exist at about 1935, 2600 & 2900Å. Molecular orbital calcns assign these bands to the following transitions: $\pi \rightarrow \pi^*$ localized on NO_2 for the 1935Å band; $n \rightarrow \pi^*$ transition of the NO_2 group for the 2600 & 2900Å bands

Galeev et al (Ref 71) used lasers to obtain light reflectivity of PETN. At 6943Å & 10600Å they obtained reflectivities of 0.79 & 0.81, respectively. Roth (Ref 46) measured the diffuse reflectivity of PETN aggregates of varying packing density, particle size & particle shape. He found that packing density and particle size have little effect on reflectivity. Particle shape appears to have some effect, in that needle-shaped particles are somewhat poorer reflectors than other shapes. Diffuse reflectivity varies between about 0.9 and 1.0 in the visible, and starts to decrease rapidly below 3500Å. Some approx absorptivity measurements suggest that absorptivity of PETN aggregates varies exponentially with the aggregate density, ρ, its thickness, h, and wavelength. Approx absorption coefficients, α, corrected for reflectivity, are shown below as a function of wavelength, λ

λ(Å)	α(cm²/g)*
2800	∼2100
2900	∼1700
3000	1300
3100	1000
3500	550
4000	420

* from $\frac{I_{trans}}{I_{inc} - I_{refl}} = \exp(-\alpha\rho h)$ for $\rho h \leq 4 mg/cm^2$

The absorption of a single crystal of PETN as measured by Deb (Ref 19) is shown in Fig 2

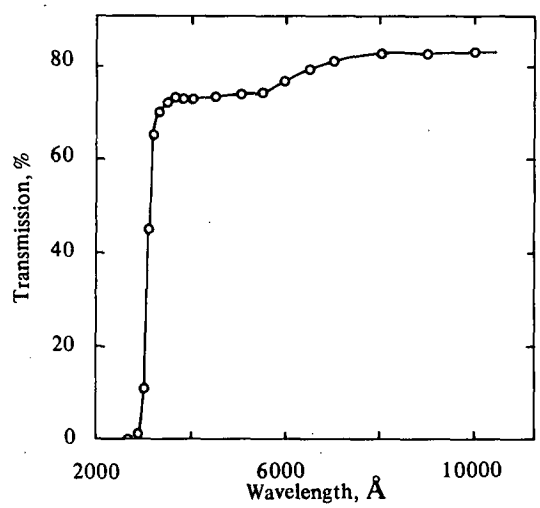


Fig 2 Absorption spectrum of a single crystal of PETN [Deb, according to Bowden & Yoffe (Ref 19)]

Mass Spectra. Obtained by Gillis et al (Ref 104). Field ionization and electron impact ionization mass spectra are given by Brunee et al (Ref 54)

Mechanical Properties & Sound Velocity. Hoge (Ref 77) obtained the following ultimate stress as a function of strain rate for machined discs (1.77g/cc) of PETN (all failures were brittle fractures)

Strain rate (sec^{-1})	Ultimate stress (psi)
10^{-3}	160
10^{-2}	215
10^{-1}	215
1.0×10^{3}	720
1.12×10^{3}	700
1.3×10^{3}	785
2.6×10^{3}	840

Cramer (Ref 17) gives the bulk modulus for 1.77g/cc PETN as 4.6×10^{10}dynes/cm^2

An important mechanical property of an expl is its behavior under shock loading. This behavior can be described by its shock *Hugoniot* (or simply Hugoniot) as discussed in Vol **7**, H179-L. For expl aggregates (not single crysts), establishing a Hugoniot presents both conceptual and exptl difficulties. However, even an approx Hugoniot can be useful in many applications. In the following tabulation we show Hugoniots for PETN aggregates at various densities. The Hugoniots are in the linearized form of U = a + bu where U is the shock velocity, u is the particle velocity, and a and b are constants

From the data of Holland et al (Ref 18a) and Campbell et al (Ref 28) one obtains U = 5.56 mm/μ sec and u = 1.14mm/μ sec for single crystal PETN (ρ = 1.77 g/cc). Use of the constants for ρ = 1.72g/cc (Ref 79) in the above tabulation gives u = 1.08mm/μ sec for U = 5.56mm/μ sec in reasonable, though possibly fortuitous, agreement with the single crystal results

Recently Bauer (Ref 107) has proposed a method of generating P–u (shock pressure–particle velocity) relationships (non-reactive Hugoniots) for any packing density ρ from the known P_1–u_1 relationship at some density, ρ_1. His equations are:

$$u^2 = u_1^2 + \frac{P}{2\rho_{cryst}}\left(\frac{p}{1-p}\right) \qquad (1)$$

and

$$u_1^2 = \tfrac{1}{2}(a/b)^2\left[1 + \frac{2Pb}{\rho_1 a^2} - \sqrt{1 + \frac{4Pb}{\rho_1 a^2}}\right] + \frac{P}{2\rho_{cryst}}\left(\frac{p_1}{1-p_1}\right) \qquad (2)$$

where a and b are the constants in the linearized form of the Hugoniot (see above), ρ_{cryst} is the crystal density of the material, and $p = 1 - \rho/\rho_{cryst}$ and $p_1 = 1 - \rho_1/\rho_{cryst}$ are porosities

Sound velocities for PETN pressings are shown in the tabulation on the following page. The writer (Ref 60) found precursor compressive waves in PETN aggregates shocked up to 10kbar

Density (g/cc)	Temp (°C)	a (mm/μ sec)	b (dimensionless)	Experimental range of u (mm/μ sec)	Refs
0.88	25	0.47	1.73	0.76–3.50	75
1.0	25	0.76*	0.66*	0.28–0.42	26
1.59	25	1.33	2.18	0.03–0.37	74 (p 222)
1.60	25	1.32	2.58	0.2 –0.5	79
1.72	25	1.83	3.45	0.2 –0.6	79
1.72	25	2.33	2.34	0.2 –0.6	94
~1.55	110	–0.6*	8.7*	0.24–0.29	74 (p 222)

* Very approximate

Density (g/cc)	Longitudinal (mm/μ sec)	Bulk (mm/μ sec)	Precursor (mm/μ sec)	Refs
1.77	–	2.42	–	75
1.72	2.933	2.326	–	94
1.67	2.8	–	–	74, p 358
1.59	2.6	–	2.45	60
1.59	2.4	–	–	74, p 358
1.55 (a)	–	–	2.25 (a)	60
1.54	1.8	–	–	74, p 358
1.48	1.7	–	–	74, p 358

(a) Heated to 110°C

Interatomic Distances. According to Booth & Llewellyn (Ref 9) the interatomic distances in PETN are: 1.50Å for C–C; 1.37Å for C–O; 1.36Å for O–N; 1.27Å for N–O (nitro)

Packing Density. The following tabulation of packing density as a function of loading press is given by Urbański (Ref 44, p 180)

Pressure, kg/cm_2	Density, g/cc
351	1.575
703	1.638
1406	1.710
2109	1.725
2812	1.740

II. Solubility

PETN is insoluble in water but is soluble in a variety of organic solvents and particularly in acetone. This is clearly shown in Table 1 which contains the data of Urbański & Kwiatkowski (Ref 3), and in Table 2 which shows the more recent results of Roberts and Dinegar (Ref 21)

Table 1
Solubility of Pentaerythritol Tetranitrate in Organic Solvents (Ref 3)

Temperature °C	PETN (g) dissolved in 100g of solution				
	Ethyl Alcohol	Ether	Acetone	Benzene	Toluene
0	0.070	0.200	14.37	–	0.150
10	0.085	0.225	16.43	0.150	0.170
20	0.115	0.250	20.26	0.300	0.230
30	0.275	0.340	24.95	0.450	0.430
40	–	0.450	–	–	–
40	0.415	–	36.16	1.60	0.620
50	0.705	–	–	2.010	1.100
60	1.205	–	–	3.350	2.490
62	–	–	42.68	–	–
70	2.225	–	–	5.400	3.290
78.4	3.795	–	–	5.400	–
80.2	–	–	–	7.900	–
90	–	–	–	–	9.120
113	–	–	–	–	30.960

Table 2
Solubility of Pentaerythritol Tetranitrate
(Ref 21)
Grams/100 Grams of Solvent

Temp °C	Acetone	Benzene	Ethanol
15	20.81	–	–
20	24.84	0.275	0.125
25	30.56	–	–
30	34.56	0.496	0.213
40	44.92	0.834	0.378
50	58.76	1.448	0.657
60	–	2.389	1.196

The solubility of PETN in acetone-water mixts was determined by Aubertein (Ref 11) and is shown in Table 3. These data are of great importance in industrial practice

Values of PETN solubility in ethyl acetate and pyridine, as reported by Desvergnes (Ref 5) are given in Table 4:

Table 4
Solubility of Pentaerythritol Tetranitrate
[Desvergnes (Ref 5)]

Temp °C	PETN (g) dissolved in 100g of solvent	
	Ethyl acetate	Pyridine
19	6.322	5.436
50	17.868	8.567

Other solubility data from various sources quoted in **AMCP 706-177** are shown on the following page:

Table 3
Solubility of Pentaerythritol Tetranitrate in Acetone-Water Mixtures
[Aubertein (Ref 11)]

Amount of PETN dissolved in 100g of solvent g	Acetone concentration				
	55%	70%	80%	90%	92%
	Temperature of solution, °C				
1	41	–	–	–	–
2	52	–	–	–	–
2.5	–	24.5	–	–	–
4	62	–	–	–	–
5	–	41.5	22	–	–
10	–	54.5	38.5	15	10
15	–	62	48	24.5	20.5
17.5	–	65	–	–	–
20	–	–	54	34.5	29
25	–	–	59	41.5	34
30	–	–	63	46.5	40.5
35	–	–	–	51.5	45
40	–	–	–	55	50
45	–	–	–	58.5	54
50	–	–	–	61.5	57.5
55	–	–	–	–	60.5
60	–	–	–	–	62.5

Solubility, grams of PETN per 100 grams (%) of:

Trichlorethylene or Alcohol		Acetone	
°C	%	°C	%
0	0.070	0	14.37
20	0.195	20	24.95
40	0.415	40	30.56
60	1.205	60	42.68

Benzene		Toluene	
°C	%	°C	%
0	0.150	0	0.150
20	0.450	20	0.430
40	1.160	40	0.620
80	7.900	60	2.490
		80	5.850
		100	15.920
		112	30.900

Methyl acetate		Ether	
°C	%	°C	%
20	13	0	0.200
30	17	20	0.340
40	22	34.7	0.450
50	31		

β-Ethoxy-ethyl-acetate		Chlorobenzene	
°C	%	°C	%
20	1.5	20	0.35
30	4.1	30	2.8
40	7.6	40	6.1
50	11.2	50	9.2
60	14.2	60	12.2

Ethylenedichloride		Methanol	
°C	%	°C	%
10	0.9	20	0.46
30	1.5	40	1.15
50	2.6	60	2.6

Tetrachloroethane		Carbon tetrachloride	
°C	%	°C	%
20	0.18	20	0.096
30	0.27	30	0.108
40	0.40	40	0.118
50	0.58	50	0.121

Dimethylformamide is also a good solvent for PETN. According to Lang (Ref 15a):

at 40°C 100g of soln contain 40g PETN
at 60°C 100g of soln contain 50g PETN
at 100°C 100g of soln contain 70g PETN

PETN forms eutectics with a number of liq or molten nitro-aromatic compds. The compns and melting points of some of these as reported by Urbański (Ref 4) are:

	mp (°C)
20% PETN with 80% m-dinitrobenzene	82.4
10% PETN with 90% 2,4-dinitrotoluene	67.3
13% PETN with 87% α-trinitrotoluene	76.1
30% PETN with 70% Tetryl	111.3
20% PETN with 80% mannitol hexanitrate	101.3

PETN forms a eutectic with NG which contains 98.5% NG and melts at 12.3° (Ref 6). A diagram of the PETN–TNT system is shown under *Pentalites* in this Vol

Unlike other nitrate esters, PETN does not form a colloid soln with NC

Solubilities of PETN in 60–95% nitric acid in the temp range of 0–50° were determined by Camera & Mauro (Ref 63), and in 20–100% nitric acid at 23–25° by Aubertein (Ref 11)

Nearly equi-dimensional PETN crystals rather than the usual needle-like crystals can be obtained by slow cooling of a 40% soln of PETN in boiling EtOAc (Ref 12)

The prepn of large single crystals of PETN (and other expls) is described by Koch (Ref 98)

III. Chemical Properties

Due to its symmetrical structure, Pentaerythritol Tetranitrate is highly resistant to many reagents. Thus PETN differs from the majority of nitrate esters by not being readily decompd by sodium sulfide at 50°. On the other hand, it is decompd quite quickly by boiling in a ferrous

chloride soln. Boiling with a 2.5% soln of NaOH causes very slow decompn, whereas NC rapidly decomps under these conditions

Aubertein & Rehling (Ref 15) have shown that treatment with water at approx 100° causes PETN to hydrolyze. At 125° and under pressure, hydrolysis proceeds quite quickly, and is considerably enhanced by the presence of 0.1% HNO_3. Regardless of whether it occurs in water alone or in water acidified with nitric acid, the hydrolysis produces mainly Pentaerythritol Dinitrate. A dil NaOH soln causes PETN to hydrolyze more rapidly than acidified water. PETN neither reduces Fehling's reagent nor enters into addition products with any aromatic nitro compd. In this respect it differs from both Erythritol Tetranitrate and Nitromannitol

Hydrolysis of PETN in concd nitric acid solns was studied by Camera & Mauro (Ref 63)

Urbański et al (Ref 7) found that the addition of mono-, di- and trinitro derivatives of benz or toluene to PETN lowers its thermal stability as detd by heating the mixt in the temp range 120–132°. The extent of thermal decompn of PETN, heated alone or in mixts, can be estimated by the decreasing pH which indicates formation of acidic decompn products. Fig 3 shows how the addition of TNT enhances PETN decompn

The authors suggest that the deleterious effect of nitro compds is due to the lowering of

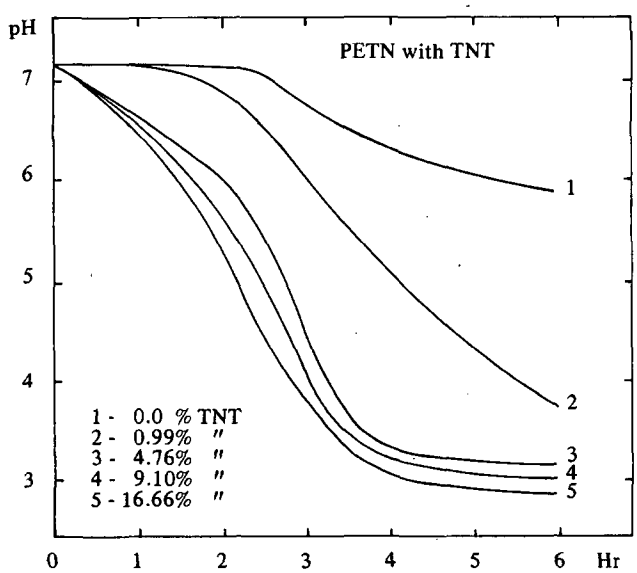


Fig 3 Change of pH of PETN alone and with TNT on heating at 120°C (T. Urbański, Kwiatkowski & Miladowski, Ref 7)

the mp of these mixts as compared to pure PETN, and a faster decompn in the liq than in the solid phase. A more detailed examination of PETN decompn will be found in Section VIII

According to **AMCP 706-177**, the compatibility of PETN with metals is:

Dry: Copper, brass, aluminum, magnesium, magnesium-aluminum alloy, stainless steel, mild steel, mild steel coated with acid-proof black paint and mild steel plated with copper, cadmium, nickel or zinc are not affected

Wet: Stainless steel is unaffected and aluminum only very slightly so after prolonged storage. Copper, brass, magnesium, magnesium-aluminum alloy, mild steel, mild steel coated with acid-proof black paint and mild steel plated with cadmium, copper, nickel or zinc are affected

IV. Specifications & Analytical

According to the "Requirements" of **MIL-P-387A** (9 Jan 1957) as modified by **EOPA-50352-2** (1 Nov 1967) & **MIL-P-387B** (7 Nov 1967), PETN for USA military use shall conform to:

Melting Point. The melting point of PETN shall be 141 degrees Centigrade (°C) plus or minus 1.0°C

Nitrogen Content. The nitrogen content of PETN shall be 17.50 percent minimum (min)

Acetone insoluble material. The acetone insoluble material of PETN shall be 0.10 percent maximum

Insoluble particle. There shall be no evidence of insoluble particles in PETN

Acidity or Alkalinity. The acidity or alkalinity shall not exceed 0.01 percent max

120°C vacuum stability. The maximum amount of gas evolved in 20 hours test time shall be 5 milliliters

Granulation. The PETN shall comply with the granulation requirements shown below, except that the granulation requirements for Class 3 PETN shall not apply to PETN used in co-precipitated pentolite

Granulation Requirements:

US Std Sieve No.	Percent Passing Specified Sieve Class 1	Class 2	Class 3	Class 4
30	–	–	95 min	100 min
80	100 min	–	–	–
100	–	–	–	20 max
100	85 min	96 min	–	5 min
140	55 max	–	–	–
200	30 max	80 max	30 max	–
200	–	65 min	–	–

Superfine PETN for use in EBW detonators and MDF is produced by quenching a hot acetone soln in cold water. The resulting particle size distribution averages 10 microns, and irregular crystals are produced which are easier to initiate (Ref 80a)

The prescribed analytical method for determining nitrogen content in PETN is the **MIL-STD-286** Method 209.3. The ferrous chloride-titanous chloride method described for NG in Vol **6**, G106–7 is also applicable to PETN

A method of analysis based on converting nitrate groups to ammonia with Devarda's alloy is described by Smeenk (Ref 103). PETN is dissolved in ethanol and the ammonia formed is titrated with standard acid soln

In recent years a number of thin-layer chromatographic methods for the qual detection of PETN have appeared in the literature. Hennig (Ref 51) used glass plates, chlf solvent, and a diphenylamine soln in concd sulfuric acid as the color developer. He experienced difficulty in distinguishing between PETN and NG. The method of Boehm (Ref 53) is similar to that of Hennig except that Boehm uses a silica gel G column and a mixt of pet-ether and EtOAc as solvent. Barnes (Ref 58) used silica gel G-H_2O plates, CCl_4-acet solvent, and diphenylamine dissolved in acet/alc as color reagent. Pariher et al (Ref 57) use Mg silicate and Al_2O_3 plates, various solvents and the Griess-Romijin color reagent. Vich et al (Ref 78) compare the effectiveness of various chromatographic methods for separating and identifying nitrate esters

Fredricks & Pristera (Ref 23) describe an IR method for determining small amounts of Dipentaerythritoltetranitrate (see Vol **5**, D1410–13) in PETN

Hetman (Ref 102) describes polarographic methods for analyzing explosives (including PETN)

V. Uses

The principal uses of PETN are in the expl core of industrial detonating fuses (eg Primacord of MDF – mild detonating fuse), and in the base charge of commercial blasting caps. It is also used as the entire expl charge in exploding-bridgewire (EBW) detonators (see Vol **6**, E353-R). In military applications PETN has been largely replaced by RDX due to the latter's better thermal stability and shlf-life. Some PETN is still needed to make **Pentolites** (see Pentolite in this Vol) which are used as expl charges in hand-grenades. A recent patent (Ref 97) claims caseless grenades and other munitions made of PETN & Al cast into a thermosetting resin. Pentolite and PETN/plastic binders are used in commercial boosters for insensitive commercial expls such as ANFO, or insensitive slurry explosives. PETN is also used in medicine as a vasodilator

In recent years PETN *sheet explosive,* consisting of PETN in a rubber-like elastic matrix, has found considerable use in metal-forming, metal-cladding and metal-hardening. Physical & expl characteristics of rubber-bonded sheet expl are described by W. Kegler & R. Schall (Ref 45, p 496), by Kegler (Ref 59), and in Refs 30c, 65a and 105a. The prepn and resulting physical properties of PETN-Epikote 871 (an epoxy resin) sheets is described by Sato (Ref 49). Extrudable, putty-like compns, consisting of 80/20 PETN/silicone rubber, capable of detonation in small diameter are described by Sherman & Vigneault (Ref 83), and Ref 91a

Low-detonation pressure composites consisting of PETN (and other expls) in a low-density (foam) plastic matrix (eg polyurethanes) are described by Abegg et al (Ref 33)

Numerous patents have been issued on PETN-plastic compns usually in the form of sheet expl. Some of these are briefly summarized below

Breza & Davis (Ref 29) claim a compn consisting of 92.5–70 parts of PETN and 7.5–30 parts of binding agent containing 25–75% of an organic rubber and 75–25% of a thermoplastic terpene resin. The product may be rolled or pressed to any desired shape. Noddin (Ref 55) claims a sheet expl based on PETN bound with Teflon. Williams (Ref 101) claims a detonating cord composed of an extrudable compn containing 60–85% PETN/10–40% polyethacrylate rubber /0–10% plasticizer

Some specialized uses of PETN are summarized below. Expendable cartridges for small arms are made by coating unglazed grains or single base smokeless powder with PETN, spraying with plasticized thermoplastic binder and compression molding to the desired shape (Ref 99). Tucker et al (Ref 85) describe a spark detonator without primary expls. Secondary

expl spark detonators have useful commercial applications because of their low cost, and because the detonators as well as the firing sets are safe. The firing set must be closely coupled to the detonator if min firing energies are to be realized. Spark detonators loaded with PETN can be fired with stored energies of 10–60 mJ if the firing circuit is capable of delivering most of its energy in a sufficiently short period of time. Spark initiation of secondary expls depends on both the amount and the rate of energy expended in the spark gap

A novel use of PETN or rather PETN detonation products in high stagnation temp lasers is claimed by Robinson (Ref 95). These N_2–CO_2 and N_2–CO gas lasers are based on expln products obtained from detonation of mixts of PETN and acrylonitrile, or detonation of PETN in O_2 or O_2/He mixts

VI. Preparation

PETN was first prepared in 1894 by the nitration of pentaerythritol, PE (Ref 1). This is still the basic method used today. Commercial production of PETN could not be realized until the formaldehyde and acetaldehyde required in the synthesis of PE became readily available about a decade before WWII

Basically, most processes for the commercial production of PETN involve pouring PE into 98+% nitric acid (sp gr 1.50–1.52g/cc) at a temp not exceeding 25°. Since PETN is only slightly sol in nitric acid it ppts near the end of the nitration. The ppt is then filtered, washed with water, "neutralized" with Na_2CO_3 soln, and recrystd from acet. In some processes the nitric acid is diluted with water after nitration. This is believed to keep some of the impurities in soln

Details of a number of manufacturing methods are given by Urbański (Ref 44, pp 185–91). These methods are rather similar. For example, a semi-continuous method used in Germany during WWII had the following material balance per 100kg of PETN: "44.4kg of PE and 224kg of nitric acid (98–99%), of which 80kg enter into the reaction, 16kg are lost, 128kg are recovered as 30% nitric acid, and resulted in 96.8% yield"

A process for making heat-stabilized PETN, claimed by Voigt (Ref 56), involves dissolving PETN and a stabilizer such as polyvinylpyrrolidinone in a solvent such as N-methyl-2-pyrrolidinone, and pptg the stabilized PETN by slowly pouring the above soln into rapidly stirred water or ethanol. The PETN thus made is claimed to meet military stability requirements

The general mechanism of nitrating alcohols to form nitrate esters is described under *Nitration* in this Vol. Several specific remarks about PETN are contained in that article. The industrial nitration of PE differs from most nitrate esters in that it employs concd nitric acid rather than mixed acid. Nevertheless nitration via the *nitronium* ion mechanism, which is the preferred mechanism in mixed acid nitrations, is also feasible in concd nitric acid. However, Eremenko and co-workers claim that the nitrating agent in PE nitrations, in mixed acid, is unionized nitric acid (Refs 39 & 76). The present writer does not find Eremenko's arguments to be very convincing. In any case, commercial production of PETN employs nitric acid and not the mixed acids of Eremenko's studies

VII. Detonation Characteristics

In general terms, PETN can be characterized as a "sensitive", brisant, and powerful high expl. Explosive sensitivity is a rather nebulous quantity, but there can be no doubt that PETN is a much more "sensitive" material than TNT, but rather less sensitive than Lead Azide. In particular, PETN requires very little priming charge (less than 1 mg LA) to initiate its detonation. This is the characteristic that makes PETN so widely used in blasting cap base charges, in detonating cord and in boosters

Brisance and "power" are quantities that can be defined more exactly than sensitivity, and PETN is one of the most powerful and brisant expls known. It is also among the most studied expls, from both exptl and theoretical points of view. In this section we will consider PETN's *steady detonation parameters, thermochemistry,* and *initiation characteristics,* including theoretical models for various types of initiation

A. *Steady Detonation Parameters*

Undoubtedly the most frequently and accurately determined detonation parameter of any expl is its *detonation velocity,* D. This is certainly true for PETN. Detonation velocity varies with packing density, ρ, charge diameter, d,

charge confinement, and expl particle size. Some results of the many published studies of D vs ρ are shown in Tables 5 and 6. As shown in Table 7, the expression, obtgained by H.C. Hornig et al (Ref 74, pp 503–512),

$D = 3.19 + 3.7(\rho - 0.37)$, in mm/sec (1)

provides a good fit to the data (particularly the data of Table 5) over the entire measurement range, although it is claimed (Ref 74) that it is valid over $0.37 \leq \rho \leq 1.65$g/cc

The same reference gives

$D = 7.92 + 3.05(\rho - 1.65)$ for $\rho \geq 1.65$g/cc (2)

$D = 2.14 + 2.84\rho$ for $\rho \leq 0.37$g/cc (3)

Cook (Ref 18) gives

$D = 5550 + 3950(\rho - 1.00)$ in m/sec. This expression fits the data for $0.5 < \rho < 1.5$g/cc reasonably well, but gives D lower than observed for $\rho < 0.5$g/cc, and higher than observed for $\rho > 1.5$g/cc

Table 5
PETN Experimental Detonation Velocities
(Ref 74)

Density (g/cc)	Detonation Velocity (mm/μsec)	Density (g/cc)	Detonation Velocity (mm/μsec)
Pin Switch Measurement			
1.773	8.30*	1.27	6.66†
1.765	8.28†	1.26	6.76†
1.765	8.16†	1.09	5.83†
1.765	8.24*	1.09	5.83†
1.763	8.27*	0.55	3.85*
1.762	8.25*	0.436	3.40*
1.762	8.26*	0.241	2.81*
1.51	7.44†	0.201	2.73*
1.51	7.49†	0.185	2.67*
Shock Electric Effect Measurement‡			
1.71	8.00	1.23	6.48
1.71	8.00	1.23	6.50
1.71	8.08	1.23	6.46
1.70	8.03	1.23	6.46
1.70	7.96	1.23	6.46
1.69	7.97	1.23	6.43
1.60	7.74	0.99	5.52
1.60	7.74	0.95	5.41
1.59	7.69	0.93	5.31
1.53	7.51	0.93	5.33
1.46	7.41	0.93	5.15
1.45	7.26	0.89	5.20
1.44	7.20	0.88	5.17
1.38	7.07	–	–

* Unconfined rate stick
† Cylinder test
‡ All other data are detonation pressure expts

There are few quant data for D vs d for PETN. However, it is certain that the diameter effect for PETN is quite small. This becomes apparent when one considers that the *critical diameter* for PETN (at ρ = 1 g/cc and 0.025–0.1 mm particle size) is only 0.9mm (Bobelev quoted in Ref 22, p 348), and becomes smaller at $\rho > 1$. Cook et al (Ref 18) show that D varies from about 4800m/sec at d=0.32cm to 5400 m/sec at d> 1.6cm, for –65 to +100 mesh PETN at 0.95g/cc. Since confinement effects parallel diameter effects, D for PETN is almost independent of confinement for any practical size charges.

Fairly large variation in PETN particle size has relatively little effect on D (this writer, unpublished results, 1949). Cook et al (Ref 18) show that there is an interaction between particle size and diameter effects. At comparable packing densities of 0.95g/cc, PETN of –35 to +48 mesh and PETN of –65 to +100 mesh detonate at about 4300 and 4800m/sec respectively at a charge diameter of 0.32cm, whereas at charge diameters of 0.63cm and larger there is no difference in D for the two particle size fractions

Stesik (Ref 81) measured D for PETN/Al and PETN/Be mixts

By depositing low concns of PETN on foamed polystyrene, Archibald (Ref 47A) obtained very low density expl systems. At an apparent PETN density of 0.09g/cc he found D = 2.05 mm/μ sec. D could be varied by changing the PETN concn

Table 6
PETN Experimental Detonation Velocities
(Various Sources)

Density (g/cc)	Detonation Velocity (mm/μsec)	Refs	Density (g/cc)	Detonation Velocity (mm/μsec)	Refs
1.77	8.50	(30)	1.00	5.55	(16)
1.73	8.35	(2)	0.97	5.33	(2)
1.66	8.10	(43a)	0.95	5.30	(43a)
1.62	7.91	(2)	0.95	5.35	(17)
1.60	7.92	(16)	0.80	4.76	(16)
1.51	7.42	(43a)	0.75	4.71	(2)
1.51	7.42	(2)	0.50	3.90	(16)
1.40	7.13	(16)	0.50	3.97	(2)
1.37	6.97	(2)	0.32	3.53	(2)
1.22	6.36	(2)	0.30	3.55	(2)
1.20	6.34	(16)	0.30	3.42	(2)
1.03	5.62	(2)	0.24	3.20	(2)

Table 7
PETN Experimental Detonation Pressures
(Ref 74)

Density (g/cc)	Dimensions of PETN Diameter x Length (inches)	Fitted Detonation Velocity (mm/μsec) (Eqs 1,2&3)	Detonation Pressure P_{CJ} (kbar)
Shock Electric Effect Measurements			
1.764	2 x 0.5	8.28	338
1.763	1 x 0.5	8.27	333
1.763	1 x 0.5	8.27	334
1.763	1 x 1	8.27	340
1.763	2 x 0.5	8.27	338
1.763	2 x 1	8.27	340
1.762	2 x 1	8.27	335
1.762	2 x 1	8.27	343
1.758	1 x 1	8.26	333
1.71	1 x 1	8.11	311
1.71	1 x 1	8.11	307
1.71	1 x 1	8.10	309
1.70	1 x 1	8.08	308
1.70	1 x 1	8.06	306
1.69	1 x 1	8.03	304
1.60	1 x 1	7.76	266
1.60	1 x 1	7.74	266
1.59	1 x 1	7.71	259
1.53	1 x 1	7.49	225
1.46	1 x 1	7.22	198
1.45	1 x 1	7.18	208
1.44	1 x 1	7.14	199
1.38	1 x 1	6.91	173
1.23	1 x 1	6.38	136
1.23	1 x 1	6.37	134
1.23	1 x 1	6.37	137
1.23	1 x 1	6.37	142
1.23	1 x 1	6.36	141
1.23	1 x 1	6.36	142
0.99	1 x 0.5	5.48	87
0.95	1 x 0.5	5.33	85
0.93	1 x 1.5	5.27	73
0.93	1 x 1	5.26	77
0.93	1 x 1.5	5.25	70
0.89	1 x 1	5.10	71
0.88	1 x 1	5.06	68

Density (g/cc)	Dimensions of PETN Diameter x Length (inches)	Fitted Detonation Velocity (mm/μsec) (Eqs 1,2&3)	Detonation Pressure P_{CJ} (kbar)
Optical (Smear Camera) Measurements			
0.48	1.5 x 1	3.60	24
0.30	1.5 x 0.5	2.99	24
0.29	1.5 x 1	2.96	15
0.27	1.5 x 0.5	2.91	5
Quartz Crystal Measurements			
0.25	1.75 x 1	2.83	8
0.25	1.75 x 1	2.83	7
0.25	1.75 x 1.5	2.83	6

The *PETN Detonation Pressure*, P (also called the CJ Pressure), is shown as a function of packing density in Table 7 and in Fig 4. Note that the measured P values in Fig 4 lie quite close to the theoretical curve developed by Lee & Hornig (Ref 72), which is based on a Wilkin's type equation of state (see Vol **4**, D294-L) with a Grueneisen ratio, Γ, for the detonation products, that is solely a function of specific volume. Shea et al obtained an effective $\Gamma = 8.077\rho - 12.288$ (Ref 74)

However, on p 511 of Ref 74, Mader shows that the BKW equation of state (see Vol **4**, D272) fits the exptl PETN pressure data just as well (compare Figs 5 and 4)

Zubarev & Telegin (Ref 40a) developed an equation of state for detonation products based on the dynamic compressibility data for these substances and the requirement that product volume be minimized. For PETN they compute the following:

ρ (g/cc)	D(m/sec)	P(kbar)
1.0	5700	88
1.25	6720	150
1.67	8160	270
1.77	8610	310

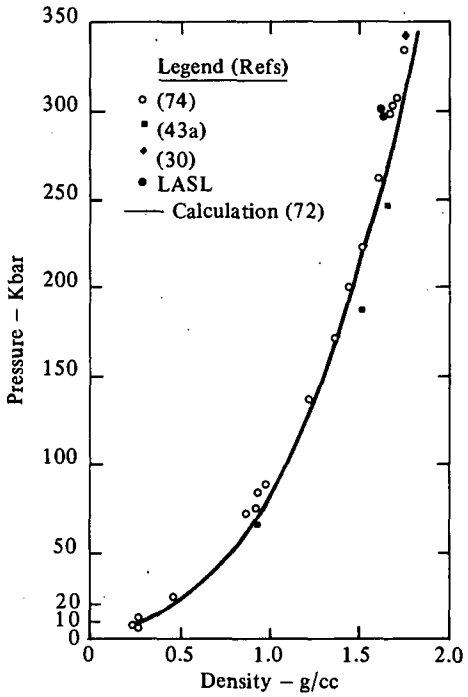


Fig 4 PETN Detonation Pressure vs Density (Ref 74, p 508)

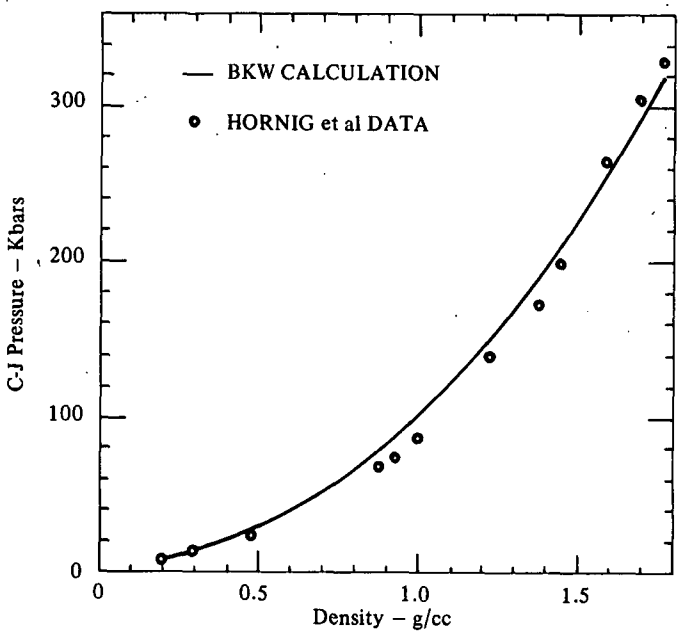


Fig 5 (Ref 74, p 511)

Note that these values are fairly close to those shown in Table 7 and Figs 4 and 5, as well as the exptl and computed D – ρ data for Fig 6 (Hornig et al, Ref 74) and Fig 7 (Mader, Ref 74). Thus it is abundantly clear that *comparison* of exptl and computed D and/or P data provides no real test of the *validity* of an *equation of state* of detonation products, since P and D data computed on the basis of widely different equations of state can be made to agree with measured P and D values

A much more rigorous test of the validity of a detonation product's equation of state is provided by the comparison of observed and computed detonation temps (CJ temps), T_{CJ} and/or detonation product compns which depend on T_{CJ} and to a lesser extent on P. Unfortunately, there are no exptl detonation product compns, and exptl T_{CJ} 's are open to serious uncertainties, particularly so in the case of solid expls. For example, Blackburn and Seely (Ref 48) in studying the light produced by the detonation of PETN, of varying degree of compaction and varying particle size, found that light intensity was not affected by the nature or even the presence of interstitial gases. For large particles,

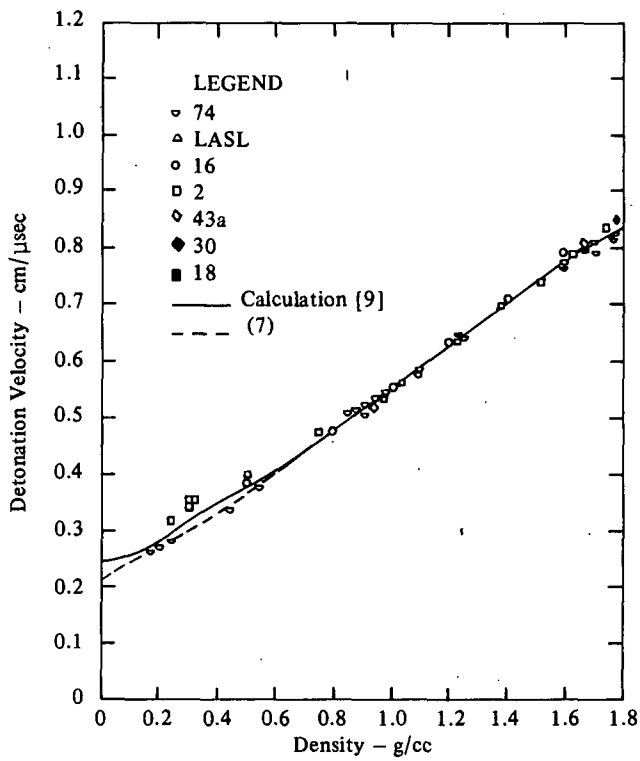


Fig 6 PETN Detonation Velocity vs Density

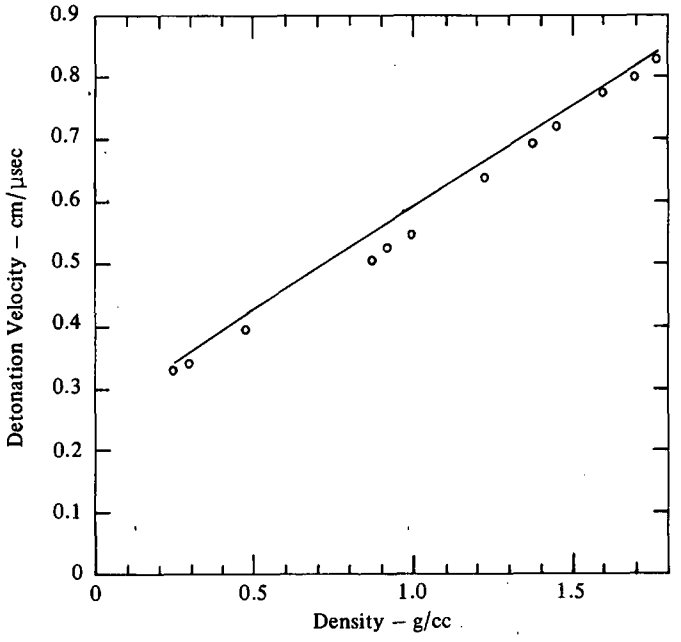


Fig 7 BKW Calculation – Hornig et al Data

they determined that the light flash consisted of discrete bursts of light about the size of the interstices. They found convincing evidence that these flashes are produced when detonation products, after expanding from a crystal into an interstice, are stagnated against the next grain. Thus "detonation light" has little relation to T_{CJ}. For PETN two values of "measured" T_{CJ} have been reported. Both were obtained by photometric methods. Voskoboinikov & Apin (Ref 24a) give T_{CJ} = 4200°K for essentially single crystal PETN. Davis (quoted in Ref 40), gives T_{CJ} = 3400±400°K for a PETN aggregate of 1.67g/cc. Theoretical values of T_{CJ} are as follows:

for ρ_o = 1.67g/cc
  T_{CJ} = 4500°K (Zubarev & Telegin, Ref 40a)
  T_{CJ} = 3018°K (Mader, Ref 40)
  T_{CJ} = 2340°K (Lee & Hornig, Ref 72)
for ρ_o = 1.77g/cc
  T_{CJ} = 4400°K (Zubarev & Telegin, Ref 40a)
  T_{CJ} = 2833°K (Mader, Ref 40)
  T_{CJ} = 2070°K (Lee & Hornig, Ref 72)
for ρ_o = 1.00g/cc
  T_{CJ} = 4850°K (Subarev & Telegin, Ref 40a)
  T_{CJ} = 3970°K (Mader, Ref 40)
  T_{CJ} = 4300°K (Lee & Hornig, Ref 72)

It is obvious that the calculated T_{CJ} depends strongly on the equation of state used in the computation. Unfortunately, as already stated, there are no unequivocal exptl T_{CJ}'s for PETN (and probably not for any expl) to compare theory and expt. However, note that for all three equations of state cited above, T_{CJ} increases as ρ_o decreases

We will not list u_p or V, the steady detonation particle velocity and detonation product specific volume, as they are completely determined by the conservation equations, namely:

$u_p = P/\rho_o D$ and
$V = 1/\rho_o(1-u_p/D)$

and can be computed from the listed P and D values of Table 7, etc

Compn of PETN detonation products and the heat of detonation will be discussed in the next subsection

Kury et al (Ref 45, p 3) made accurate measurements of the fragment velocity of expl-filled copper cylinders. Based on the kinetic energy of the fragments, they were able to obtain a relative energy scale (ie, a measure of the efficiency of various expls in propelling metal fragments) for several expls. On this scale Comp B grade A is chosen as a standard and assigned a value of 1.00. Other common expls have the following relative energies:

HMX	1.30
PETN	1.21
TNT	0.74
NM	0.56

Initial velocities of explosively driven metal fragments can be accurately estimated by the so-called Gurney formula (see Vol **6**, G195-R). The writer (Ref 81a) used the Ref 45 data referred to above to compute a Gurney constant $\sqrt{2E'}$ (for tangential detonation) of 3.04mm/μsec for 1.765g/cc PETN

AMCP 706-177 (1971) gives the *power* of PETN as 145% of TNT in the Ballistic Mortar and 173% of TNT in the Trauzl block. It also lists PETN's *brisance* at 1.5g/cc as 129% of TNT as detd in plate dent test. The Russians use a somewhat different measure of power which they call "total efficiency". This involves computing expln product expansion to 1 atm. Andreev & Belyaev (Ref 25, p 655) list the "total efficiency" of 1.6g/cc PETN as 134% of TNT

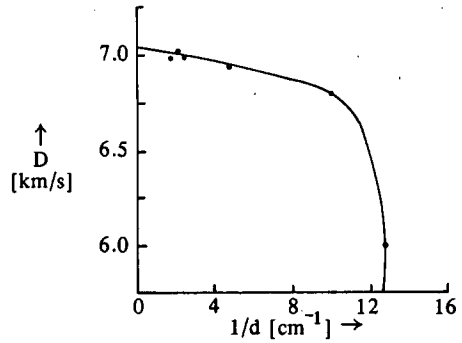


Fig 8 Detonation rate of PETN sheets (Δ = 1.4, 15% natural rubber) as a function of inverse thickness d (Ref 45)

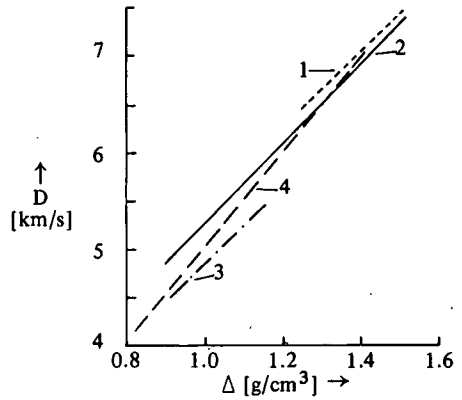


Fig 9 Density effect of stretched and unstretched explosives: curves 1–3 refer to unstressed sheets; 1 = 15% natural rubber, 2 = 15% depolymerized rubber, 3 = 20% depolymerized rubber. Curve 4 refers to a stretched 15% rubber containing explosive of 1.4g/cc initial density (Ref 45)

PETN is an effective underwater expl. Its shockwave energy and bubble energy relative to Pentolite (see in this Vol) are 1.15 and 1.13, respectively (Ref 21a)

Because PETN sheet expl (PETN/elastomer in sheet form) has assumed such importance in a variety of expl applications, we now present some of its detonation parameters

Detonation velocity of sheets containing 15% natural rubber is given in Figs 8 & 9 as functions of sheet thickness and density. These data are taken from Kegler & Schall (Ref 45, p 499), who show that the decrease in D produced by stretching the sheet is due to a decrease in sheet density

Jones (Ref 88, p 125) gives D = 7.0mm/μsec and P = 184kbar for Dupont **Detasheet C** (63% PETN, 8% NC, 29% elastomers)

Another Dupont sheet explosive is **EL506D.** It contains about 70% PETN and has a density of 1.4g/cc. Gurney constants for it are 2.50mm/μsec (Roth, Ref 81a) and 2.28mm/μsec (Kennedy, Ref 88, p 117)

XTX-8003, an extrudable expl, contains 80% PETN and 20% silicone rubber at a nominal density of 1.53g/cc (its theoretical max density is 1.556g/cc). At around its nominal density, D = 7.3mm/μsec and P = 170kbar. Its heat of detonation is 1.16kcal/g (Ref 92)

B. *Thermochemistry.* Ornellas (Ref 52a) obtained some very accurate measurements of the heat of reaction and reaction product compn of PETN decompd in an inert atm, for both highly confined and unconfined PETN samples. His results are shown in Table 8. Also included in this table are computed decompn products calcd under the assumption that the product gases are ideal and at equil at 1600°K and 1 atm

It is clear from these data that neither ΔH nor the major products for PETN are affected by sample confinement. It is most interesting that measured product compn and ΔH's match closely the computed ideal gas equil compn for T = 1600°K and 1 atm. This implies that as the products expand and cool, equil is *frozen* at around 1600°K, ie, reaction rates become so slow below 1600°K that the product compn remains essentially unchanged upon further product expansion and cooling

Under CJ conditions, where pressures are extremely high, the so-called *soot reactions*

$$CO + H_2 = C_S + H_2O$$

$$2CO = C_S + CO_2$$

should favor formation of free carbon and depletion of CO. Of course, for an expl that is oxygen balanced or nearly so, there is little CO or H_2 in the products under most conditions. It seems that Lee & Hornig (Ref 72) chose to ignore the soot reactions and they write

$$C_5H_8N_4O_{12} = 4H_2O + 3CO_2 + 2CO + 2N_2$$

Table 8
PETN Decomposition*
(according to Ornellas, Ref 52a)

	Confined Sample	Unconfined Sample	Computed**
ΔH***kcal/g	1.49	1.50	1.52
Product Composition (moles/mole PETN)			
CO_2	3.39	3.50	3.50
CO	1.64	1.59	1.50
CH_4	0.003	< 0.0002	none
C_s	none	none	none
H_2O	3.50	3.45	3.50
H_2	0.45	0.51	0.50
N_2	2.00	2.00	2.00
NH_3	0.037	< 0.002	1.5×10^{-5}
HCN	none	none	none

* ρ_o = 1.74g/cc
** Ideal gas equilibrium at 1600°K and 1 atm
*** $(H_2O)_\ell$

for the CJ reaction. This leads to a heat of detonation, Q, of 1.38kcal/g

Mader (Ref 40), on the other hand, did take the soot reactions into account and he obtains the following CJ products (minor products ignored):

$C_5H_8N_4O_{12}$ =

$3.95CO_2+0.096CO+0.95C_s+4.00H_2O+2N_2$ at ρ_o = 1.77g/cc

$3.89CO_2+0.22CO+0.88C_s+4.00H_2O+2N_2$ at ρ_o = 1.67g/cc

$3.04CO_2+1.96CO+3.96H_2O+0.025H_2+2N_2$ and minor amounts of CH_4, NH_3 & NO at ρ_o = 1.2g/cc

$3.04CO_2+1.96CO+3.94H_2O+0.050H_2+1.99N_2+0.02NO$ and minor amounts of NH_3, H, OH & CH_4 at ρ_o = 1.0g/cc

The Q's for these reactions are respectively 1.51, 1.50, 1.38 and 1.38kcal/g

Measurements of the electrical conductance of PETN detonation products, obtained by Hayes (Ref 45, p 599) show that conductance increases with PETN packing density. Since the peak conductivities of PETN, NM, Comp B and liq TNT appear to be a linear function of the free carbon content of their respective detonation products (as calculated by Mader, Ref 40), Hayes justifiably claims that the amount of free carbon in detonation products controls the conductivity of such products. If so, the dependence of PETN detonation product conductance on initial PETN density favors Mader's detonation product computations since, as shown above, Mader calculates that the amount of free carbon decreases with a decrease in PETN packing density

The product compns measured by Ornellas (Table 8) and the Mader CJ compositions differ appreciably. The Q's are, however, very similar. The agreement between calorimeter and computed Q's is certainly unexpected in view of the different product compns. Nevertheless, as stated in Vol **7**, H38–39, there is rather good agreement between calorimeter Q's for confined samples and the CJ Q's computed by Mader (Ref 40) for expls that are not too deficient in oxygen. The following tabulation illustrates this:

	Q_{exper} (kcal/g)	Q_{comput}(kcal/g)
PETN	1.49	1.51
HMX	1.48	1.48
RDX	1.51	1.48
9404	1.41	1.38
LX-04	1.31	1.31
NM	1.23	1.30
TNT	1.09	1.27

Note that disagreement between exptl and computed values increases as the oxygen deficiency of the expl increases

Orlenko & Parshev (Ref 48b) determined that the ratio of PETN underwater shockwave energy to Q is 0.77 at ρ_o = 1.6g/cc and 0.47 at ρ_o = 0.7g/cc

Initiation Characteristics. Usually the initiation characteristics of an expl are examined from two different points of view, namely, how to obtain reliable initiation, and how to avoid accidental initiation. It is the latter point of view that we will emphasize, since, as stated at the beginning of this section, there is no problem in initiating PETN reliably. Conversely, PETN, because of its "sensitivity", is prone to accidental initiation. We will now proceed with the description of various modes of initiation of PETN. For general modes of expl initiation see Vol **7**, I106–109

Initiation by exploding bridge. This subject has been studied extensively by Leopold (Refs 32a, 41 & 43). He used a smear camera to observe the growth of expln in PETN, and a condenser discharge to explode the bridge wire. He found that the diameter of the wire can be chosen so as to favor time reproducibility of expln, reliability of detonation, or vigor of the bridge-wire output. To cause detonation, there is an optimum length for each wire material, apparently governed by the energy density in the wire, and a min critical volume of expl that must be initiated. No single parameter was found to be correlated with the ability of the wire to effect detonation over a wide range of parameters. Beneficial trends, however, are readily apparent. These include a high-power input producing high temps and pressure; a sustained electrical-energy input just after the wire bursts to provide simultaneous electrical and chemical energy contributions during the critical growth to the detonation period; vigorous wire explns to ensure ignition of a definite critical volume of expl, and use of wire materials with low bp and heats of vaporization for greater heat transfer (Ref 41)

In a subsequent study (Ref 43), Al, Au, Pt and W wires were investigated to determine the effect of the wire material on the initiation of PETN by exploding wires. The wires were exploded by a 1-μf capacitor charged to 2000v. The results indicate that favorable wire materials are those into which energy is deposited at a rapid rate. They also have low bp's and heats of vaporization. Heat of oxidation of the wire material plays only a minor role. Different wire materials have different optimum lengths for effecting detonation

Blackburn & Reithel (Ref 42) also studied the initiation of PETN by exploding bridge wires using smear camera techniques. Photographs thru the transparent head of a detonator revealed that the shock wave generated by the exploding wire accelerates until it becomes a detonation wave in the expl. The rate of this evolution is increased by increasing the sp surface of the granular expl and by increasing the intensity of the bridgewire expln. Initiation was studied by pressing PETN into a transparent container against a bridgewire. Photographs of the initiation to detonation of the expl were taken both by the self-light of the process, and by external illumination from a second exploding wire

Initiation by Electrostatic Discharge. Jackson (quoted in Vol **5**, E45) found the max non-ignition voltage and non-ignition energy for 2.6μ PETN to be 12000v and 0.036 joules at 500MMF capacitance and a spark gap of 0.005 inches. Previous investigations (also quoted in the above Ref) showed max non-ignition energies of 0.062 and 0.085 joules for PETN of unspecified (but probably larger than 2.6μ) particle size. Circuit parameters for these tests were also not specified in Vol **5**. In any event, PETN handling is not a particularly hazardous operation from the static discharge point of view

Recently Romanov and Sten'gach (Ref 89) found that discharge energies for 50% explns of PETN increased with: PETN particle size, packing density, water content, circuit inductance, and a decrease in ambient temp. The discharge energy-interelectrode distance curve

passes thru a minimum. They claim that shock waves have a significant role in the discharge initiation process

Initiation by flame and heat will be described in sections **VIII** and **IX**

Impact and Friction Initiation of PETN have been extensively studied. This general subject is summarized in Bowden & Yoffe (Refs 13 & 19), Afanas'ev & Bobolev (Ref 85a), and Vol **7**, I35–55, which contains a rather complete description of impact initiation with many refs to the impact and friction initiation of PETN. There is general agreement that impact and friction initiation proceed via a *hot spot* mechanism (see Vol **7**, H170–75). There is, however, considerable doubt and controversy about the mechanisms of hot spot formation

As discussed in Vol **7**, it is rather futile to assign numerical values to the impact or friction sensitivity of PETN (or any other expl), although the average critical stress of ∿5kbar for PETN impact initiation (Ref 85a) may be significant. It is significant, however, that in most, and probably all, relative rankings of the impact sensitivities of solid expls (see Vol **7**, I42-R), PETN ranks as the most sensitive secondary expl (primary expls, such as Lead Azides, Mercuric Fulminate, etc, are more sensitive)

Aside from the question of how hot spots are formed, there is general agreement about the subsequent stages of the initiation of PETN by impact. Bowden & Yoffe (Ref 13), and more recently Bobolev et al (Ref 70) have observed the following sequential stages in the impact (also friction and spark) initiation of PETN layers:

1) Over a short time interval, deflagration near the point of initiation proceeds at several tens of meters/sec

2) At about 5–15mm from the point of initiation, the propagation velocity increases to several hundred meters/sec

3) At the end of the second stage there is a sharp increase in propagation velocity to about 1000m/sec. Depending on exptl conditions, this "low velocity detonation"(LVD) can propagate over considerable distances, or it can go over into a normal detonation whose propagation velocity is determined by the density and dimensions of the PETN layer. It is possible to observe local ignitions *ahead* of the LVD front (Ref 70)

Bobolev et al (Ref 70) have shown that the LVD in stage 3 is a compression wave phenomenon and not a combustion front. For PETN they found that this compression wave must have a min velocity of 700–800m/sec, otherwise stage 3 cannot occur. They postulate that the initial combustion (stage 1) releases gaseous decompn products which raise the pressure of the reacting region and accelerate combustion. Hot combustion products penetrate into unreacted regions to produce new ignition sites and a further pressure increase, accelerated combustion, etc. This *avalanching* process accounts for stage 2. In an enclosed volume, ie, in a cased charge, an accelerating flame front acts like a piston and drives a compression wave into the virgin material ahead of it. On attaining sufficient intensity this compression wave deforms and fragments the virgin material. Bobolev et al (Ref 70) claim that this deformation and fragmentation create new reaction sites (hot spots) in a manner similar to that postulated in Ref 85a. A balance between energy losses and energy release by the new reaction sites maintains the process at an approximately stable propagation velocity, namely the LVD of stage 3. If such a compression wave, travelling at around 1000m/sec in a confined layer of PETN at around 90% of crystal density, enters a region of lower density (80% crystal density or lower), Bobolev & Dubovik (Ref 48a) observed sharply accelerating propagation and establishment of normal detonation

Some valuable insight into the mechanism of the initial hot spot formation (the processes preceding stage 1) during impact of PETN is provided by Heavens & Field (Ref 87). Their high-speed framing sequence of 5kg–1 meter impact on 15mgs of polycrystalline PETN shows: a) compression to a layer about 0.1mm thick; b) cessation of lateral spreading of the layer (about 10microsec after a) and jetting at 150m/sec; c) in an additional 10–15microsec the initially opaque PETN layer becomes gradually translucent, and completely transparent in 15–20microsec; d) transparency and rapid mobility of the PETN is associated with surface fusion followed by melting of the entire sample; and e) some 25microsec after b), the jetting velocity increases to 300m/sec, and some 5micro-

sec thereafter several initiation sites appear simultaneously, and burning at 300–400m/sec develops shortly thereafter

Heavens & Field suggest that both gas cavities, sealed off during fusion of the sample, and high flow rate shearing near the impacting striker edge contribute to hot spot formation during PETN impact initiation

Initiation by LASERS. Several investigators have used lasers (see Vol **7**, L4) to initiate PETN. Brish et al (Ref 50) initiated detonation in PETN with Q-switched neodymium glass lasers (10600Å), focused to produce a power density in excess of 0.08MW/mm^2 at the surface of 5mm thick, 1 g/cc PETN samples. It appears that the delay in producing steady detonation under these conditions is of the order of 1.5 to 2microsec. In a later study (Ref 69), using both neodymium glass and ruby lasers (6943Å), Brish et al found a critical diameter, d_o, for the laser initiation of PETN. For PETN with a specific surface of 550cm^2/g (finer than normal production grade), $d_o \simeq 0.6$mm. For finer PETN (larger specific surface), d_o decreases. The laser energy required for initiation increases as the PETN packing density is increased. Brish et al claim that laser initiation is a thermal process, and that the laser energy rapidly absorbed in a thin layer of expl produces a shock wave which initiates detonation

A series of papers by Menichelli & Yang (Refs 82, 84 & 86) showed that Q-switched ruby lasers could initiate steady detonation in PETN (and RDX or Tetryl) in <0.5 μsec when a 1000Å-thick Al layer was deposited on the face of the sample, and subsequently exposed to laser radiation of 0.5 to 4.2 J with a pulse width of 25nanosec

Initiation by Light. Neither Deb (quoted in Ref 19, p 111) nor the writer (Ref 47) could produce detonation of PETN exposed to high-intensity light. The writer used PETN cores at 0.8 to 1.5g/cc, with and without small additions of graphite (in attempts to increase light absorbency), in 1/4 inch ID plastic holders, and exposed them up to around 25microsec to the radiation of Argon flash bombs (T=29000°K). In a few instances there was evidence of a deflagration, but no detonations were observed

Initiation by Shock is undoubtedly the most quantitatively reproducible of all the modes of initiation. In spite of this there is still no general agreement as to its mechanism, although most authorities now agree that it is a thermal process. A distinction is usually made between *homogeneous* and *heterogeneous* shock initiation. The former refers to initiation of single phase liquids or single crystals, while the latter refers to initiation of cast, pressed or loosely-packed solid expls

Generally, shock initiation measurements are carried out in a system consisting of a *donor* charge (some standard expl), an inert barrier, and an *acceptor* charge (test sample). The donor can be a plane wave expl lens (Ref 28) or an ordinary cylindrical charge (Ref 74, pp 220 & 261). The acceptor can be in the form of a wedge (Ref 28 & Ref 74, p 221) or a cylinder similar to the donor (Ref 74, pp 229 & 261). The cylindrical donor/barrier/acceptor systems are commonly called *gap tests.* Inert barriers are usually PMMA (polymethylmethacrylate) or brass. The information obtainable from plane wave shots and instrumented gap tests is: the input shock amplitude, and the run-up distance and time to detonation, if the shock is sufficiently strong to initiate detonation. In plane-wave/wedge shots one also obtains a record of the shock velocity during run-up. Obviously both types of tests, if made in sufficient numbers, provide a shock-initiation threshold. Shock initiation data are very reproducible in any given system, but can vary from system to system depending on test geometry, since test geometry controls rarefaction effects which in turn affect test results

For single crystal PETN (a homogenous system) Campbell et al (Ref 28) indicate that a shock of 112kbar will produce detonation after a delay of about 0.3microsec. They claim that the initiation process is essentially identical to that observed by them in single-phase liq expls (see Vol **7**, L31). Quantitative verification of their postulates is still in some doubt, because there is no general agreement about the temps that a 112kbar shock produces in the crystal, nor is there agreement about the values of the kinetic parameters that are necessary to compute the PETN thermal expln delay. However, in a qualitative sense their mechanism appears to be quite sound

In their original publications (Ref 28) Campbell et al claimed that the shock initiation process

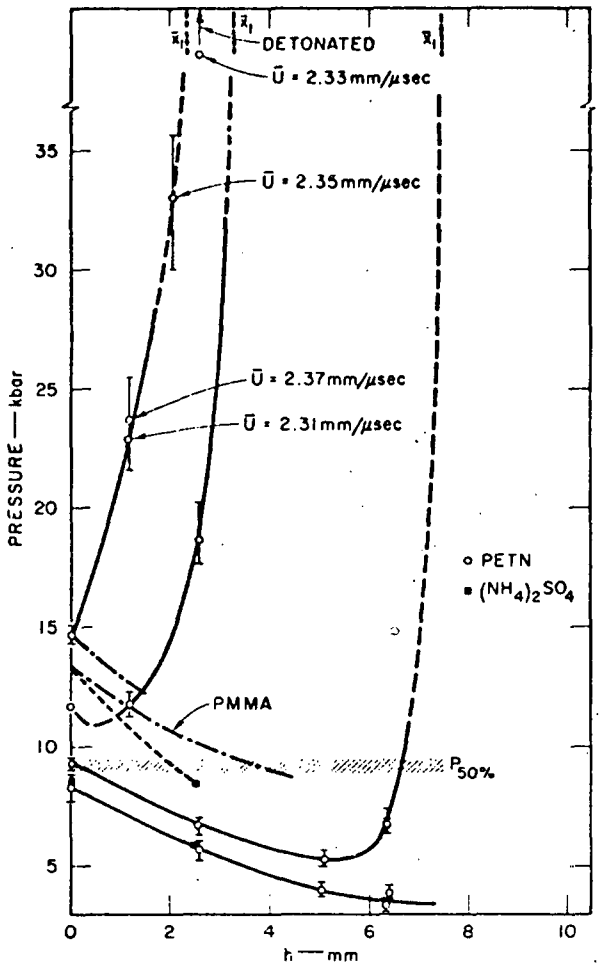


Fig 10 Pressure-Distance History in 1.59g/cc PETN (Ref 74, p 226)

in heterogenous expls is quite different from that of homogenous expls. Recent studies (Ref 74, pp 219, 321 & 435 and Ref 94), however, strongly suggest that shock initiation in expls pressed to 90% (or higher) of their crystal density is rather similar to that in homogenous expls, namely, that substantial reaction takes place well behind the shock front, and that stable detonation results when the compression waves produced by this reaction catch up with the initial shock front

Exptl evidence showing that shock initiation in high density PETN pressings proceeds rather similarly to that in homogenous expls was obtained by the writer (Ref 74, p 219) and by Wackerle and coworkers (Refs 79 & 94). Fig 10, taken from Ref 74, summarizes the results of an instrumented gap test on unconfined one-half inch diameter 1.59g/cc PETN pressings. Quartz pressure gauges were placed on one face of the cylindrical PETN pressings of thickness h, while the other face was in contact with a PMMA barrier. All pressures are in the PETN either at the barrier/PETN interface (at h = 0), or at the PETN/quartz gauge interface (h > 0). The shock initiation threshold, $P_{50\%}$, is indicated by the horizontal striped band. In the bottom curve, with the input shock $P_0 > P_{50\%}$, the pressure decreases monotonically with h. In the next curve $P_0 = P_{50\%}$. Up to h~5mm this curve parallels the bottom curve, but for h ≥ 5mm the pressure rises rapidly. The dashed extrapolated portion is drawn to approach x_i, the run-up distance to detonation (also called *build-up distance*), asymptotically. The curve at P_0 ~12kbar may or may not have the "dip" as drawn. It certainly has a "dip" or a "flat" for h ≤ 2mm. The top curve at P_0 = 15kbar (well above $P_{50\%}$) shows no indication of a "dip" or "flat". To ensure that the gauges produced no anomalous records at $P > P_{50\%}$, P–h curves were obtained with PMMA or $(NH_4)_2SO_4$ pressings substituted for the PETN. The PMMA Hugoniot in this low pressure region is fairly similar to that for 1.6 g/cc PETN (it lies slightly above the PETN Hugoniot in the P–u plane), and $(NH_4)_2SO_4$ has the same crystal density as PETN, and consequently qualifies as an inert "substitute" for PETN. Although not shown in Fig 10, the PMMA P–h curve for $P_0 < P_{50\%}$ is quite similar to the bottom curve of Fig 10. The main conclusion to be drawn from the data in Fig 10 is that at $P_0 = P_{50\%}$, for which half the samples tested detonate, the pressure in the PETN *decreases* during some 80 to 90% of the run-up distance before the pressure begins its rapid increase. This is certainly inconsistent with a shock front reaction, and strongly suggests that some type of disturbance occurring well behind the shock front sends out a pressure pulse that eventually overtakes the initial shock front

Wackerle & coworkers (Ref 79) have photographically recorded a "second wave phenomenon" for 1.72g/cc PETN pressings, but not for 1.6g/cc pressings. However, in a later study (Ref 94) using quartz gauges to impact the PETN sample and shock it, as well as target gauges on the other PETN face, they found

that 1.72g/cc and 1.6g/cc pressings behave quite similarly. Their data indicate a reaction-generated pressure pulse originating well behind the shock which eventually overtakes the initial shock front and intiates detonation

It was already stated that shock initiation data are very reproducible within a system, but not necessarily reproducible among different systems. PETN appears to be somewhat of an exception – presumably because it is so "sensitive" (for lack of a better word). Generally, one expects a lower shock initiation "threshold" (see footnote (a) of Table 9) for plane wave systems than for small-scale unconfined gap tests. As shown in Table 9, the difference between the plane wave and unconfined gap test results for PETN is fairly small. As expected agreement between plane wave and confined gap test data is even closer. Examination of the last two rows of Table 9, and comparing them with the first three rows, suggests that preheating sensitizes PETN to shock more than by just decreasing its density (see below for a discussion of the density effect, although the data in Table 8 already suggest that PETN shock sensitivity increases as its packing density decreases). Shock sensitization by preheating was also observed for other explosives (Ref 74, p 219)

The shock sensitivity of PETN increases (ie, the 50% firing stimulus decreases) as packing density decreases. This trait common to practically all expls, is illustrated in Fig 11

The shock sensitivity of PETN increases slightly as PETN particle size is increased, ie, as specific surface is decreased (Refs 34 & 74, p 265)

Chick (Ref 45, p 353) found that increasing the inert gas pressure in the interstices of a PETN pressing decreased its shock sensitivity. These effects were further examined by Dinegar et al (Ref 96), whose results are summarized in Fig 12. The desensitizing action of inert gases, and the sensitizing action of oxygen or air, in PETN pressings of about 3000cm^2/g specific surface is quite similar to that shown in Fig 12 for about 12000cm^2/g PETN, except that all curves are slightly displaced towards greater attenuator thickness (greater sensitivity) in accord with the results of Refs 34 & 74, p 265

Table 9
Shock Initiation of PETN

Test Conditions	Packing Density (g/cc)	Specific Surface (cm^2/g)	Shock Pressure Threshold (kbar)	Refs
Plane-wave	1.6	∿3000	≥ 7 (a)	79 & 94
Unconfined gap test	1.59	3350	9.1	74, p 227
Confined gap test	1.6	–	7.5 (b)	100a
Plane-wave	1.72	∿3000	≥ 14	79 & 94
Confined gap test	1.72	–	∿12 (b)	100a
Unconfined gap test	1.55	3350	6.7 (c)	74, p 224
Confined gap test	1.55	–	∿6.5 (b)	100a

(a) There is no real shock pressure initiation threshold in a plane-wave system. These are pressures in the region where the pressure-run up distance curve begins to be steep

(b) Ref 100a does not specify whether these pressures are in the PETN or in the PMMA barrier. If these are PMMA pressures, the threshold pressures in the PETN would be lower than shown in the Table. The pressures in Refs 74 & 79 are pressures in the PETN at the PETN–barrier interface

(c) PETN (originally at 1.59g/cc) pre-heated to 110°

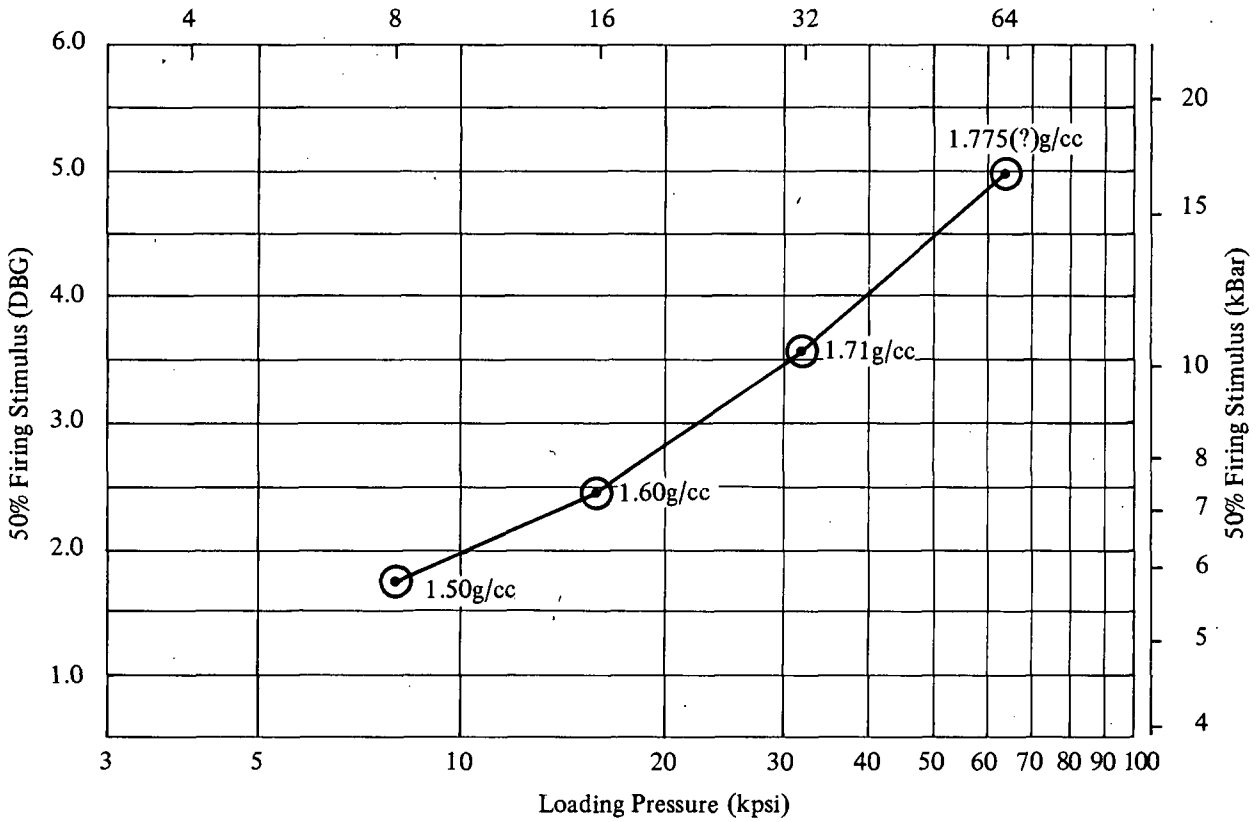


Fig 11 Small Scale Gap Test (SSGT) Data for PETN (Ref 100a)

Table 10
Relation Between Buildup Parameters for 1.6 and 1.72g/cm^3 PETN
(Ref 94)

The coefficients listed were determined by non-linear least-squares fitting of the data of Ref 79, and have dimensions appropriate for x_i in mm, t_i in μsec, and P_1 in kbar

Initial Density (g/cc)	Formulation	A	B
1.6	$x_i = AT^B$	2.585	0.890
	$x_i = AP_1{}^{-B}$	567.1	1.985
	$x_i = AP_1{}^{-B}$	390.3	2.196
1.72	$x_i = AT^B$	3.209	0.850
	$x_i = AP_1{}^{-B}$	593.2	1.678
	$t_i = AP_1{}^{-B}$	487.2	1.989

Algebraic expressions for run-up distances, x_i, and times to detonation, t_i, for the shock initiation of high density PETN pressings, taken from Wackerle & Johnson (Ref 94), are shown in Table 10. Although these parameters are for a plane-wave system, they agree quite well with the writer's gap test data (Ref 74) down to input pressures just slightly greater than $P_{50\%}$

Dinegar et al (Ref 34) found that at $P_0 \geq P_{50\%}$, t_i decreases as PETN specific surface is increased. For $P_0 >> P_{50\%}$, t_i is independent of specific surface

Even if all the input shock energy of the data of Table 9 or Fig 11 went into the *uniform* heating of shocked PETN pressings, the resulting temp rises would amount to only several tens of degrees. This is, of course, grossly insufficient to produce any appreciable decompn in the PETN, to say nothing of decompn that is complete on a microsecond time scale, which is a typical t_i for the shock initiation of PETN. The input shock must obviously produce localized and not bulk heating of the shocked material. How this occurs is still unclear. For example, Wackerle & coworkers (Ref 79) show that even

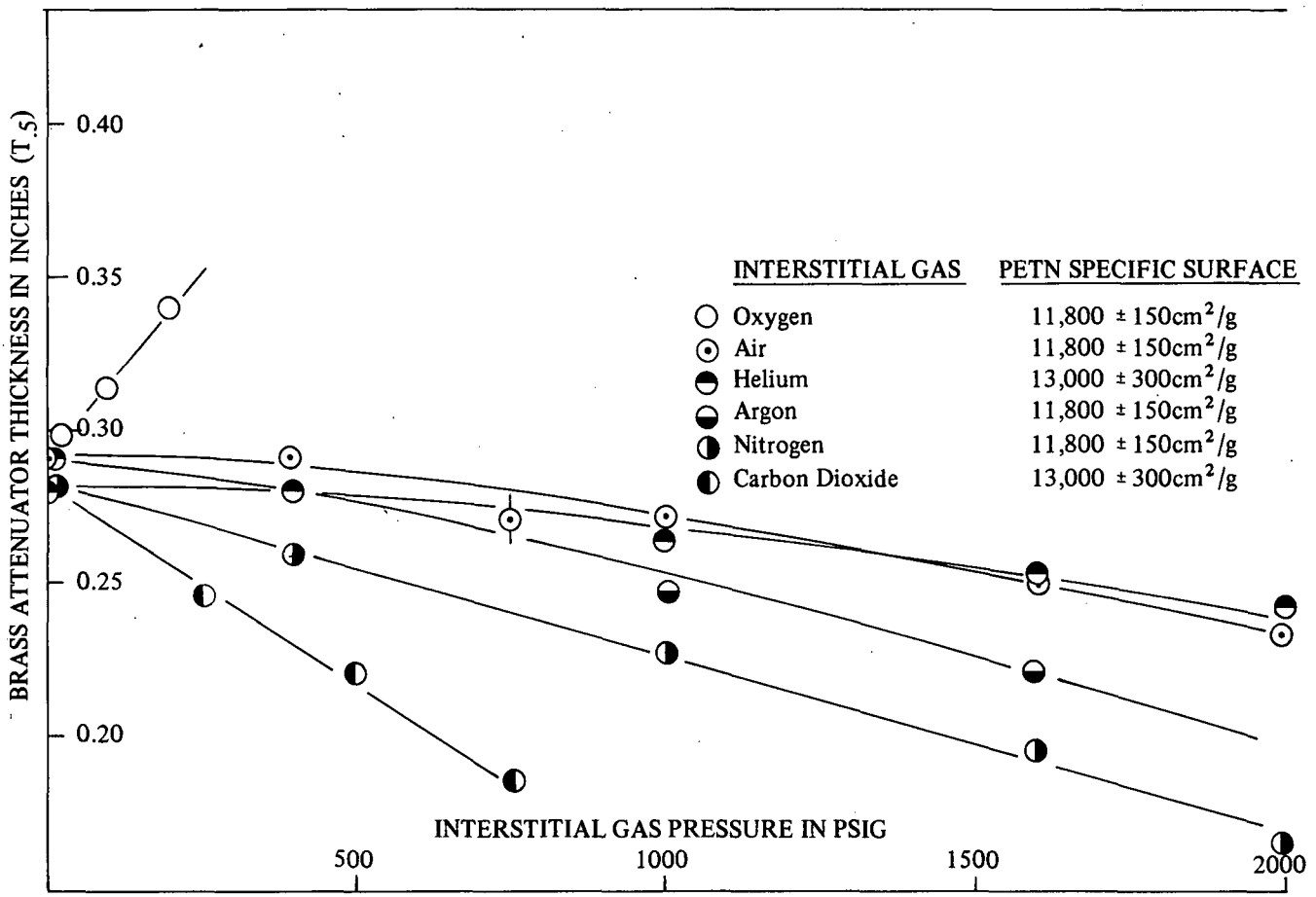


Fig 12 Effect of Interstitial Gas Pressure on the Small-Scale Gap-Test Sensitivity of High Specific Surface PETN (Ref 96)

at $P_0 \doteq 30$kbar, the mean "bulk" temp rise for 1.6g/cc PETN is less than 200°C. For a single crystal at $P_0 = 112$kbar they compute a $\Delta T \simeq$ 420°C. This agrees roughly with a rather different method of computation made by Voskoboinikov et al (Refs 65 & 66) who get $\Delta T = 400$°C for $P_0 = 122$kbar. However, Dremin et al (Ref 75), using yet another computational procedure, get $\Delta T = 170$°K at $P_0 = 100$kbar and $\Delta T =$ 300°K at $P_0 = 150$kbar for single crystal PETN; and $\Delta T = 130$°K at 25kbar, and $\Delta T = 230$°K at 50kbar for PETN at 1.475g/cc. Obviously much work remains to be done before the mechanism of shock initiation of heterogeneous expls is fully understood

VIII. Thermal Decomposition

A complete understanding of the initiation processes in an expl requires knowledge of its thermal decompn kinetics. Kinetic data are also necessary for the complete description of most facets of detonation phenomena, eg, detonation failure, diameter effect, LVD, etc. The thermal decompn kinetics of PETN have been studied repeatedly (Refs 10a; 10b; 20, pp 174–82; 26a; 38; 52; 62 & 106), but as yet there is no general agreement about the decompn mechanism or on the values of its Arrhenius parameters (see Vol **7**, K9). Most of the above studies used manometric techniques to follow pressure changes during decompn. Cook (Ref 20) followed the reaction by measuring weight loss as a function of heating time. Rogers (Ref 106) employed DSC techniques (differential scanning calorimetry) to follow heat evolution as a function of time. The writer (Ref 10b) followed the

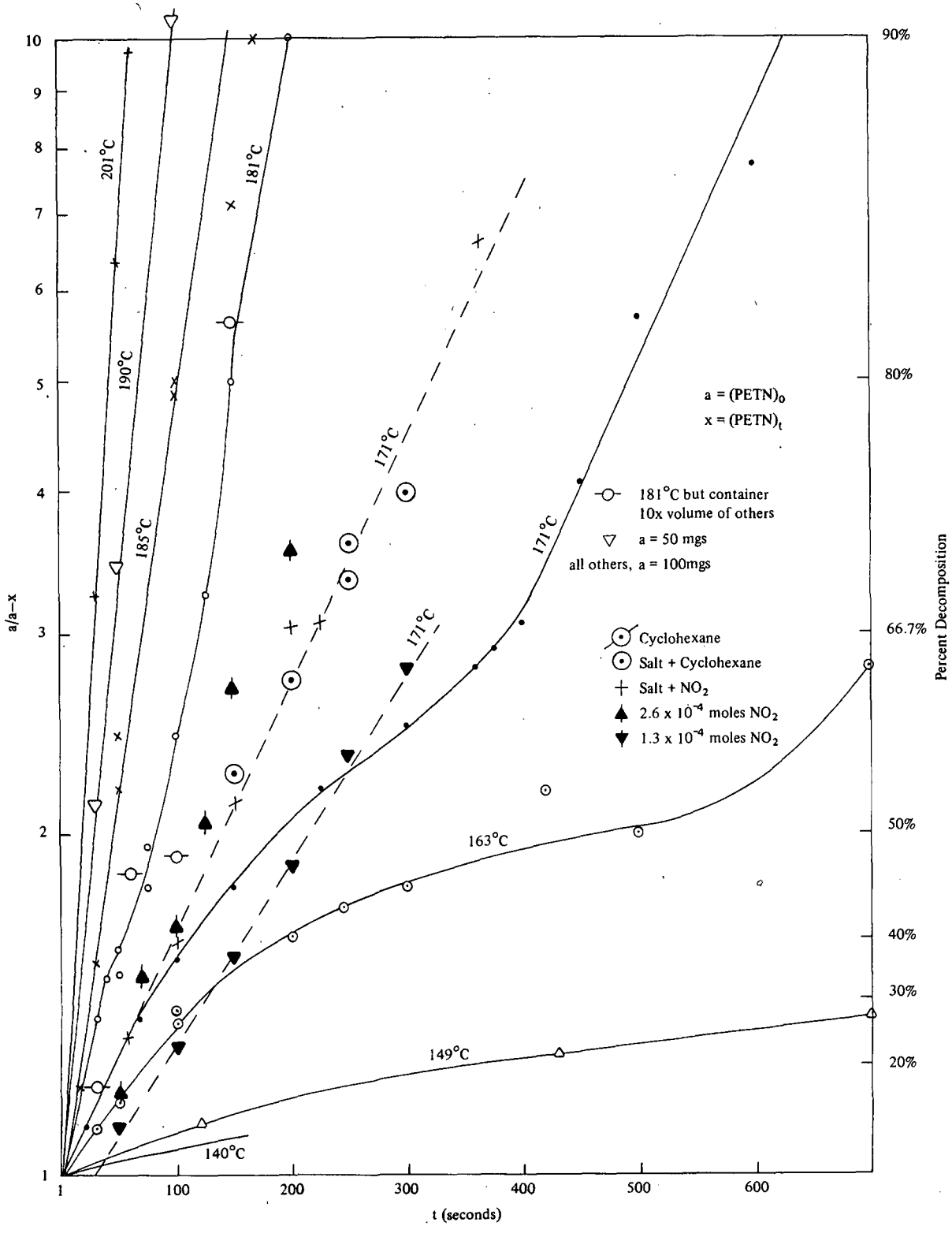


Fig 13 Thermal Decomposition of PETN

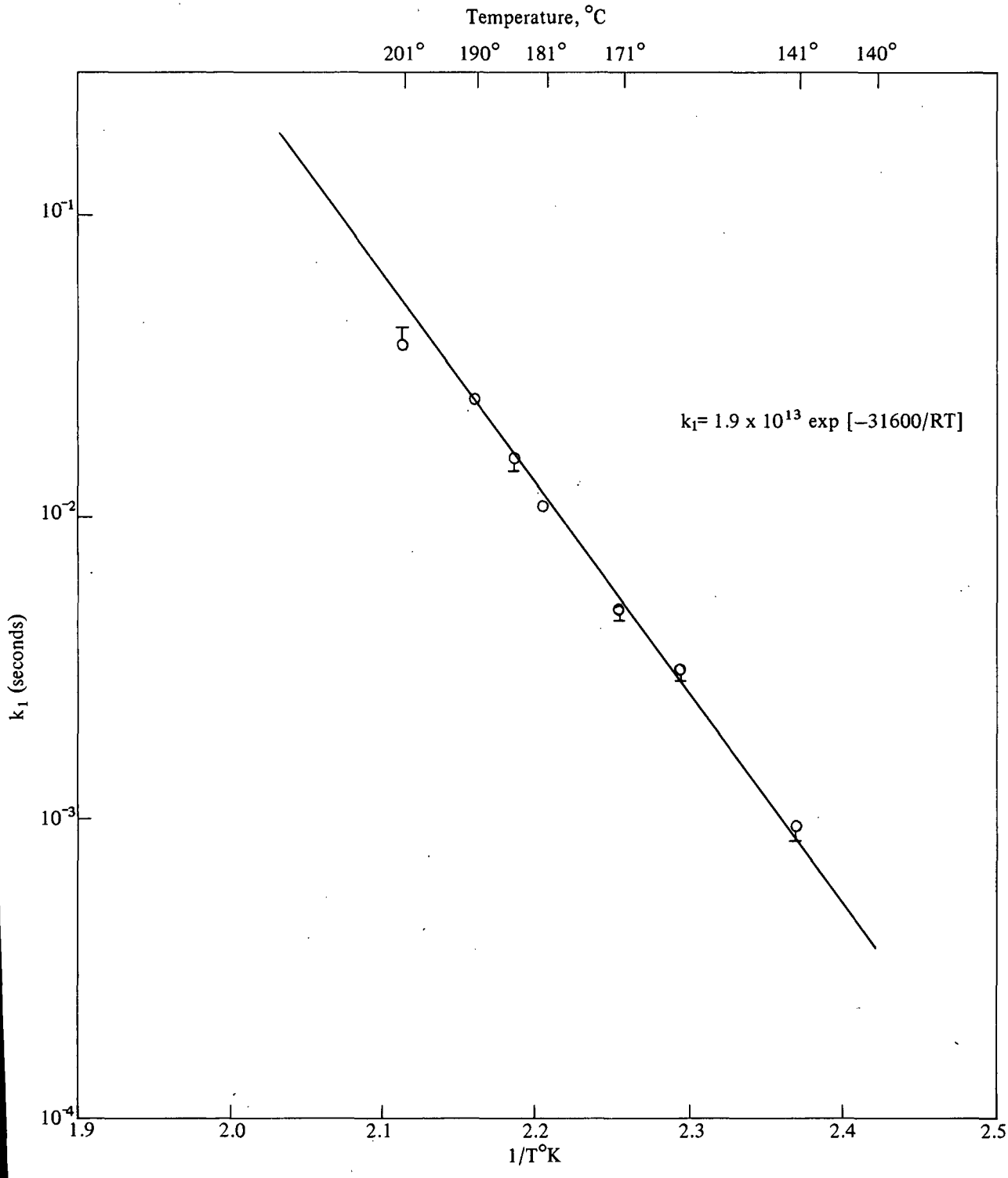


Fig 14 Arrhenius Plot for the Thermal Decomposition of PETN

decompn by chemical analysis of the PETN remaining after varying periods of heating. As will be shown below, the decompn is complex, involving retardation, autocatalysis, product interaction and other complications. Thus, it is more than pride of authorship that makes the writer suspicious of at least some of the conclusions of the *indirect* methods of following the decompn, and makes him favor the conclusion of his own *direct* method of chemically analyzing for the PETN remaining

Most of the results of the writer's study are summarized in Figs 13 & 14. A closed system (an Al bomb of about 2.4cc) was used in conjunction with a Wood's metal heat bath. After a given period of heating, the Al bomb was quickly placed in ice-water, opened, and the condensed residue removed. The PETN remaining was separated and analyzed by the $FeCl_2$–$TiCl_2$ method. In the studied temp range, decompn was for PETN in the liq phase (mp 141°), since even at the highest temp the PETN vapor press was only about 11mm Hg (according to Ref 73)

The following conclusions may be drawn for the decompn without additives:

1) Above 185° the decompn is first order over its entire course

2) At 181° and below the decompn is first order over 20 to 40% of its course, then it slows down and eventually re-accelerates above about 50% decompn

3) The first order rate constant of

$$k_1 = 1.9 \times 10^{13} \exp(-31600/RT)$$

holds for all the data except at the highest (201°) and lowest (140°) temps. At 201° the observed rate constant is lower than expected (ie, decompn is slower than expected), probably because heat-up time of the sample is no longer negligible in comparison with the total heating time. At 140° there are insufficient data

4) The effect of added surface (fine salt or powdered glass) is complex (not shown in Fig 13). At 171° the decompn with added surface at first (up to about 30% decompn) follows the 171° curve of Fig 13, then dips below it and finally (at about 50% decompn) rises above it

Additives introduced into the bomb before heating provide some interesting data. Inert additives, such as cyclohexane or CO_2 (not shown in Fig 13), that raise the pressure in the bomb appear to make the decompn at 171° first order over its entire course (upper dashed line in Fig 13). In the presence of salt (NaCl), NO_2 addition [both (1.3 & 2.6) x 10^{-4} moles] acts the same way. In the absence of salt, however, 2.6 x 10^{-4} moles of NO_2 first slow down the 171° decompn, and then make it faster than first order. With 1.3 x 10^{-4} moles of added NO_2, the decompn (lower dashed line in Fig 13) is pseudo first order with an apparent induction time, or more probably a much slower decompn in its initial stages

Not shown in Fig 13 is the effect of added water, which was found to greatly accelerate decompn at both 140° and 171°. Addition of 5 x 10^{-4} moles of acetaldehyde did not alter the initial decompn rate at 163°. However, addition of larger amounts (1.5 x 10^{-3} moles) produced explns. In a separate series of expts, it was found that about 0.5 mole of NO_2 was formed for every mole of PETN decompd, and this ratio decreased rapidly in the middle stages of decompn and then increased again in the final stages

The following macroscopic reaction scheme accounts for many of the observed effects (for simplicity PETN will be designated by RCH_2ONO_2):

(1) $RCH_2ONO_2 \xrightarrow{k_1} RCH_2\dot{O} + NO_2$

(2) $NO_2 + RCH_2\dot{O} \xrightarrow{k_2} RCH_2ONO_2$

(3) $RCH_2\dot{O} \rightarrow$ intermediate decompn products (IDP) such as H_2CO

(4) $IDP + NO_2 \rightarrow NO + N_2O + N_2 + CO + CO_2 + H_2O$

(5) $RCH_2ONO_2 + H_2O \xrightarrow{HNO_3} RCH_2OH + HONO_2$

(6) $H_2O + 3NO_2 \rightarrow 2HNO_3 + NO$

There is general agreement about step (1). Step (2) is supported by the observed slowing down of the initial decompn stages when NO_2 is added. It is also supported by Levy's studies of the decompn of ethyl nitrate (Ref 15b). At the higher temps, steps (3) and (4) remove both $RCH_2\dot{O}$ and NO_2 so rapidly that there is essentially no back reaction (step 2). Thus the reaction is first order (step 1) over its entire course. It would appear steps (3) and (4) are heterogenous reactions (at least at lower temps) that are favored by the combination of added surface and increased pressure (upper dashed line in Fig 13). The reacceleration

of the decompn in its final stages at temps of 181° and below (the reacceleration is off-scale for the 149° and 163° curves in Fig 13) could be due to hydrolysis (step 5) after enough water had been produced via (4) and nitric acid via (6), since hydrolysis is much faster in acidified water. This supposition is supported by Andreev & coworkers (Refs 26a & 38) who showed that the hydrolysis reaction accelerates PETN decompn at the lower decompn temps

In the writer's study, the addition of NO_2 most likely also introduced small amounts of water and/or nitric acid. These impurities could possibly account for the accelerated decompn rate observed in the middle and later stages of expts with added NO_2, but without salt. It is not clear why the presence of salt apparently prevents the hydrolysis reaction (see Fig 13 – with salt & NO_2 the decompn is first order over its entire course)

At the highest temps, water will be mostly in the vapor state (eg, at 185° the vapor pressure of water is about 11 atm while the estimated pressure in the bomb of the gaseous products for 50% decompn is about 6 atm) while the PETN is still liq. Thus the hydrolysis reaction does not take place unless there is appreciable soln of water vapor in the liq PETN. At 163° the vapor pressure of water is roughly equivalent to the total pressure in the bomb at 50% decompn. Thus, for the hydrolysis reaction to be significant at lower temps, but not at higher temps, there must be appreciable solubility of water vapor in liq PETN in the 160–70° temp range, and at lower temps, but not at temps above 185°

In Ref 10b the step

$RCH_2ONO_2 + RCH_2\dot{O} = RCH_2OH + R\dot{C}HONO_2$

was proposed as part of the decompn scheme. We now rule it out in view of the convincing evidence by Levy (Ref 15b) that the analogous step is absent in the ethyl nitrate decompn. However, some RCH_2OH may form via step 5. It, or further hydrolysis products should be water soluble. Water soluble nitrate-containing material was found in the wash water during separation of PETN from the rest of the residue in the bomb

By analogy with Levy's studies we might expect the formation and subsequent decompn of nitrite esters:

$RCH_2\dot{O} + NO = RCH_2ONO$

It has been suggested (Ref 38) that the above reaction may proceed differently:

$RCH_2\dot{O} + NO = RCHO + N\dot{O}H$

$2NOH = N_2O + H_2O$

This sequence could account for some of the reacceleration in the late decompn stages (when there is appreciable NO via step 4) by removing $RCH_2\dot{O}$, thus preventing step 2, and by providing H_2O for hydrolysis. The sequence could also account for N_2O, which is a known decompn product

According to Andreev and coworkers (Refs 26a & 38) and Kaidymov (Ref 62) the decompn of solid PETN is much slower than that of molten PETN. They suggest that paritial melting occurs during decompn at temps below the PETN mp and this increases the decompn rate. The increase in the PETN decompn rate in the presence of TNT (observed by Urbański et al, Ref 3) is claimed to be brought about similarly, ie, the PETN–TNT system forms low melting eutectics and PETN decompn proceeds, in effect, in a TNT soln (Ref 38)

The published PETN Arrhenius parameters are quite horrendous. They are summarized in the tabulation below:

Refs	Technique	E (kcal/mole)	Z (sec^{-1})
Robertson (10a)	Manometric	47,000	$10^{19.8}$
Robertson (10a)	Manometric	39,500 (a)	$10^{16.1}$
Rogers (106)	DSC	47,000	$10^{19.8}$
Cook (20)	Weight Loss	38,600	$10^{15.2}$
Andreev (26a)	Manometric	39,000	$10^{15.6}$
Andreev (26a)	Manometric	40,100 (b)	$10^{15.8}$
Roth (10b)	Chemical Analysis	31,600	$10^{13.3}$

(a) 5% solution in dicyclohexylphthalate
(b) 5% solution in TNT

It is instructive to compare, insofar as possible, the gaseous products of PETN decompn and expln. This is done on a water-free basis in Table 11. Note the absence of oxides of nitrogen in the expln products and the increase in CO_2 from decompn to expln

Table 11
Gas Compositions of PETN Decomposition and Explosion
(Water-free Basis; in Mole %)

	NO_2	NO	N_2O	N_2	CO_2	CO	H_2
Thermal Decomposition 210° (Ref 10a)	12.0	47.6	9.5	1.6	6.3	21.0	2.0
Impact (Ref 13, p 96)	–	24.3	5.3	9.4	19.1	35.4	6.5
Explosion in Calorimeter (unconfined sample) (Ref 52a)	–	–	–	26.3	46.1	20.9	6.7

Effect of Irradiation with Nuclear Particles

Decompn of expls can be induced by irradiation with nuclear or atomic particles (Ref 19, pp 113–21). Urizar et al (Ref 31a) found that neutron irradiation produces about 14% weight loss in PETN, mostly as CO_2. Some Petrin and PE-dinitrate were formed

The effect of nuclear reactor irradiation on PETN was studied by Avrami and Voreck (Ref 71a). Weight losses ranged from 3.65% for an 8.7 minute irradiation (0.61×10^8 R gamma) to 10.53% for 25 minutes (1.78×10^8 R gamma). Infrared, DTA and mp data revealed that the decompn of PETN increased greatly as a function of total dose. For example, at the 25 minute exposure (1.9×10^{-16} nvt, fast neutrons and 1.78×10^8 R gamma), the mp was decreased by 7–13°

Avrami et al (Ref 96a) made an extensive study of the effects of ^{60}Co irradiation on both powdered and pelletized expls. For PETN they found significant changes even at their lowest radiation exposure of 1×10^7 R [1 R (of dry air) = 87.7 ergs (absorbed)/g]. At 9×10^7 R there was 7.1% weight loss and swelling of the pellets. Irradiation up to 9×10^7 R produced little change in the PETN DTA thermogram. In TGA (thermogravimetric analysis) measurements, irradiation drastically reduced the onset of decompn – from 160 to 173° for unirradiated samples, to 70° for samples irradiated at 9×10^7R. Total weight loss or temp for 10% weight loss were, however, not greatly affected by irradiation. Irradiation at 9×10^7R lowered the mp by 5°, and irradiation at 1.06×10^9R reduced the PETN to a white sticky paste. There is some indication that irradiation increases PETN impact sensitivity, although the real effect was to make the already erratic impact results even more erratic. Irradiation at 9×10^7R lowered the 5 sec expln temp from 228 to 222° – an almost insignificant effect. However, the slope of the log expln time vs 1/T plot appeared to be less for the irradiated samples (large scatter in the measurements) than for the controls. The detonation velocity of PETN pellets irradiated at 9×10^7R was about 400m/sec lower than the controls

Explosion Temperature is not a precisely defined entity, since it depends on test geometry, heating rate, etc. It is better to speak of an explosion temp after a certain heating time, eg, 1 sec-expln temp, 5 sec-expln temp, etc. An even better procedure is to plot the log of expln time vs 1/T. These plots are generally linear

For PETN we obtain the following 1 sec and 5 sec "expln temps" from various sources:

Table 12
PETN "Explosion Temperatures"

1 sec Expl Temp °C	5 sec Expl Temp °C	Min Observed Expl Temp °C	Refs
255	222	215	13a
–	225	–	10b
–	225	205-215	25
276	228	< 214	96a
270	227	175	32b

Lee et al (Ref 74, p334) find that expln temps of PETN increase as the ambient pressure on the sample is increased. Bowden and Yoffe (Ref 19, p40) also observed this effect

IX. Combustion & DDT

Combustion.

PETN is difficult to ignite at atm pressure. According to Andreev (quoted in Ref 44, p 185), PETN will not burn even in a tube as large as 18mm diameter unless it is preheated to 95°; then burning propagates at the low rate of about 0.05cm/sec. Andreev & Popova (Ref 30b) found that the mass burning rate of 1.25 to 1.3g/cc PETN pellets follows the linear burning rate law, $u_m = 0.0193P$ over the range of 16 to 750 atm (where the mass burning rate u_m is in g/cm²sec and the ambient pressure P is in kg/cm²). At 1 atm and room temp the critical diameter for PETN was 30mm. Molten PETN burns more readily and its burning rate approaches that of NG and EGDN. Taylor (Ref 32) gives a mass burning rate of 0.86g/cm²sec for 1.25g/cc PETN at 52 atms. This agrees fairly well with the 1.00g/cm²sec computed by the Andreev-Popova rate law shown above. Actually, packing density appears to have little effect on mass burning rate, eg, Taylor finds u_m = 0.99, 0.86 & 0.99g/cm²sec respectively for 0.67, 1.25 & 0.95g/cc pellets (of about 5 micron particle size PETN). He ascribes this apparent constancy of u_m to the formation of a continuous layer of molten material over the burning expl. Heat transfer from the gas phase burning reactions to the solid, now controlled by this molten layer and essentially independent of the physical state of the solid, becomes nearly constant. A constant heat transfer implies a constant mass burning rate. However, if this molten layer becomes too thin (in comparison with pore diameter), *convective burning* can be established and burning rates will increase sharply (Ref 31). In *convective burning*, propagation is via the flow of hot gases thru the pores of the burning material at a speed determined by the existing pressure gradients. Similar conclusions were reached by Belyaev et al (Ref 37) in their study of PETN combustion in a manometric bomb. For PETN of about 0.1 micron pore size, transition to convective burning occurs at pressures of about 330 bars. Taylor (Ref 24, p 79 & Ref 31) gives the following mass burning rates for 500-853 micron PETN at around 0.92g/cc:

Pressure (psig)	Burning rate (g/cm²sec)
375	0.53
525	13.9
750	59.0

Obviously the pressure dependence of the burning rate in Taylor's expts with porous PETN is much greater than linear

The development of combustion in PETN by shock was studied by Dubnov et al (Ref 93). Unfortunately, the original article is unavailable to us, but it appears that the effects of incident shock velocity, reflected shock pressure and temp, surrounding gas, and surface roughness of the PETN were examined

Deflagration-to-Detonation Transition (DDT)

DDT is discussed in some detail in Section VII of the article on *Propellants, Solid* in this Vol. That discussion emphasized the importance of *convective burning.* A convective flame front is an ignition wave which is propagated by the passage of hot combustion gases thru the pores of the expl mass, with the hot gases being forced into the pores by confinement. However, this penetration does not result in the immediate formation of a flame front. The gases heat the pore walls and are consequently cooled. It is the *continuous* flow of gases which raises the pore wall temp sufficiently to produce ignition, and the *avalanching* of such a process produces what becomes the head of the convective front. At some later time compressive waves develop in the region behind the convective flame front. These waves coalesce and reinforce each other, and eventually produce a shock which overtakes the convective flame front, and shortly thereafter a shock-to-detonation transition occurs

DDT in PETN has been the subject of many studies (Refs 10c, 13, 24b, 35, 36, 67, 68 & 70). The highlights of these investigations, most of which favor the DDT process outlined above, are presented below

Griffith & Groocock (Ref 24b) found that the DDT run-up distance decreases as packing density is increased but at high packing density DDT is difficult to achieve. The particle size–run-up distance curve goes thru a minimum, with the optimum PETN size falling in the range of 76–124 microns. Streak camera records show detonation *starting well ahead of the flame front*

Andreev & Chuiko (Ref 35) observed stable burning in PETN of 5 micron particle size and relative density δ = 1.17, up to 60 atm pressure. At higher pressures (up to 100 atm) burning rate increased rapidly. The pressure at which transition from stable to accelerating

burning occurs increases with δ and decreases as particle size is increased

Andreev & Gordunov (Ref 36) define a critical pressure P_c above which the pressure in the burning PETN increases drastically in a short time interval τ

The studies of Bobolev et al (Ref 70) on the transition from burning to detonation have already been described in Section VIII under *Initiation by Impact & Friction*

Korotkov et al (Ref 67) also stress the importance of convective burning in DDT. They claim that the length of the run-up zone to detonation is determined by dp/dt in the burning zone. The value of dp/dt in turn is determined by the specific burning surface and the permeability, pore size and compressibility of the expl

In a subsequent study (Ref 68) these authors formulate the DDT model shown in Fig 15. In this model, Region I is surface combustion; Region II, convective combustion with a ragged front; Region III, convective combustion with a smooth front; Region IV, LVD; and Region V, detonation. Surface combustion is propagated by heat conduction, while propagation in Region

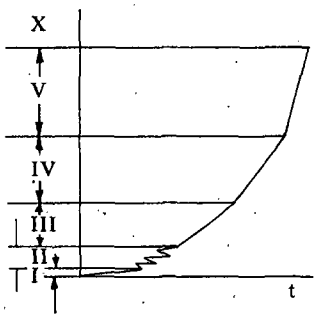


Fig 15 Model of transition from combustion to detonation in porous explosives (Ref 68)

II is via penetration of hot combustion products into the existing pores of the expl. Propagation in Region III is via convective flow between the charge surface and its confinement. This regime is claimed to be affected by confinement expansion (due to pressure), and by fragmentation of the peripheral portions of the expl column. The phenomena in Regions IV and V have already been described in Section VIII under *Initiation by Impact & Friction*

In agreement with the results of Bobolev et al (Ref 70), Obmenin et al (Ref 68) find that the critical velocity for establishing LVD (Region IV) in PETN, of 500 micron particle size and porosities of 0.04 to 0.2, is 800m/sec. High porosity, large charge diameter and long columns favor DDT. For PETN, the min porosity for DDT is 0.18 for 10mm diameter charges. LVD depends on confinement material. Thus LVD is 900, 2600 & 3200m/sec respectively for low-porosity PETN in Plexiglas, brass and steel. LVD in PETN is not affected by decrease in particle size or increase in charge diameter. However, in metal confinement, DDT occurs at lower porosities than in Plexiglas, probably because higher pressure can be achieved before the confining tube ruptures. The max pressure in the confining tube prior to rupture also appears to control the actual velocity of the LVD regime (as shown above, the LVD in steel is higher than the LVD in Plexiglas)

Related to both DDT and initiation by shock is the initiation of solid expls by gas detonations. Weiss et al (Ref 61) found that PETN at 0.7g/cc could be initiated by a gas detonation of 21 atm initial pressure, which produced an initial (presumably in the PETN) pressure of 2kbar. Under these conditions initiation delay in the PETN was less than one microsecond

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Pentaerythritol Tetra-acetate (PETA). $C_{13}H_{20}O_8$, mw 304.29, OB to CO_2 –147.4%; needles, mp 83–4°; (Refs 1 & 2); prepd by the action of Ac_2O on PE in the presence of Na acetate (Ref 2). The IR absorption peaks are given in Ref 5; CA Registry No 597-71-7

To evaluate its use as a plasticizer for NC, a mixt of 70% NC and 30% PETA was examined by the vac stability test at 110°. The gas evolution vs time curve was found to be slightly concave downward with a value of 7.5ml of gas/g after 80 hours (Ref 4). Comps of 50–64% NC, 28–42% NG, and 2–8% PETA have been patented as rocket proplnts (Ref 3); and comps of 50–80% TNT or PETN and 20–50% PETA as bursting expls (Ref 3). Other comps of 15–60% TNT or PETN, 20–80% AN, and 5–25% PETA are in the same patent

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Pentaerythritol Acetate Trinitrate. $C_7H_{11}N_3O_{11}$, mw 313.18, N 13.4%, OB to CO_2 –43.5%; a cryst solid, mp 87–8°. It has been prepd by the nitration of PE monoacetate with 100% nitric ac at 0°, yield 99% (Ref 3); by the nitrolysis of PE monoacetate cyclic arsenite, yield 97% (Ref 5); or by the acetylation of Petrin with Ac chloride (Ref 2), or Ac_2O (Ref 4). In the latter ref the acetate is used as a deriv for the iden of Petrin. Its Q_e is 845cal/g. It has a Taliani slope of 0.27mm/min at 110°, and has a 17min KI test at 82° (Ref 2)

Refs: 1) Beil **2**, ⟨264⟩ 2) Anon, **ABL MPR No 6** (Apr 1952), 8 3) N.S. Marans et al, JACS **76**, 1305 (1954) 4) A.T. Camp et al, JACS **77**, 751 (1955) 5) T.E. Stevens, JOC **24**, 1715 (1959)

Pentaerythritol Allyl Ether Trinitrate. $C_8H_{13}N_3O_{10}$, mw 311.21, N 13.5%, OB to CO_2 –64.3%; a liq, d 1.373g/cc at 20°, RI 1.4797 at 20° (Ref 3), visc 66 centipoises at 20° (Ref 2); prepd by the nitration of PE monoallyl ether (Ref 3)
Expl Properties:
Brisance by Sand Crushing Test. A 0.5g sample when initiated with 0.5g of MF crushed 7.4g of sand (NG 53.5g) (Ref 2)
Drop Test by Filter Paper Method. 175mm for 100% explns (NG 100mm) (Ref 2)
Friction Sensitivity by Sliding Rod Test. At a 75° angle and a 10 lb wt, no explns in 5 tries (NG 5 explns in 5 tries) (Ref 2)
Heat of Combustion. 3437cal/g (Ref 2)
Heat of Explosion. 837cal/g (Ref 2)
Methyl Violet Heat Test at 120°. 285 min (propyl ether trinitrate 120 min (NG 65 min). It is suggested that the unsaturated allyl group has a stabilizing effect giving an improved heat test (Ref 2)
Uses. It has been proposed as a high energy plasticizer for NC for use in rocket proplnts (Ref 2)
Refs: 1) Beil **1**, ⟨2816⟩ 2) R. Evans, "The Mono and Diallyl Esthers (sic) of Pentaerythritol and some of the Properties of their Nitrates", Bulletin of 4th Army-Navy Solid Propellant Group Meeting, Chicago (19–20 Apr 1948), 83 3) R. Evans & J.A. Gallaghan, JACS **75**, 1248 (1953)

Pentaerythritol Formate Trinitrate. $C_6H_9N_3O_{11}$, mw 299.16, N 14.1%, OB to CO_2 –29.4%; a solid, mp 62–3°; prepd by the action of 90% formic ac on Petrin in the presence of sulfuric ac, yield 84.1% (Refs 2 & 3)
Refs: 1) Beil **2**, ⟨38⟩ 2) N.S. Marans et al, JACS **76**, 1304 (1954) 3) Urbański **2** (1965), 193

Pentaerythritol Methacrylate Trinitrate. $C_9H_{13}N_3O_{11}$, mw 339.22, N 12.4%, OB to CO_2 –63.7%; a colorl to yel liq, d 1.435g/cc at 20°, RI 1.4918 at 20°; CA Registry No 19363-43-3

Prepd by the action of methacrylyl chloride on Petrin, yield 82.5% (Refs 2 & 3). It is readily polymerized to an insol flammable polymer (Ref 3) which has been patented as an ingredient in high energy rocket proplnts (Ref 4)
Refs: 1) Beil, not found 2) J. Legocki et al, PrzemysłChem **43**, 148 (1964) & CA **61**, 16166 (1964) 3) J. Simecek et al, Explosivst **17**, 1 (1969) & CA **70**, 116763 (1969) 4) J. Foltyl & J. Simecek, CzechP 131644 (1969) & CA **72**, 122566 (1969)

Pentaerythritol Methyl Ether Trinitrate. $C_6H_{11}N_3O_{10}$, mw 285.17, N 14.7%, OB to CO_2 –42.1%; a solid, mp 79–80° (Ref 3); prepd by nitration of PE monomethyl ether (Ref 4). Impact sensy using a 2kg wt 165cm for no explns (PA 35cm); power by Pb block expansion 128% of PA, 133% of TNT (Ref 3). It has been patented as an ingredient for expls, proplnts, and ign devices (Ref 2)
Refs: 1) Beil, not found 2) Westfälische-Anhaltische Sprengstoff AG, GerP 638432–3 (1936) & CA **31**, 1212 (1937) 3) Blatt, OSRD **2014** (1944) 4) Urbański **2** (1965), 192

Pentaerythritol Monochlorohydrin Trinitrate [2-Chloromethyl-2-hydroxymethyl-1,3-propanediol Trinitrate (Name preferred by CA)]. $C_5H_8ClN_3O_9$, mw 289.59, N 14.5%, OB to CO_2 –24.9%; a white cryst solid, mp 65–6° (Ref 3); prepd by the action of P pentachloride on Petrin, yield 22.5% (Ref 3). It has been patented as an ingredient for expls, proplnts, and ign devices (Ref 2). For the expl props of a mixt of this compd with PE dichloride dinitrate, see above under the latter name
Refs: 1) Beil **1**, ⟨2782⟩ 2) Westfälische-Anhaltische Sprengstoff AG, GerP 638432–3 (1936) & CA **31**, 1212 (1937) 3) D.E. Elrick et al, JACS **76**, 1374 (1954)

Pentaerythritol Nitrobenzoates Trinitrate.
Ortho-Nitrobenzoate. $C_{12}H_{12}N_4O_{13}$, mw 420.24, N 13.3%, OB to CO_2 –64.8%; a solid, mp 94–5°; prepd by the action of o-nitrobenzoyl chloride on Petrin in pyridine, yield 64% (Ref 3)
Meta-Nitrobenzoate. A solid, mp 102–3°; prepd the same way as the ortho isomer using m-nitrobenzoyl chloride, yield 71% (Ref 3). Impact sensy with a 2kg wt, no explns at 175cm

(PA 35cm) (Ref 2)

Para-Nitrobenzoate. A solid, mp 106–8°; prepd the same as above using p-nitrobenzoyl chloride, yield 60%. Urbański states that this compd has great expl strength and low sens to shock (Ref 4)

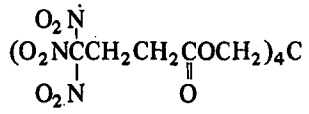
3,5-Dinitrobenzoate, $C_{12}H_{11}N_5O_{15}$, mw 465.24, N 15.1%, OB to CO_2 –49.9%; a solid, mp 109–10°; prepd the same as above using 3,5-dinitrobenzoyl chloride, yield 70% (Ref 3)

Refs: 1) Beil, not found 2) Blatt, OSRD **2014** (1944) (found on Class of Compounds page "Nitrates") 3) N.S. Marans et al, JACS **76**, 1304 (1954) 4) Urbański **2** (1965), 193

Pentaerythritol Tetrabenzoate, $C_{33}H_{28}O_8$, mw 552.55, OB to CO_2 –208.5%; needles, mp 99–101°; prepd by the action of Bz chloride on PE (Refs 1 & 2). A mixt of PETN with PE tetrabenzoate and a PE cinnamate (structure unspecified) has been patented as a progressive burning gun proplnt (Ref 3)

Refs: 1) Beil **9**, 144 & {688} 2) P. Rave & B. Tollens, Ann **276**, 61 (1893) 3) T.L. Davis, USP 1432321 (1923) & CA **17**, 472 (1923)

Pentaerythritol Tetrakis (4,4,4-trinitrobutyrate), $C_{21}H_{24}N_{12}O_{32}$, mw 972.40, N 17.3%, OB to CO_2 –36.2%; w crysts from glac acet ac, mp



174–5° (Ref 2); prepd by the addn of nitroform to PE tetra-acrylate, yield 41.6% (Ref 2); Q_e 904cal/g (Ref 3). The compd was incorporated at a level of 10% in a NG/NC proplnt formulation. The burning rate vs temp curve was plotted and was found to increase from 0.26 inches/sec at 300psi to 0.79 inches/sec at 4000-psi (Ref 3)

Refs: 1) Beil, not found 2) RHC(H), "Quarterly Progress Report on Organic Chemistry", P-52-1, Contr W-01-021-ORD-334 (June 1952), p 23 3) RHC(H), "Quarterly Progress Report on Propellant Chemistry", P-52-5, Contr W-01--21-ORD-334 (Oct 1952), pp 6 & 7

Pentaerythritol Diacetate Dipropionate (Pentaerythritol Acetate Propionate, PEAP). $C_{16}H_{28}O_8$, mw 348.38, OB to CO_2 –174.7%; a liq, bp 173–80° at 2mm (Ref 2); prepd by the reaction of PE with two moles of Ac_2O, then two moles of propionic anhydride, or by the reaction of PE with an equimolar mixt of the two anhydrides (Refs 3 & 4). The analysis of a coml sample of PEAP is given in Ref 5, and the Specs for PEAP for use in proplnt powd are in **MIL-P-23313** (22 Jan 1962). It has been used instead of triacetin in casting liq (see under "Cast Propellants" in Vol **2**, p C84) for the prepn of proplnt grains for Terrier sustainer. For specific formulations see Refs 6 & 7 in the closed literature

Refs: 1) Beil, not found 2) F.J. vanAntwerpen, IEC **34**, 68 (1942) 3) R.H. Barth & H. Burrell, USP 2356745 (1944) & CA **39**, 223 (1945) 4) E. Berlow et al, "The Pentaerythritols", ACS Monograph **136**, Reinhold (1958), 219–20 5) P. Fuller et al, "The Analysis of Penta-erythritol Diacetate Dipropionate", **ERDE 11/M/58** (Oct 1958), AD 206266 (DDCSTI users only) 6) V. Pasquale, "Feasibility Study on Using Low Acetyl Cellulose Acetate Inhibitor for Production Cast Grains", **NOSIH TR 317** (10 July 1970), AD 510578 (Conf) 7) CPIA "Solid Propellant Manual", **CPIA/M2** (28 Jan 1974), unit 1069 (Conf)

Pentaerythritol Propionate Trinitrate. $C_8H_{13}N_3O_{11}$, mw 327.21, N 12.8%, OB to CO_2 –56.3%; a solid, mp 39–40° (Ref 3); prepd by the action of propionyl chloride on Petrin in eth, yield 83% (Ref 3); Q_e 663cal/g; Taliani test 0.25ml of gas evolved/min at 110°; KI test 20 min at 82° (Ref 2)

Refs: 1) Beil, not found 2) Anon, **ABL MPR No 6** (Apr 1952), 8 3) N.S. Marans et al, JACS **76**, 1305 (1954)

Pentaerythritol Propyl Ether Trinitrate. $C_8H_{15}N_3O_{10}$, mw 313.22, N 13.4%, OB to CO_2 –69.0%; a liq, d 1.332g/cc at 20°, RI 1.4654 at 20° (Ref 3), visc 66 centipoises (Ref 2); prepd by the nitration of PE monopropyl ether (Ref 3)

Expl Properties:

Brisance by Sand Crushing Test. A 0.5g sample when initiated with 0.5g of MF crushed 6.1g of

sand (NG 53.5g) (Ref 2)
Drop Test Using Filter Paper Method. 200mm for 100% explns (NG 100mm) (Ref 2)
Friction Sensitivity by Sliding Rod Test. At a 75° angle & a 10 lb wt, no explns in 5 tries (NG 5 explns in 5 tries) (Ref 2)
Heat of Combustion. 3540cal/g (Ref 2)
Heat of Explosion. 804cal/g (Ref 2)
Methyl Violet Heat Test at 120°. 120 min for color change (NG 65 min) (Ref 2)
Uses. It has been proposed as a high energy plasticizer for NC to be used in rocket proplnts (Ref 2)
Refs: 1) Beil **1**, ⟨2816⟩ 2) R. Evans, "The Mono and Diallyl Esthers (sic) of Pentaerythritol and some of the Properties of their Nitrates", Bulletin of 4th Army-Navy Solid Propellant Group Meeting, Chicago (19–20 Apr 1948), 83 3) R. Evans & J.A. Gallaghan, JACS **75**, 1248 (1953)

Pentaerythritol Trinitrate Tris(difluoramino) methyl Ether (FA-PETRIN). $C_6H_8F_6N_6O_{10}$, mw 438.16, N 19.2%, OB to CO_2 −11.0%; a

$$(F_2N)_3COCH_2\overset{\displaystyle CH_2ONO_2}{\overset{|}{C}}CH_2ONO_2$$
$$\qquad\qquad\quad\ \ CH_2ONO_2$$

shock sens liq, prepd by the addn of perfluoroguanidine to Petrin, followed by fluorination of the adduct (for refs to the prepn of this type compd see under Pentaerythritol Mononitrate, **FA-PEMON**)
Expl Properties. Q_f −136kcal/mole, Q_e 1535 cal/g; impact sensy on PA app 5.6cm (NG 10cm), on Bruceton app 2.1cm (NG 10cm)
Refs: 1) Beil, not found 2) J.A. Brown et al, "Desensitization of Available High Energy NF Compounds", Esso Research & Engrg Co Report **ED-8** (Dec 1966) AD 397575, 60

Pentaerythritol Tetrakis[tris(difluoramino) methyl Ether] (FA-PE). $C_9H_8F_{24}N_{12}O_4$ mw

$$(F_2NCOCH_2)_4C$$
$$\qquad\quad F_2N$$

804.19, N 20.9%, OB to CO_2 & HF −11.9%; a shock sens solid, mp 53–4°, vap press below 0.05mm at 25° (Ref 2); prepd by the addn of perfluoroguanidine to PE followed by fluorination of the adduct (Ref 2). For examples of the prepn of this type compd see Refs 3, 4 & 5
Expl Properties. Q_f −172kcal/mole, Q_e 1659 cal/g, impact sensy on PA app below 1 cm (PETN 50cm, NG 10cm) (Ref 2)
Refs: 1) Beil, not found 2) J.A. Brown et al, "Desensitization of Available High-Energy NF Compounds", Esso Research & Engrg Co Report **ED-8** AD 379575 (Dec 1966), p 59 3) A.V. Fokin et al, IzvestAkadN,SerKhim **1970**, 199 & CA **72**, 110701 (1970) 4) L.J. Engel et al, USP 3692837 (1972) & CA **77**, 151449 (1972) 5) J.L. Zollinger et al, JOC **38**, 1065 (1973)

Pentaerythritol Vinyl Ether Trinitrate [2-(Hydroxymethyl)-2-(vinyloxymethyl)-1,3-propanediol Trinitrate (name preferred by CA)]
$C_7H_{11}N_3O_{10}$, mw 297.18, N 9.43%, OB to CO_2

$$CH_2{:}CHOCH_2\overset{\displaystyle CH_2ONO_2}{\overset{|}{C}}CH_2ONO_2$$
$$\qquad\qquad\quad\ \ CH_2ONO_2$$

−51.2%; a solid, mp 54–5°; CA Registry No 22769-89-7

It is prepd by the interaction of vinyl 2-chloroethyl ether and Petrin in methyl alc catalyzed by a mixt of Hg and Na acetates. Q_c 2982cal/g, Q_e 855cal/g; impact sensy with 1 kg wt 20.8 inches for 50% explns; Taliani test: $m_{100} = 0.050$, $t_{100} = 5.5$ hrs

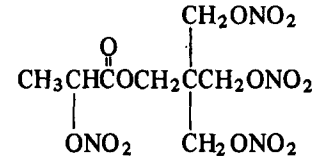
It can be polymerized and copolymerized with acrylates to give useful proplnt ingredients
Refs: 1) Beil, not found 2) S.F. Reed, USP 3427295 (1969) & CA **70**, 96158 (1969)

Pentaerythritol Diglycolate Tetranitrate.
$C_9H_{12}N_4O_{16}$, mw 432.21, N 13.0%, OB to CO_2

$$(O_2NOCH_2\overset{\displaystyle O}{\overset{\|}{C}}OCH_2)_2\overset{\displaystyle CH_2ONO_2}{\overset{|}{C}}CH_2ONO_2$$

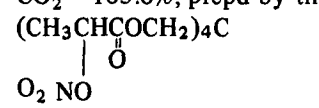
−29.6%; power by Pb block expansion is 79% of PA
Refs: 1) Beil, not found 2) Blatt, OSRD **2014** (1944) (found on Class of Compounds page "Nitrates")

Pentaerythritol Monolactate Tetranitrate. $C_8H_{12}N_4O_{14}$, mw 388.21, N 14.4%, OB to CO_2 −33.0%; a liq, prepd by the nitration of PE



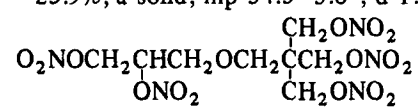
monolactate. A mixt of this compd with a small amt of PE dilactate tetranitrate has been patented as an expl plasticizer for NC and Nitrostarch
Refs: 1) Beil, not found 2) J.A. Wyler, USP 2086146 (1937) & CA **31**, 6010 (1937)

Pentaerythritol Tetralactate Tetranitrate [Pentaerythritol Tetrakis (2-nitroxypropionate)]. $C_{17}H_{24}N_4O_{20}$, mw 404.37, N 13.9%, OB to CO_2 −103.0%; prepd by the nitration of PE



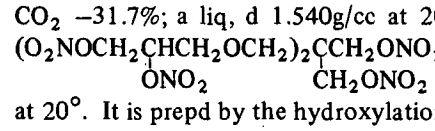
tetralactate with mixed ac. Other nitrated PE esters of hydroxy acids are also claimed. The compds are useful expl ingredients
Refs: 1) Beil, not found 2) J.A. Wyler, USP 2086146 (1935) & CA **31**, 6010 (1937)

Pentaerythritol Monoglyceryl Ether Pentanitrate. $C_8H_{13}N_5O_{16}$, mw 435.21, N 16.1%, OB to CO_2 −23.9%; a solid, mp 54.5–5.0°, d 1.57g/cc at



20°, RI 1.531 at 31° (Ref 3); prepd by the hydroxylation of PE monoallyl ether followed by nitration of the pentahydroxy compd (Ref 3). Other phys and expl props are given in Ref 2
Refs: 1) Beil **1**, ⟨2816⟩ 2) Anon, **SPIA M3a** (June 1949), Unit 119 (Conf) 3) R. Evans & J.A. Gallaghan, JACS **75**, 1248 (1953)

Pentaerythritol Diglyceryl Ether Hexanitrate. $C_{11}H_{16}N_6O_{20}$, mw 554.30, N 15.16%, OB to CO_2 −31.7%; a liq, d 1.540g/cc at 20°, RI 1.4878



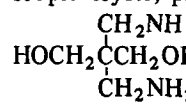
at 20°. It is prepd by the hydroxylation of PE diallyl ether (see above) with 3% H peroxide, followed by nitration. Although the expl props of this compd have not been reported, from the combination of high mw and low neg OB, it should be a good expl
Refs: 1) Beil **1**, ⟨2817⟩ 2) R. Evans & J.A. Gallaghan, JACS **75**, 1248 (1953)

Written by **C. H. McDONNELL**

Pentaerythritylamines

Monoamines. No derivs of pentaerythritylmonoamine (PE derivs in which one hydroxyl group has been replaced by an amino group) have been reported which are sens or expl

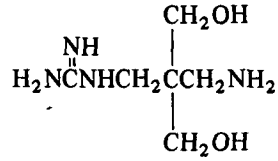
Diamines. Pentaerythrityldiamine [2,2-Bis (aminomethyl)-1,3-propanediol (name preferred by CA)]. $C_5H_{14}N_2O_2$, mw 134.18, hygroscopic crysts, prepd in two steps from the



diacetate ester of 2,2-bis(bromomethyl)-1,3-propanediol, yield 45.8%; and isolated as the dihydrochloride salt, mp 246–7° (Refs 1 & 3)

Dipicrate. $C_5H_{14}N_2O_2.2C_6H_3N_3O_7$, mw 592.38, N 24.1%, OB to CO_2 −75.7%; golden yel ndls, mp 223° with decompn (Refs 2 & 3)

Pentaerythritylmonoaminemonoguanidine [3-Amino-2,2-bis(hydroxymethyl) propylguanidine (name preferred by CA)]. $C_6H_{16}N_4O_2$, mw 176.22; prepd by the action of $H_2NC(=NH)SMe$ on

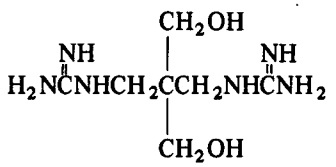


PE diamine and isolated as the dinitrate salt, mp 128–9° (Ref 3)

Dipicrate. $C_6H_{16}N_4O_2.2C_6H_3N_3O_7$, mw 582.43, N 24.0%, OB to CO_2 −90.7%; crysts from Me alc, mp 209.5–11.5° with decompn (Ref 3)

Pentaerythrityldiguanidine[1,1'-2,2-Bis(hydroxy-

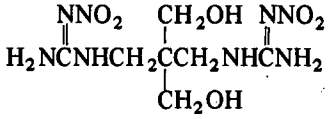
methyl)trimethylene diguanidine (name preferred by CA)]. $C_7H_{18}N_6O_2$, mw 218.26; prepd by the action of an excess of the nitrate salt of $H_2NC(=NH)SEt$ on PE diamine and isolated as the



dinitrate salt, $C_7H_{18}N_6O_2.2HNO_3$, mw 344.30, N 32.5%, OB to CO_2 −74.4%; mp 196–8° with decompn (Ref 3)

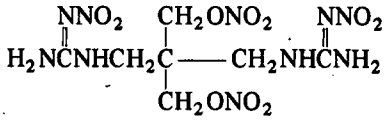
Dipicrate. $C_7H_{18}N_6O_2.2C_6H_3N_3O_7$, mw 676.47, N 24.8%, OB to CO_2 −80.5%; a solid, mp 257–9° with decompn (Ref 3)

1,1′-[2,2-Bis(hydroxymethyl)trimethylene] bis (2-nitroguanidine). $C_7H_{16}N_8O_6$, mw 308.26, N 36.4%, OB to CO_2 −83.1%; prepd by the



reaction of an excess of $O_2NN{:}C(SEt)NH$ on PE diamine, yield 26%, mp 200–1° with decompn (Ref 3)

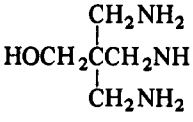
1,1′-[2,2-Bis(hydroxymethyl)trimethylene] bis (2-nitroguanidine) Dinitrate. $C_7H_{14}N_{10}O_{10}$, mw 398.25, N 35.2%, OB to CO_2 −44.2%;



a cryst solid, prepd by the nitration of the above dihydroxy compd with 99% nitric ac, yield 85.5%; mp 158–60° with decompn (Ref 3)

Refs: 1) Beil **4**, {850} 2) Beil **6**, {952} 3) L.S. Hafner & R. Evans, JACS **79**, 3783 (1957)

Triamines. Pentaerythrityltriamine [3-Amino-2,2-bis(aminomethyl) propanol (name preferred by CA)]. $C_5H_{15}N_3O$, mw 133.19; prepd in three steps from PE tetrabromide and isolated as the hydrated **tripicrate,** $C_5H_{15}N_3O.3C_6H_3N_3O_7$,

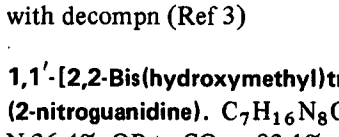


mw 820.51, N 26.1%, OB to CO_2 −70.2%; crysts from w, mp 145° with decompn (Refs 1 & 2)

Trinitrate. $C_5H_{15}N_3O.3HNO_3$, mw 322.23, N 26.1%, OB to CO_2 −44.7%; mp 239° with decompn (Refs 1 & 3)

Refs: 1) Beil **4**, {809} 2) A. Litherland & F.C. Mann, JCS **1938**, 1588 3) M. Bayaert & F. Govaert, ProcAcadSciAmsterdam **42**, 776 (1939) & CA **34**, 5414 (1940)

Pentaerythrityltetrakis(dichloramine) [N,N,N′,N′-Tetrachloro-2,2-bis(dichloraminomethyl)-1,3-propanediamine (name preferred by CA)]. $C_5H_8Cl_8N_4$, mw 407.87, N 13.7%, OB to CO_2 & HCl −39.2%; a solid, mp 54.0–4.5°; prepd by



the action of Cl (from NaOCl) on $(PhCH{:}NCH_2)_4C$. It decomps on standing above −15°, and the authors report it to be a powerful expl more sens than MF

Refs: 1) Beil, not found 2) E. Gryszkiewicz-Trochinowski et al, MP **40**, 109 (1958) & CA **55**, 2527 (1961)

Pentaerythrityltetrakis(nitramine) [Tetrakis(nitraminomethyl)methane, PETX]. $C_5H_{12}N_8O_8$, mw 312.20, N 35.9%, OB to CO_2 −61.5%; colorl cryst,

mp 175° with decompn (Ref 4). It is prepd by the action of aq ammonia on $(EtOOCCNO_2CH_2)_4C$ in w on a steam bath, yield 88% (Ref 4)

Explosive Properties.

Explosion Temperature. Deflagrates at 295° (Ref 2)

Heat Test at 120°. At 30 hours there was 32.4% wt loss and 35.6% decompn (Ref 3)

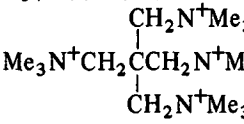
Impact Sensitivity. Using the Bruceton No 3 app & a 5kg wt, 27cm for 50% explns was obtained (RDX 48–50cm) (Ref 2)

International Heat Test at 75°. A zero wt loss was noted (Ref 2)

Power by Ballistic Mortar. 129% of TNT (Ref 2)

Thermal Stability at 100°. No acid fumes in 300 min (Ref 2); at 135° ignited in 240 min (Ref 2)
Vacuum Stability at 100°. 10.20cc of gas were evolved in 48 hours (Ref 2)
Refs: 1) Beil, not found 2) R. McGill, "Preparation and Properties of Explosives" in "Preparation and Testing of Explosives" NDRC, OSRD Div 8 Interim Report **PT-9** (15 Apr–15 May 1943), table betw pp 29 & 30 3) H. Henkin, "Stability of Ethylenedinitramine (Haleite) and Related Nitramines", OSRD **1743** (Aug 1943), 25 4) A.T. Bloomquist, "Certain Aliphatic Nitramines and Related Compounds", OSRD **4134** (Nov 1944), 91

Pentaerythrityltetrakis(trimethylammonium Bromide) ([2,2-Bis(dimethylaminomethyl)trimethylene] bis[trimethylammonium Bromide], Dimethobromide [name preferred by CA]). $C_{17}H_{44}Br_4N_4$, mw 624.18; prepd by heating

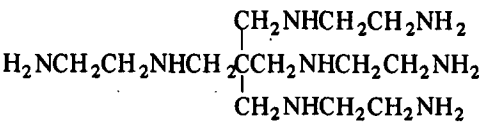


in a sealed tube a mixt of PE tetrabromide and trimethylamine in 95% Et alc for 18 hours at 230°, yield 72% (Refs 1 & 3)

Tetraperchlorate. $C_{17}H_{44}N_4^{+4}.4ClO_4^-$, mw 560.55, N 10.0%, OB to CO_2 & HCl –108.4%; crysts from dil perchloric ac, decomps explosively at 380° (Refs 1 & 3)

Tetrapicrate. $C_{17}H_{44}N_4^{+4}.4C_6H_2N_3O_7^-$, mw 1217.0, N 18.4%, OB to CO_2 –105.2%; yel crysts, mp 310° with decompn (Refs 2 & 3)
Refs: 1) Beil **4**, {634} 2) Beil **6**, {942} 3) F. Govaert & J. Cazier, NatuurwTijdschr **23**, 149 (1942) & CA **37**, 6245 (1943)

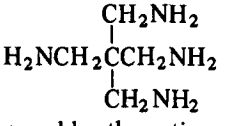
Pentaerythrityltetrakis(2-aminoethylamine) [N,N'-Bis(2-aminoethyl)-2,2-bis(2-aminoethylamino)methyl-1,3-propanediamine (name preferred by CA)]. $C_{13}H_{36}N_8$, mw 304.48, N 36.8%; a light yel oil, bp 265–75° at 18mm;



prepd by the action of an excess of ethylenediamine on PE tetrabromide and obtained as a hydrate (Refs 1 & 3)

Octapicrate. $C_{13}H_{36}N_8.8C_6H_3N_3O_7$, mw 2137.4, N 36.8%, OB to CO_2 –71.9%; a yel amorphous solid; mp, softens and decomps betw 120 and 160° (Refs 2 & 3)
Refs: 1) Beil **4**, {635} 2) Beil **6**, {942} 3) J. vanAlphen, Rec **57**, 265 (1938) & CA **32**, 4546 (1938)

Tetramines. Pentaerythrityltetramine[2,2-Bis(aminomethyl)-1,3-propanediamine (name preferred by CA)]. $C_5H_{16}N_4$, mw 132.19. It is



prepd by the action of ammonia in Et alc on PE tetrabromide (Refs 1, 3 & 5), or better by the action of p-toluenesulfonamide on the same bromide followed by hydrolysis of the tetrasulfonate (Ref 4)

Tetranitrate. $C_5H_{16}N_4.4HNO_3$, mw 384.26, N 29.2%, OB to CO_2 –50.0%; ndls, mp 220–2° with decompn, decomps explosively on rapid heating (Refs 1 & 7)

Tetranitroform Salt. $C_5H_{16}N_4.4HC(NO_2)_3$, mw 736.35, N 30.4%, OB to CO_2 –8.7%. It is prepd by the action of nitroform on the amine in 20% aq Et alc. The differential thermal analysis (DTA) thermogram shows a decompn exotherm at 90° (Ref 6)

Tetraperchlorate. $C_5H_{16}N_4.4HClO_4$, mw 534.03, N 10.5%, OB to CO & HCl –6.0%. It is prepd by the action of aq perchloric ac on the tetramine in w. The DTA thermogram shows no mp, but a decompn exotherm at 246.5° (Ref 6)

Tetrapicrate. $C_5H_{16}N_4.4C_6H_3N_3O_7$, mw 1048.6, N 21.4%, OB to CO_2 –50.0%; ndls, prepd by the action of excess Na picrate on the

amine in w and isolated as a hydrate which can be dehydrated in vacuo; mp of hydrate 196–7° with decompn (Refs 2 & 4), of the anhydrous salt 206–8° (Ref 5)

Written by **C. H. McDONNELL**

Refs: 1) Beil **4**, {633} 2) Beil **6**, {942} 3) F.J. Govaert, ProcAcadSciAmsterdam **37**, 156 (1934) & CA **28**, 4038 (1934) 4) A. Litherland & F.G. Mann, JCS **1938**, 1588 5) J. vanAlphen, Rec **57**, 267 (1938) & CA **32**, 4546 (1938) 6) C.J. Barnes & A.J. Matuszko, "Amine Salts", **NPP TR 128; NavWeps 8028** (May 1963), AD 415706 7) L.J. Zompa & R.F. Bogucki, JACS **88**, 5186 (1966)

Pentaglycerol. See M116-R & M120-R in this Vol

Pentaglycerin Trinitramine. See M117-L in this Vol

Pentaglycerin Trinitrate. See M117-L & M120-R in this Vol

Pentaglycol. See Vol **5**, D1357-R

Pentaglycol Dinitramine. See Vol **5**, D1369-R

Pentaglycol Dinitrate. See Vol **5**, D1358-L

n-Pentane. $CH_3(CH_2)_3CH_3$; mw 72.15; colorl liq; mp −129.72°; bp 36.07°; d 0.6262g/cc at 20/4°; RI 1.35748. Sol in acet, benz, chlf, ethanol, eth and heptane. V sl sol in w. The compd was first isolated in 1863 by Pelouze and Cahors from American petroleum. Synthetic prepn is by treating 1,4-dibromopentane with Zn dust in 75% ethanol (Ref 2); however, the usual commercial method is by fractional distn of petroleum followed by purification by rectification (Ref 4). Lab prepn consists of redn of an alkyl halide such as 2-bromopentane with Mg in an acid medium (Refs 5 & 21)

n-Pentane has a Q_c of 19339Btu/lb; its deton limits and initiation temp in chlorine are 2.42–.43% and 20–2°, in oxygen 1.4–8.0% and 20–2°; a closed cup flash pt of −49°; an ign temp of 330°; and a visc of 0.279 centipoises at 0° (Refs 7–12 & 14–20)

Toxicity. Max allowable concn for an 8 hr exposure is 1000ppm or 2950mgs/cm of air. Higher concns produce a narcotic effect and eventual asphyxia (Refs 16a & 22)

Uses. n-Pentane has found use as an anesthetic; an expl suppressant when mixed with a halogenated hydrocarbon and included in aircraft fuel (Ref 13); a jet engine fuel (Ref 16a); as a base for synthetic rubbers and plastics; a parent compd for the formation of nitropentanes and azido nitro pentanes used as expls and proplnts (Refs 15a, 15b & 21a); also, as a parent compd for fluorine-contg resin binders which impart both thermal stability and, in conjunction with metal hydrides, high impulse to solid proplnts (Ref 15b)

Refs: 1) Beil **1**, 130, (42, 50), [92] & {238} 2) O. Filipov, JPraktChem **93**, 178 (1916) & CA **9**, 1904 (1916) 3) R.P. Anderson & A.M. Erskine, IEC **16**, 263 (1924) & CA **18**, 1048 (1924) 4) G.G. Brown & A.R. Carr, IEC **18**, 720 (1926) & CA **20**, 2742 (1926) 5) C.S. Marvel, Ed, "Organic Synthesis", **11**, 84 (1931) 6) J. Powling, Fuel **28** (2), 25–8 (1949) & CA **43**, 2404 (1949) 7) A. Yoffe, ProcRoySoc **A198**, 373–88 (1949) & CA **44**, 2243 (1950) 8) H. Titman & J. Haig, **Research Rept No 11**, MinFuelandPower(Brit) (1950) & CA **45**, 2647 (1951) 9) P. Dugieux & E. Fréling, CR **238**, 349–50 (1954) & CA **48**, 6123 (1954) 10) Ya.B. Zel'dovich et al, ZhurTekhFiz **26**, 1744–68 (1956) & CA **51**, 10908 (1957) 11) A. Pilc, PrzemystChem **35**, 433–42 (1956) & CA **53**, 3695 (1959) 12) M. Lucquin, JChimPhys **55**, 827–36 (1958) & CA **53**, 19534 (1959) 13) W.G. Glendinning, USP 2921897 (1960) & CA **54**, 14690 (1960) 14) J.H. Burgoyne & M.J.G. Wilson, ProcSympChem Process Hazards, Spec Refs Plant Design, Engl, 25–9 (1960) & CA **54**, 10035 (1960) 15) D.J. Rasbash & Z.W. Rogowski, CombFlame **4**, 301–12 (1960) & CA **55**, 5908 (1961) 15a) H. Feuer, "Research In Nitromonomers and Their Application to Solid Smokeless Propellants", Purdue Res Found, Lafayette (1962) 15b) R.L. Johnson, "Propulsion Research Program, Synthesis and Evaluation of Polyfunctional Fluorocarbon and

N- Fluoro Compounds", **TDR62-16**, Aerospace Corp, El Segundo, Contract AF 04 647930 (1962) 16) G.F.P. Harris & P.G. Briscoe, CombustFlame **11** (4), 329–38 (1967) & CA **67**, 83540 (1967) 16a) Kirk & Othmer **14** (1967), 707–16 16b) Urbański **3**, (1967), 296 17) M. Gros et al, SympCombust **11**, 1107–14 (1966) & CA **68**, 51471 (1968) 18) R. Vandamme et al, BullFr **1970** (4), 1290–6 (1970) & CA **73**, 37079 (1970) 19) V.M. Berry & B.H. Sage, "Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures: n-Pentane and Methane-m-Pentane", **NSRDS-NBS 32** (1970) 20) A.S. Mal'tseva et al, KhimProm(Russ) **47** (1), 33–5 (1971) & CA **74**, 128323 (1971) 21) A. Zlatkis et al, "A Concise Introduction to Organic Chemistry", McGraw-Hill, NY (1973), 24–52 21a) L.P. Kuhn & A.C. Duckworth, "The Preparation of Some New Polyfunctional Organic Azides–Part II", **BRL-MR-2384** (1974) 22) Sax (1975), 998 23) ChemRubHdb (1975), C-407 24) J.D. Macewen & E.H. Vernot, "Toxic Hazards Research Unit Annual Technical Report: 1975", **AMRL TR-75-57**, Cal Univ Irvine, Contract F33615-73-C-4059 (1975)

3,3-Diazido-2,4-Dinitratopentane. $CH_3.CHONO_2.C(N_3)_2.CHONO_2.CH_3$, mw 276.24; N 40.58%; OB to CO_2 –46.34%; white cryst; mp 64–6°, bp 135° (decompn); sol in benz and eth. Prepn is by first mixing acetic anhyd (10.68cc) at 0–5° with 100% nitric acid (4.56cc) by dropwise addn of the acid. Solid diazidopentadiol (4.2g) is then added over a period of 20 min while maintaining the temp at 5–15°. Crystn occurs after 30 min of stirring. Pptn is completed by drowning the react mixt in ice-w. The prod is extrd with eth and recryst from hexane. The yield is 85%

The diazido compd can be detond by friction. It has an expl temp of 165°; a Q_c of 825.4 (avg) kcal/mole; a Q_f of 78.9kcal/mole; and an impact sensy of 5.7cm using a 2kg wt and an Aberdeen Impact app with No 12 tools (vs 26.7cm for PETN). Theoretical calcns using the TIGER computer code detd the flame temp (3120°K), force (4.46 inch-lbs/b) and chamber press (39800 psi) of M-2 proplnt when the diazide was substituted for NG in the formulation, (19.34%).

Another suggested application for the diazido nitrato compd is that of a combustible percussion primer for caseless ammo

Ref: L.P. Kuhn & A.C. Duckworth, "The Preparation of Some New Polyfunctional Organic Azides", **BRL Rept 1607** (1972)

Mononitropentanes, $C_5H_{11}NO_2$. The only compd of expl interest here is 2-Nitropropane which can be used as a rocket fuel constituent (Ref 3):

2-Nitropentane. $CH_3.CHNO_2.CH_2.CH_2.CH_3$, mw 117.18, N 13.60%, OB to CO_2 –184.33%, colorl oil, bp 148–50°, d 0.938g/cc at 25/4°, RI 1.4092 at 25°. Sol in aq NaOH. Prepn is by reacting at 0° with stirring an ethereal soln of 2-nitroprop-1-ene with ethylmagnesium bromide, which is added v slowly. An additional hr of stirring at 20° is reqd to complete the reaction. Subsequent decompn of the Mg complex is obtd by cautious addn of aq acet acid. The compd is purified by steam distn, washing with aq sodium hydrogen sulfite, drying, and then fractionization

Refs: 1) Beil **1**, {350} & ⟨318⟩ 2) G.D. Buckley & E. Ellery, JCS **1947** (290), 1497 (1947) & CA **41**, 1232 (1947) 3) Urbański **3** (1967), 296

Dinitropentanes. $C_5H_{10}(NO_2)_2$, mw 162.15, N 17.21%, OB to CO_2 –108.5%. There is only one compd that is of expl interest here.

1,5-Dinitropentane. $O_2N.CH_2.CH_2.CH_2.CH_2.NO_2$, colorl oil, bp 134° at 1.2mm; RI 1.461. Sol in benz. Prepn is by reacting 1,5-diiodopentane with Ag nitrite in eth. Its disodium salt is v sl sol in ethanol, and explds weakly when heated

Refs: 1) Beil **1**, {350} 2) ChemRubHdb (1975), C-409

Alkyl substituted dinitropentanes. There are two such compds of interest:

1,2-Dinitro-2-Methyl-Propane. See Vol **5**, D1391-R and Vol **2**, B368-R where it is described as Dinitro-iso-butane

The Sodium salt of 1,1-Dinitro-2-Methoxy-Pentane. $CH_3.CH_2.CH_2.CH(OCH_3).C.(Na)(NO_2)_2$, mw 142.15, yel ndls, mp, explds. Prepn is by slow (drop by drop) addn of Na methyl alco-

holate (2.3g Na/25cc of methanol) to 9.7g of 1-brom-1-nitro-1-amylene while cooling the reaction vessel with cold w. The salt is recryst from w. The compd explds on heating
Ref: J. Loevenich et al, Ber **63**, 642 (1930) & CA, not found

Polynitropropanes. There are three compds of interest:
(±)-1,1,1,3-Tetranitropentane.
$CH_3.CH_2.CH(NO_2).CH_2.C(NO_2)_3$, mw 252.21, N 22.22%, OB to CO_2 −38.06%, colorl cryst, mp 24.0–0.5°, bp 112° at 0.2mm, d 1.4656 g/cc at 25/4°, RI 1.4712 at 25°. Sol in hexane. It is described in Russ lit as a tautomeric compd obtd from urea dissolved in methanol and reacted with the *aci* form described next. The Tetranitro compd can be detond
1,1-Trinitro-3-*aci*-nitro Pentane.
$CH_3.CH_2.C(:NOOH).CH_2.C(NO_2)_3$; mp 70.5–71° (decompn). Prepd by reacting 2-Nitrobutene-(1) with trinitromethane
Ref: Beil **1**, ⟨319⟩
1,1,1,3,5,5,5-Heptanitropentane.
$(O_2N)C.CH_2.C(NO_2)_2.CH_2.C(NO_2)_3$, mw 387.24, N 25.33%, OB to CO_2 −26.86%, white cryst, mp 104° (decompn), d 1.74g/cc. Sol in acet, eth, chlf, ethanol, dinitrobutyl acrylate and toluene. V sl sol in w. Prepn is by dropwise addn of a cold soln of 7.5g of nitroallyl acetate in 20cc of methanol over a period of 60 mins, to a continuously stirred mixt which is maintained at 0° of 15.1g of nitroform in 150cc of w, using 1 ml of a 20% aq soln of NaOH as the catalyst for the reaction. The prod is first w-washed and then recrystd from 70% nitric acid at 75°. The 66% recryst yield is then dessicator dried

The expl has a Q_c of 1560cal/g (avg) using liq w at 25° as ref, a negligible hygroscopicity; an ign temp of 196°; an impact sensy of 65–70cm at the 50% pt using a BM app with a 2kg wt (PETN ref is 26–8cm); power by BalMort is 143 (150 for RDX ref); power by Trauzl test is 181 (157 for RDX ref); a thermal stability at 65.5° of failure after 25 min using KI-starch indicator paper; a thermal stability at 134.5° of failure after 4 min (charred residue after 5 hrs) using methyl violet indicator paper; a storage stability of several weeks at RT; and a vac stability of 6.1cc of gas/g at 90° in 48 hrs
Ref: L.T. Carleton et al, "Explosives Research", Aerojet Engrg Corp, Calif Report **No 512**, ONR Contract N7onr-46208 (1951), 3, 4, 5 and appendix 1-4

Iso-Pentane or 2-Methylbutane (called Isopentan or Dimethyläthylmethan by Beil).
$(CH_3)_2.CH.CH_2.CH_3$; mw 72.15, colorl liq, mp −159.9°, bp 27.85°, d 0.6201g/cc at 20/4°, RI 1.35370. Sol in ethanol, ether, hydrocarbons and oils, insol in w. First prepd by Frankland in 1850 by treating iso-amyl iodide with Zn in w at 140° (Ref 2). It was isolated by Young from American petroleum (Ref 3). Present methods of prepn include fractional distn of petroleum and subsequent purification of the crude isopentane by rectification, as well as cracking and reforming of crude oil components and natural gasolines in oil refineries (Refs 4 & 7)

Isopentane has expl limits in air of 1.4 to 7.6% and a closed cup flash pt of −51° (Refs 5 & 7). It can be nitrated in the vapor phase, but these derivs have not been used as expls (Refs 1 & 6)
Refs: 1) Beil **1**, 134, 140, 141, (45 & 50), [99 & 104] & {352} 2) E. Frankland, Ann **74**, 53 (1850) 3) S. Young et al, JCS **71**, 442 (1897); Ibid **73**, 906 (1898) 4) R.P. Anderson & A.M. Erskine, IEC **16**, 263 (1924) & CA **18**, 1048 (1924) 5) G.G. Brown & A.R. Carr, IEC **18**, 720 (1926) & CA **20**, 2742 (1926) 6) L.W. Seigle & H.B. Hass, IEC **31**, 648–50 (1939) & CA **34**, 1993 (1940) 7) Kirk & Othmer **14** (1967), 707–16 8) Sax (1968), 849 9) ChemRubHdb (1975), G-213 10) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 455

Pentanitrocellulose. See Vol **2**, C100-R

Pentanitroaniline (PNA). See Vol **1**, A414-L

Pentanitroazobenzene. See Vol **1**, A649

Pentanitrobenzocarbazole. See Vol **2**, B66-R

Pentanitrodiethylenediamine. See Vol **5**, D1247-R

Pentanitrodimethylaminodiphenylamine. See Vol **5**, D1310-L

Pentanitrodimethylaniline. See Vol **5**, D1316-L

Pentanitrodimethyl-m-phenylenediamine. See Vol **5**, D1363-R

Pentanitrodiphenylamine. See Vol **5**, D1434-R

Pentanitrodiphenylethanol. See Vol **5**, D1459-L

Pentanitrodiphenylether. See Vol **5**, D1453-L & R

Pentanitrodiphenylsulfide. See Vol **5**, D1477-R

Pentanitrodiphenylsulfone. See Vol **5**, D1480-L

Pentanitroethylaniline. See Vol **6**, E207-R

Pentanitromethylaniline. See in this Vol, M101-R

Pentanitronaphthol. See this Vol, N20-R

Pentanitrophenylmethylnitramine. See this Vol, M102-R

2-Pentanone (Methyl n-propyl ketone, MPK). $CH_3.\overset{\overset{O}{\|}}{C}.(CH_2)_2.CH_3$; mw 86.13; colorl liq; mp −77.8°; bp 101.7°; d 0.8089g/cc at 20/4°; RI 1.3895. Miscible with acet, benz, CCl_4, eth, heptane, methanol, etc; insol in w. A coml prepn reacts acet with ethylene at 300–50° & ca 140 atms press over Ni oxide as a catalyst. Many other prepns are shown in Beil. MPK has a closed cup flash pt of 7.2°, and the expl limits with air are 1.6 to 8.2% (Ref 5). MPK deton in contact with bromine trifluoride at −15° (Ref 1a)
Refs: 1) Beil **1**, 676, (350), [736], {2799} & ⟨3271⟩ 1a) T.E. Stevens, JOC **26**, 1629 (1961) & CA **55**, 233310 (1961) 2) I. Mellan, "Ketones", Chem-Pub, NY (1968), 78–9 3) Sax (1968), 999 4) ChemRubHdb (1975), C-414 5) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 451

3-Pentanone (Propionone, Diethylketone or DEK). $CH_3.CH_2.\overset{\overset{O}{\|}}{C}.CH_2.CH_3$; mw 86.13; colorl liq; mp −39.8°; bp 101.7°; d 0.8138 g/cc at 20/4°; RI 1.3924. V sol in w; sol in ethanol and acet. Prepn is by the dehydration of 3-pentanol using copper-chromium oxide as a catalyst at 275–300°. Other methods of prepn are listed in Beil. DEK has a lower expl limit of 1.6% in air and a closed cup flash pt of 13° (Ref 3)
Refs: 1) Beil **1**, 679, (351), [738], {2806} &⟨3279⟩ 2) I. Mellan, "Ketones", Chem Pub, NY (1968), 94 3) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 451 4) ChemRubHdb (1975), C-414

Pentastit. Trade name for Swiss military expls prepd by phlegmatizing PETN with pentaerythritol tetrastearate (called pentaerythrit-tetrastearat in Ger). These expls were manufd by the Schweizerische Sprengstoff Fabrik AG at Dottikon, Switzerland

The properties and compns of some Pentastit expls, with and without Al are reported as follows:

	93/7 Pentastit		96.5/3.5 Pentastit	
	100%	20% Al	100%	20% Al
Melting point, °C	137	137	138	138
Explosion temp (20°C/minute, °C	192	190	198	198
Impact sensitivity, 5 kg hammer, cm	30	29	23	22
Density, g/cc	1.56	1.68	1.60	1.67
Velocity of deton, meters/second	8000	7700	8100	7700
Trauzl test value, cc/10g sample	408	467	420	512
Copper cylinder compression test, mm	3.50	3.34	3.63	3.36

Refs: 1) Schweiz Sprengstoff-Fabrik AG, SwissP 220756 (1942) & CA **42**, 6538 (1948) 2) Stettbacher (1948), 67 & 122–3 3) M. Freiwald, Explosivst **6**, 133 (1961)

Pentazenes (Pentazdienes). These are derivatives of a compd contg five nitrogens in an open chain, such as RN:N.NR.N:NR, where R stands for hydrogen, or an alkyl or aryl radical. These compds contain high percentages of nitrogen, and therefore release large volumes of gas on decompn. Listed below are representative examples of those reported to expld on heating, impact or friction.

In naming the derivatives of pentazenes, the numeration of the nitrogens of the open chain is in Roman numerals, I, II, III, IV and V; the numeration of any substituent attached to the nitrogens is in Arabic numerals

I,V-Diphenyl-pentazene. (called 1,5-Diphenyl-pentazdien-(1,4) or Bisdiazobenzolamid by Beilstein). $C_6H_5.N:N.NH.N:N.C_6H_5$, mw 225.25, N 31.09%, yel prisms, mp explds. Was prepd by Griess (Ref 2) by adding a cold satd aq soln of benzenediazonium nitrate to ammonia. Insol in w, sol in alc and eth with decompn. In the dry state, it explds violently when heated, or on impact or friction
Refs: 1) Beil **16**, 753 2) P. Griess, Ann **137**, 81 (1866) 3) H. von Pechmann & L. Frobenius, Ber **27**, 898–9 (1894); **28**, 171 (1895)

[I,III-Diphenyl,V-tolyl] pentazene. [Called 1,3-Diphenyl-p-tolyl-pentazdien-(1,4) or Benzol-diazo-p-toluoldiazoanilin by Beilstein; Diazo-benzol-p-diazotoluolanilid by von Pechmann]. $C_6H_5.N:N.N(C_6H_5).N:N(C_6H_4.CH_3)$, mw 315.37, N 22.21%, yel needles, mp (explds at about 72–73°). Can be prepd from diazoamino-benzene and p-toluenediazonium chloride in the presence of Na methylate in methanol. Insol in w, sol in acet. Explds on heating
Refs: 1) Beil **16**, 754 2) H. von Pechmann & L. Frobenius, Ber **28**, 171 (1895)

[I,V(Di-4-tolyl),3-ethyl] pentazene. [Called 3-Aethyl-1,5-di-p-tolyl-pentazdien-(1,4) or Bis-p-toluoldiazo-äthylamin by Beilstein]. $(CH_3.C_6H_4).N:N.N(C_2H_5).N:N.(C_6H_4.CH_3)$, mw 281.35, N 24.89%, pale yel needles from ligr, mp 121° (with violent evolution of gas). Was prepd from p-toluene diazonium chloride and ethylamine. Easily sol in eth and benz, more difficultly in alc and ligr
Refs: 1) Beil **16**, 754 2) H. Goldschmidt & H. Holm, Ber **21**, 1025 (1888)

[I,V-Di-4-tolyl] pentazene. Called Di-p-tolyl-pentazdien-(1,4) by Beilstein; Bis-p-diazotoluol-amid by von Pechmann). $(CH_3.C_6H_4).N:N.NH.N:N.(C_6H_4.CH_3)$, mw 253.30, N 27.65%, needles, mp (deflagrates at 79–83°). Can be prepd by adding p-toluenediazonium chloride soln dropwise to an excess of ammonia at 0°. Deflagrates when heated; explds on impact or friction

Refs: 1) Beil **16**, 754 2) H. von Pechmann & L. Frobenius, Ber **27**, 899 (1894)

[I & III-Di-4-tolyl, V-phenyl] pentazene. (Called 1-Phenyl-3,5-di-p-tolyl-pentazdien-(1,4) or Benzodiazo-p-toluol-diazo-p-toluidin by Beilstein; Diazobenzol-p-diazotoluoltoluidin (by Pechmann). $(CH_3.C_6H_4).N:N.N(C_6H_4.CH_3)N:N.C_6H_5$, mw 329.39, N 21.26%, yel needles, mp (explds at 76°). Can be prepd by adding a methanolic soln of benzoldiazonium chloride to a methanolic soln of p,p'-diazoaminotoluol (Beil **16**, 709) and Na methylate. Sol in acet. Explds on heating

Refs: 1) Beil **16**, 754 2) H. vonPechmann & L. Frobenius, Ber **28**, 170 (1895)

[I,III,V-Triphenyl] pentazene. (Called 1,3,5-Triphenyl-pentazdien-(1,4) or Bis-benzoldiazoanilin by Beilstein; Bisdiazobenzolanilin or Benzoldiazoanilindiazobenzol by vonPechmann). $C_6H_5.N:N.N(C_6H_5).N:N.C_6H_5$, mw 301.34, N 23.24%, yel leaflets, mp (explds at 80–81°). Can be prepd by treating a methanolic soln of 2 moles of N-nitrosoacetanilide (Beil **12**, 581) with 1 mole of K methylate or ethylate. Difficultly sol in alc and eth, sol in acet, chlf and benz. Explds on heating or light impact

Refs: 1) Beil **16**, 753 2) H. vonPechmann & L. Frobenius, Ber **27**, 703–4 (1894)

[I,III,V-Tri-4-tolyl] pentazene. (Called 1,3,5-Tri-p-tolylpentazdien-(1,4) or Bis-p-toluoldiazo-p-toluidin by Beilstein; Bis-p-diazotoluol-p-toluid by vonPechmann). $(CH_3.C_6H_4).N:N.N(C_6H_4.CH_3).N:N(C_6H_4.CH_3)$, mw 343.42, N 20.39%, yel needles, mp (deflagrates at 88°). Can be prepd by adding methanolic Na methylate to a methanolic soln of p-toluidine, followed by methanolic p-toluenediazonium chloride. Difficultly sol in alc, eth or ligr; easily sol in chlf and benz. Explds on heating or on strong impact

Refs: 1) Beil **16**, 754 2) H. vonPechmann & L. Frobenius, Ber **27**, 705 (1894) 3) E. Bamberger, Ber **27**, 2597 (1894)

Pentek. A proprietary trade name for a mixt of approx 88% pentaerythritol (PE) and 12% related polyhydric alcohols, mostly dipentaerythritol (DPE). It is prepd in the same manner as PE, starting with acetaldehyde, formaldehyde and alkali, except that the purification procedure is more simple. This mixt has found extensive use in the protective coating industry and in the manuf of synthetic drying oils. It can also be used (price permitting) for the prepn of a commercial expl which would consist chiefly of Pentaerythritol tetranitrate (PETN), the balance being Dipentaerythritol hexanitrate (DPEHN), Tripentaerythritol octanitrate (TPEON), Tetrapentaerythritol decanitrate (TePEDeN), nitrated formals of PE, etc

Ref: T.M. O'Neil, PaintIndMag **62**, 370–84 (1947) & CA **42**, 1065 (1948) (Correction in CA **42**, 5686 (1948))

Penthrinits (Swiss). See Vol **3**, C443-R and Vol **6**, G51-L & 52 (Table G17)

Pentrite, Pentrit. Same as Pentaerythritol Tetranitrate (PETN)

Pentofive. Expl contg PETN 50, Fivonite 50% (see Vol **6**, F41)

Ref: D.P. MacDougall et al, OSRD **5744**, **5745** & **5746** (1945)

PENTOLITES

Pentolites are castable expl mixts containing PETN and TNT. The most commonly used blend consists of 50/50 PETN/TNT, but other blends such as 75/25, 40/60, 30/70 and 10/90 have been occasionally employed. Molten TNT dissolves appreciable amounts of PETN as shown in Fig 1. The eutectic in the TNT-PETN system occurs at 76.7° for a 87/13 TNT/PETN mixt. Because correspondingly more PETN than RDX dissolves in TNT, the viscosity of Pentolites at casting temperatures is less than that of comparable Cyclotols (RDX/TNT blends)

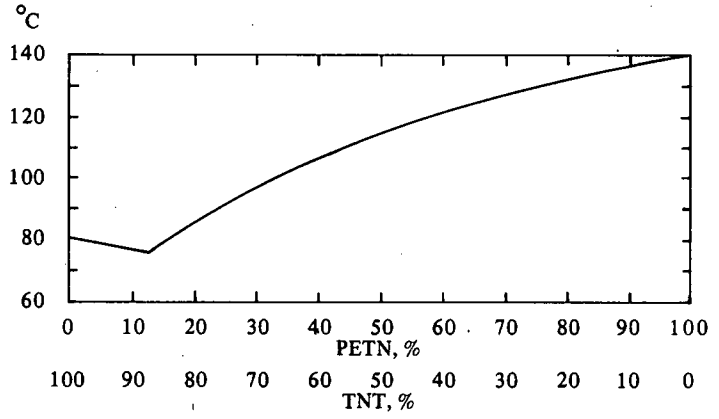


Fig 1 PETN and TNT System Melting Points (Ref 1)

The cast density of Pentolites does not vary appreciably with blend compn. 50/50 Pentolite (hereafter to be referred to simply as Pentolite) has a cast density of 1.63–1.67g/cc (Ref 8a), while 10/90 Pentolite has a cast density of 1.60 g/cc (Ref 12). The density of pressed Pentolite lies between 1.60 and 1.65g/cc. Since Pentolites are blends (no compound formation) they are soluble in the same solvents as their constituents (PETN & TNT). Pentolite has a compressive strength of 2000–2200psi at 1.68g/cc (Ref 12)

Boyle et al (Ref 7b) give a Hugoniot for "unreacted" Pentolite of 1.67g/cc in the form of U=2.83+1.91u where U is the shock velocity and u is the particle velocity

Uses. During WWII cast Pentolite was used as the main charge in hand and anti-tank grenades and as a pressed charge in some detonators (Ref 8a). Currently it still finds limited use in boosters and primer charges in commercial blasting

Casting is usually accomplished at around 90°. Constant stirring is required to keep the PETN suspended as only about 20% PETN dissolves at this temp. It is desirable to use small elongated PETN crystals to minimize settling of the PETN, thus preventing the production of non-uniform charges. W.O. Williamson (Ref 4) claims that in 50/50 Pentolites cast at 90–4°, PETN crystals retain their original shape characteristics, since little soln occurs at such temps. These crystals were enclosed by cryst TNT. Added wax caused no obvious changes in the microstructures, and at least some persisted as segregations. Microstructures resembled those of TNT

Pressing. The same methods as used in the press-loading of *Amatols* (see Vol **1**, A160–61) can be used for Pentolites

Specification. **JAN-P-408** (1946) contains the following general requirements for Pentolite: Volatile matter: 0.5% max; Composition: 50 ± 2% TNT; Total acetone insol: 0.04% max: Inorganic acetone insol: 0.02% max; Acidity or Alkalinity: 0.005% max; Grit: non; PETN granulation: thru No 30 sieve, 95% min; thru No 200 sieve 30% max; and Stability: not more than 5ml of gas in 100° heat test

Preparation. Two methods have been used in large scale Pentolite production. In the more modern *slurry* method, PETN in water is stirred and heated above 80°, and then TNT is added. The molten TNT coats the PETN particles. The resulting slurry is cooled under rapid stirring, and the separated granules are filtered out and dried at below 75°. In the *coprecipitation* method, PETN and TNT are dissolved separately in acet and the solns are then mixed. The Pentolite is pptd by pouring the mixed solns into cold water using vigorous agitation. After filtering, the Pentolite is air dried (Ref 12). The slurry method permits better particle size control than the coprecipitation method. It is also more economical of acet (acet is used in the slurry method for obtaining PETN of the desired particle size), and takes less time per complete production cycle

Explosive Properties (50/50 blend). Ref 12

gives the following expl properties for Pentolite: OB to CO_2 −42%; Detonation velocity 7465 m/sec at d 1.66g/cc in one-inch diameter; Ballistic mortar 126% TNT; Trauzl test 122% TNT; Impact sensitivity (2kg wt) 34cm in BuMine App and 12 inches in PicArsn App; Friction pendulum – unaffected; Explosion temp 0.1 sec at 290° and 1 sec at 266°

Dobratz (Ref 13) summarizes other Pentolite properties as follows: Detonation Velocity (D) = 7470m/sec at d 1.67g/cc, and $\Delta D/\Delta T = -0.4 \times 10^{-3}$ (mm/microsec °C); Small scale LASL gap test (50% thickness for brass spacers), 105–140 mils at 1.68g/cc and 32–38 mils at 1.70g/cc; Measured ΔH_{det} = 1.23kcal/g and ΔH_f° = −23.4kcal/mole; Calc ΔH_{det} = 1.41kcal/g; Theoretical max density, 1.71g/cc; Vapor press, 0.1 mm Hg at 100°C

Cook (Ref 4a, pp 45 and 48) gives the variation of D with packing density ρ as: D = 5480 + 3100 (ρ−1.0) in m/sec, and shows that "ideal" D is attained for one-inch diameter charges

Jameson & Hawkins give the CJ pressure of Pentolite as 245 ± 10kbar (Ref 10a)

Shear (Ref 6) quotes an exptl CJ pressure, obtained by Gehring & Dewey, of 237kbar, and D = 7620m/sec at d 1.66g/cc

Figures 2 and 3 show Urbański's data (Ref 1) for the expln properties of low density Pentolite charges as a function of the PETN/TNT compn

Dobratz (Ref 13) lists a computed CJ pressure of 250kbar at d 1.66g/cc and a polytropic exponent (Γ) of 2.73. Theoretical computations by Shear (Ref 6) give CJ pressure (232kbar), detonation product compn, and isentropic expansion for Pentolite

Macek (Ref 5) used Pentolite (and DINA) to study the transition from deflagration to detonation (DDT). He found that in Pentolite, heavily confined and ignited by a hot wire, a low-velocity regime (1–2mm/microsec) precedes steady detonation for 30–80microsec. Compression waves precede the burning front in this pre-detonation region and appear to coalesce into a shock wave

Obmenin et al (Ref 10b) found LVD (low velocity detonation) at 1000–2000m/sec in cast Pentolite enclosed in 5mm ID steel tubes whose wall thickness was varied from 1.3 to 17mm. LVD was initiated by an igniter pin at the closed end of the tube and propagated for about 15 to

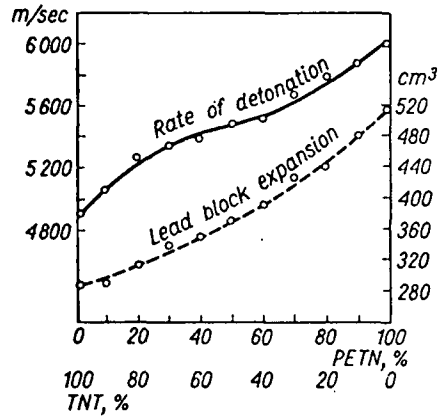


Fig 2 The relation between the rate of detonation (density 1.04) and lead block expansion of mixtures of PETN and TNT, and their composition (according to T. Urbański) (Ref 1)

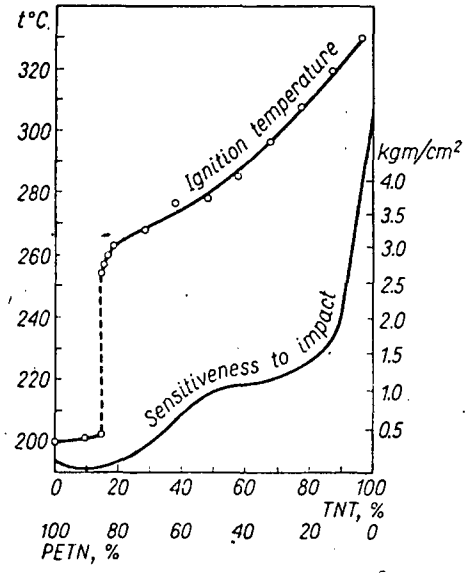


Fig 3 The relation between the ignition temperature and sensitiveness to impact of mixtures of PETN and TNT, and their composition (according to T. Urbański) (Ref 1)

40 charge diameters. Tube-wall thickness increased the LVD value up to a wall thickness of 8mm. Above 8mm, LVD was independent of tube thickness

Urakawa and Masutomi (Ref 8b) studied the heat stability of Pentolite using gas chromato-

graphy and DTA. Slow decompn starts at 110° and is followed by the main pyrolysis reactions which generate NO_2 rapidly. The rate of pyrolysis of the mixt (ie, the Pentolite) is faster than that of either TNT or PETN

Pentolite at d 1.56g/cc is used as the standard donor charge in the NOL "Large Scale Gap Test" (Ref 10)

Pentolite is also used as a standard charge for both air blast and underwater blast measurements. Extensive air blast measurements using Pentolite were made by Stoner & Bleakney (Ref 3). Theoretical air blast computations for Pentolite (and TNT) have been given by Shear & Wright (Ref 7) and by Shear (Ref 7a)

Underwater blast effects for Pentolite are given by Cole (Ref 2). Recent peak pressure measurements (Ref 9) confirm Cole's results. Cole (Ref 2) gives the following equations for the underwater shock effects of Pentolite at d 1.6 g/cc:

Peak pressure $= 2.25 \times 10^4 (W^{1/3}/R)^{1.13}$ psi

Impulse $= 2.18\, W^{1/3}(W^{1/3}/R)^{1.05}$ psi-sec

Energy $= 3.27 \times 10^3 W^{1/3}(W^{1/3}/R)^{2.12}$ inch-lb/inch^2

where W is the charge weight in lbs and R is the distance, in feet, from the center of a spherical charge

Orlenko & Parshev have computed the ratio of underwater shock energy of Pentolite to its total chemical energy to be 0.57 to 0.59 (Ref 8)

Nomograms for obtaining both air and underwater blast effects for Pentolite (and other explosives) are given in **Navord 2986** (1955)

Sternberg & Walker (Ref 11) calcd the flow following the detonation of a centrally initiated Pentolite sphere in fresh water at sea level, up to the time the main shock in the water is 100 charge radii from the center. Pressure, particle velocity, and temp vs distance at various times are obtained; also peak pressures, time constants, and pressure vs time at fixed positions. Partial steam formation in the water close to the gas bubble is shown to be possible but unimportant at the distances covered. The partition and distribution of kinetic and internal energies in the water and the gas sphere, and the energy dissipated by shock heating are found. The calcd dissipated energy is 33% of the total energy released in the detonation when the shock front is 10 charge radii from the center, and 40.5% when the distance is 100 charge radii

Written by **J. ROTH**

Refs: 1) T. Urbański, MF **20**, 237 (1946); CA not found 2) R. Cole, "Underwater Explosions", Princeton Univ Press, Princeton, NJ (1948) 3) R.G. Stoner & W.J. Bleakney, JApplPhys **19**, 670 (1948) 4) W.O. Williamson, JApplChem(London) **8**, 661 (1958) & CA **53**, 8627 (1959) 4a) Cook (1958) 5) A. Macek, 8th SympCombust, 847 (1960) & CA **57**, 6198 (1962) 6) R.E. Shear, **BRL 1159** (1961) 7) R.E. Shear & E.Q. Wright, **NASA Doc N 62-17060** (1962) & CA **60**, 10467 (1964), and R.E. Shear **BRL 1262** (1964) 7a) R.E. Shear, US ArmyDeptSciConfProc **2**, 391 (1965) & CA **66**, 4564 (1967) 7b) V.M. Boyle et al, 4th SympDet (1965), 245 8) L.P. Orlenko & L.P. Parshev, ZhPriklMekhiTekhnFiz **5**, 130 (1965) & CA **64**, 3274 (1966) 8a) Urbański **3** (1967) 249–53 8b) T. Urukawa & Sh. Masutomi, KogyoKayakuKyokaishi **28**, 132 (1968) & CA **68**, 14607 (1968) 9) T. Kazumi et al, KygyoKayaku **30**, 233 (1969) & CA **78**, 6083 (1973) 10) D. Price, **NOLTR 70-25** (1970) 10a) R.L. Jameson & A. Hawkins, 5thSympDet (1970), 23 10b) A.V. Obmenin et al, FizGoreniyaVzryva **6**, 571 (1970) & CA **75**, 89727 (1971) 11) H.M. Sternberg & W.A. Walker, PhysFluids **14**, 1869 (1971) & CA **75**, 111351 (1971) 12) Anon, "Explosives Series, Properties of Explosives of Military Interest", EngrDesHndb, **AMCP 706-177** (1971), 273–5 13) B.M. Dobratz, "Properties of Chemical Explosives & Explosive Simulants", **UCRL-51319**, Rev 1 (1974)

Pentonal. Expl contg PETN 47, TNT 33 & Al powder 20%
Ref: D.P. MacDougall, OSRD **5744**, OSRD **5745** (1945)

Pentralite or Tetralite. Same as Pentanitromethylaniline (See in this Vol, M101-R to M102-L)

Pentrinits. Same as Penthrinits

Pentrit or Pentrit (Swiss). Same as Pentaerythritol Tetranitrate (PETN)

Pentritol (Ger). Same as Pentolite, according to Stettbacher, NC **11**, 63–7 (1940)

Pentryl. Same as 2-(2′,4′,6′-Trinitro-n-nitranilino)-ethanol nitrate. See Vol **1**, A425-L to A429-R

Pentryl and Pentro. Trade names for Swiss military expls contg mixts of PETN and TNT in various proportions. They are prepd by dissolving PETN and TNT in acetone and precipitating them with water. They are manufd by the Schwazerische Sprengstoff-Fabrik AG, Dottikon, Switzerland

The properties & compns of some Pentryl expls, with and without Al, are reported as below

Note: 70/30 Pentryl contains 70% PETN and 30% TNT. See also under Swiss Commercial Explosives of Nonpermissible Type in Vol **3**, C443-R

Refs: 1) Stettbacher (1948), 123 2) B.T. Fedoroff, private communication with A. Stettbacher, Dec 14, 1953

Pentyl. Swedish name coined by the Bofors Co in the 1930's for PETN, because the Ger name "Nitropenta" used at that time was not considered suitable

Ref: B.T. Fedoroff, Private communication with C.M. vonArbin of the Bofors Co (March 6, 1963)

Pentyl azide. See under Amylazide in Vol **1**, A395-R to A396-L

Pentyl nitrate. See under Amyl nitrate in Vol **1**, A397-L

PEP-3. One of the US plastic high expls developed during WWII, consisting of PETN 86 and Gulf Crown E Oil 14%. Its sensitivity, stability and performance properties are detailed below:

Density, g/cc.	1.47
Explosion Temp, °C.	257
Impact Test, 2kg wt.	
BM App, cm	92
PicArsn App, inches	10–12
Ballistic Mortar Test, TNT equiv.	118
Hygroscopicity (90% RH, 30°).	
% Gain in wt in 200 hours	0.04
Pendulum Friction Test, Steel Shoe.	
Number of trials	10
Unaffected	10
Plate Dent Test.	
Block (Engineer Corps Special Blasting Cap used for initiation), dent, inches	0.109
Cylinder (35g Tetryl Booster plus Engineer Corps Special Blasting Cap used for initiation), dent, inches	0.215
Rate of Detonation, m/sec.	7780 (d 1.47g/cc)
TNT at d 1.60g/cc	6795

	70/30 Pentryl		60/40 Pentryl		50/50 Pentryl	
	100%	15% Al	100%	15% Al	100%	15% Al
Melting point, °C	70-130	70-130	70-125	70-125	70-120	70-120
Explosion temp (20°C/minute), °C	202	202	200	200	200	190
Impact sensitivity, 5-kg hammer, cm	23	22	24	22	25	24
Density, g/cc	1.58	1.65	1.56	1.68	1.55	1.62
Velocity of detonation, meters/second	7800	7400	7600	7200	7450	7000
Trauzl test value, cc/10g sample	394	498	370	490	362	450
Copper cylinder compression test, mm	3.48	3.49	3.39	3.38	3.24	3.38

Rifle Bullet Impact Test.

Number Trials	5
Partial Detonation	0
Burned	0
Unaffected	5

100° Heat Test.

% Loss in 1st 48 hrs	0.06
% Loss in 2nd 48 hrs	none
Explosion in 100 hrs	none

Sand Test.

Sand Crushed, g (TNT=44.1)	46.8

100° Vacuum Stability Test.

CC gas in 40 hrs	0.32–0.48

120° Vacuum Stability Test.

CC gas in 40 hrs	11+

PEP-3 did not possess the important property of remaining essentially unchanged in physical characteristics over a −65°F to +169°F temp range. It did not remain plastic at −65°F, and exuded badly at only slightly elevated temps. The residue left by this exudation was markedly more sensitive than the original expl. It was concluded that plastic expl PEP-3 did not have sufficiently promising characteristics to warrant attempted improvement by modification (Ref 1)
Refs: 1) S. Livingston & S. Fleischnick, PATR **1695** (1948) 2) L.H. Eriksen & R.C. Grass, PATR **1713** (1949)

Pepperbox. A firearm with a cluster of barrels, often a revolver, each barrel of which fires separately. Some weapons with fixed barrels and rotating hammers may also be classed as pepperboxes
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 345

Pepper Pot. An Allied WWII term for coordinated fire, sweeping enemy front lines at relatively short range. Such fire would include all available tank guns, anti-tank guns, light anti-aircraft guns, medium machine guns, and heavy mortars
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 345

Peracids, Organic (Peroxy Acids). See Peroxides, Organic of Structure RC(:O)OOH

Perafex. An Allied mechanical deception device produced during WWII. They would be dropped from the air and, on hitting the ground, would imitate the sound of rifle fire and the expln of hand grenades
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 345

Peragon. See under Paragon in this Vol

Peralite. Large grain proplnt contg K nitrate 63, charcoal 30 and Sb sulfide 7%
Ref: Daniel (1902), 604

Perammons. See under Parammons in this Vol
Percarbonates. Salts of the hypothetical percarbonic acid, $H_2C_2O_6$, contg the $C_2O_6^{-2}$ radical, some of which are expl. Guided by analogy with persulfates, Constam and von Hansen (Refs 1 & 2) prepd several percarbonates by electrolysis of aq solns of corresponding carbonates, maintained at low temp. For details of the procedure, see Mellor (Ref 2)
Note: According to Mellor (Ref 2, p 86), A. Bach claimed that percarbonic acid can exist in cold ethereal soln. When such a soln was treated with an alc KOH soln, a bluish-white ppt of K percarbonate was formed. Of the percarbonates, the K salt is the easiest to prepare and is available commercially (see below)
Refs: 1) E.J. Constam & A. von Hansen, Zeit-Electrochem **3**, 137 (1897) & GerP 91612 (1896) 2) Mellor **6** (1925), 82–87 3) Hackh's (1972), 498-L

Potassium Percarbonate. $K_2C_2O_6.H_2O$, mw 216.23; white, granular mass; mp 200–300°. Was first prepd in 1896 by E.J. Constam & A. von Hansen (Ref 2, p 85) by the electrolysis of a concd aq soln of K carbonate, cooled to −15°. A more modern prepn of practically anhydr compd is reported by Partington et al (Ref 3)

K percarbonate is sparingly sol in alc; it dissolves in ice cold w almost without decompn, but at RT and higher, it decomps with the evolution of H_2

A percarbonate possesses, according to Daniel (Ref 1), some expl properties because it can be detonated if a sufficiently powerful detonator is used. According to Mellor (Ref 2, p 86), a violent reaction took place when a soln of 0.5g of solid phosphoric acid, some ether, and a few drops of w were added to 2g of K percarbonate. It was used by Turpin in Fr in expl mixts, ie, "Pyrodialytes" (qv) (Ref 1)

K percarbonate is highly toxic, and a strong irritant to tissue. It is also a fire risk in contact with organic materials (Refs 4 & 5)

Refs: 1) Daniel (1902), 778 (under Turpin) 2) Mellor **6** (1925), 82–87 3) J.R. Partington et al, JChemSoc **1950**, 1934 4) Merck (1968), 856-L 5) CondChemDict (1971), 724-L 6) Hackh's (1972), 541-L

Perchlorates. See under Perchloric Acid and Perchlorates

Perchloratits or Perchloratites. Industrial blasting expls, based on perchlorates, used in Ger before and after WWI. Naoûm (Refs 1 & 2) lists the compns shown in Table 1:

Table 1

Ingredients:	Composition, %		
	1	2	3
K perchlorate, of which up to 10% of the total expl may be replaced with Am nitrate and/or K nitrate	60-75	62-75	-
K and/or Am perchlorate	-	-	30-40
Am nitrate	-	-	35-45
Note: When Am perchlorate is incorporated some of the Am nitrate is replaced by K nitrate in an amt chemically equiv to the amount of Am perchlorate.			
Vegetable meal	1-5	-	-
Vegetable meal and/or solid hydrocarbon	-	1-8	3-8
Nitroglycerin (ungelatinized)	3-6	-	-
Nitroderivatives of toluene and/or naphthalene and/or diphenylamine in which up to 4% of the total expl may be substituted with NC	20-30	20-30	15-20

Perchloratminensprengstoffe. A castable perchlorate expl suitable for use in trench mortars (Wurfminen) contg K perchlorate 56, DNB 32 and DNN 12%. It was developed during WWI at Zentralstelle für wissenschaftlichtechnische Untersuchungen in Neubabelsberg, Ger

Note: Davis (Ref 2) refers to this expl as Perdit, but Naoûm and Stettbacher give different formulations for Perdit (qv)

Refs: 1) Naoûm, Expls (1927), 133 2) Davis (1943), 364 3) PATR **2510** (1958), Ger 129-L

Perchloratsprengstoffe (Perchlorate Explosives). Expls based on the perchlorates of Amm, K or Na were used to a limited extent in Ger during WWI, as for example, Parammon, Perchloratite, Perchlorit, Perdit, Perkoronit, etc. According to Davis (Ref 1), the perchlorates recovered from surplus WWI munitions were used in Ger post WWI commercial expls, such as Perchloratit, Perchlorit, Perkoronit and Persalit. When the Stettbacher (Ref 3) details the Perchloratites listed in Table 2:

Table 2

Composition, %	Perchloratites:		
	1	2	3
K perchlorate	68	35	34
Am nitrate	10	42	48
TNT and DNT	-	14	-
DNT	16	-	12
Wood (or vegetable) meal	1	5	6
NG (nitroglycerin)	4	4	-
MNN (mononitronaphthalene)	1	-	-

Refs: 1) Naoûm, Expls (1927), 134 2) Naoûm, NG (1928), 431 3) Stettbacher (1933), 316 4) Pepin-Lehalleur (1935), 347. 5) Vivas, Feigenspan & Ladreda **2** (1946), 348

supply of surplus perchlorates were exhausted, the manuf of perchlorate expls was nearly discontinued because of the high cost of perchlorates from new sources

Refs: 1) Davis (1943), 364 2) PATR **2510** (1958), 129

PERCHLORIC ACID AND PERCHLORATES

Historical Introduction and Perchlorates in General History. The early history of perchlorates and the perchlorate industry has been thoroughly discussed (Refs 12 & 14, p 2), so it will be only briefly reviewed here. Early exptl work on chlorates and perchlorates was closely tied to the discovery and identification of Cl. Several workers, notably Priestly, Lavoisier, and Scheele reported the isolation of volat liqs and gases which probably were oxides or oxyacids of Cl, but they failed to identify and characterize the compds isolated. Scheele, for example, treated muriatic ac (HCl) with Mn dioxide and obtained a volat liq which he called "muriatic ac derived of its phlogiston" (Ref 14, p3). The first perchlorate definitely identified was the K salt which was prepd by Stadion in 1816 by the thermal decompn of K chlorate (Ref 2). From this he prepd a hydrate of perchloric ac by heating the K salt with sulfuric ac (Ref 3). Pure (anhyd) perchloric ac was first prepd by Roscoe in 1862 by distn of the hydrated ac (Ref 4)

At present most perchlorate salts are prepd from Na perchlorate or perchloric ac by exchange or displacement reactions (Ref 13, p4). Na perchlorate is prepd in two steps by the electrolysis of Na chloride; first to Na chlorate, then in a second electrolysis to Na perchlorate (Ref 13, p 4)

General Information Valid for all Perchlorates. In perchloric ac and perchlorates the Cl is in its highest oxidn state. Hence they are good oxidizing agents and have been widely used in the expl, proplnt, and other inds for their oxidizing power. In addn, perchloric ac is a strong ac, pH of a 0.72M soln is 1.02 (Ref 7), and salts have been prepd from most metals as well as inorganic and organic bases (for individual compds see in the text below)

Analytical Procedures (general procedures useful for the analysis of all perchlorates). For a review of procedures used prior to 1953 see Ref 9. 1) *Qualitative.* The presence of the perchlorate ion is best detd qualitatively by the addn of a 0.2% aq soln of methylene blue. A violet ppt forms which, when dried, deflagrates on heating (Ref 5). 2) *Quantitative.* The first effort to develop a gravimetric procedure for the detn of perchlorates was by Loebich who proposed the use of Nitron as a precipitant (for the structure of this reagent see Ref 10) (Ref 6). It was found that chlorides, chlorates, and nitrates interfere by forming insol ppts (Ref 6). Later it was found that w sol perchlorates could be analyzed gravimetrically by pptn of the perchlorate ion as tetraphenylarsonium perchlorate (K_{sp} at 20° = 2.60 ± 0.14 x 10^{-9}). The ppt can be dried at 105° and weighed directly (Ref 16). Still more recently a specific perchlorate ion electrode has been developed (Ref 17) which can be used for the potentiometric titration of the perchlorate ion using a soln of tetraphenylarsonium chloride as the titrant (Ref 15). Tetraphenylphosphonium chloride has been similarly used, but the corresponding Sb compd is too insol in w for practical use (Ref 8). For routine assay of perchlorates for use by the armed forces, a Na carbonate fusion procedure is described in Mil Specs **MIL-A-23946** (19 Aug 1964) & **MIL-A-23948** (19 Aug 1964) (see also under Ammonium Perchlorate). The tetraphenylarsonium chloride procedure has also been proposed for use in Mil Specs (Ref 11)

Safety. As stated above, perchlorates are strong oxidizing agents and will react with reducing substances, with expl violence when hot (Ref 13). The impact sensy of perchlorate salts depends to a great extent on the cation present. Metal perchlorates are relatively insens; while organic perchlorates, particularly those in which the OB is close to 0, are extremely sens. For details see below under individual perchlorates

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PERCHLORIC ACID

Überchlorsäure (Ger in the older lit), Perchlorsäure (Ger), Acide Perchlorique (Fr), Acido Perclorico (It), Ácido Perclórico (Sp), Khlornaya Kislota (Russ); $HClO_4$, mw 100.46, OB to HCl +64%; mp −102° (anhyd) (Ref 34) (for mp of hydrates see below); bp 16° at 18mm with decompn (Ref 17); d 1.7676g/cc at 20° (Ref 4); RI 1.38189 at 20° (Ref 19); visc 0.946 centipoise at 20° (Ref 19); CA Registry No 7601-90-3

Preparation. As stated above, perchloric ac was first obtained as a hydrate in 1818, and the anhyd ac was prepd in 1862. At present the anhyd ac is best prepd by vacuum distn of a mixt of 72% ac and fuming sulfuric ac, yield up to 75% (Ref 21). The anhyd ac is unstable, however, and yellows on standing at room temp. The colored ac is extremely sensitive and may expld without warning. Hence anhyd perchloric ac should only be prepd in small amts as needed (Ref 29). Other prepns of anhyd perchloric ac are by distn of a mixt of 92% sulfuric ac and K perchlorate (this gives an aq soln of perchloric ac which can be dehydrated as described above) (Ref 10); by passing gaseous HCl thru a satd soln of Na perchlorate, the pptd NaCl filtered off, and the excess HCl driven off during the concn step (Ref 2); and by the action of aqua regia (a mixt of HCl and nitric ac) on AP. Runs on a 500g scale are described, and the process can be readily scaled up (Ref 3). On the coml scale it is prepd by the electrolysis of a soln of chloric ac. Construction details of the electrolysis cell and of its operation are in Ref 38

Physical Properties. The IR spectra of solid, liq, and gaseous perchloric ac as well as deuteroperchloric ac are in Ref 33. Its Q_f is −11.1kcal/mole (anhyd) (Ref 20), and −31.6 ± 1.7kcal/mole (aq soln) (Ref 11)

Chemical Reactions

Water. The freezing point/compn diagram for w/perchloric ac mixts (Fig 1) shows that at least 6 hydrates are formed (Ref 1, B-2, p 433). The most important of these are:

1) *A Monohydrate,* $HClO_4.H_2O$, or $H_3O^+ClO_4^-$ as shown by X-ray diffraction (Ref 27) and nuclear magnetic resonance spectral data (Ref 18). It is a hygroscopic solid, mp 49.905 ± 0.005° (Ref 7), bp 40–50° at 25mm (Ref 1, B-2, p 436); d_4 2.040g/cc below −24.9°, 2.095g/cc above −24.9° (Ref 26); RI 1.4136 at 50° (Ref 5); CA Registry No 15979-03-0

It is best prepd by mixing 54.3 parts of 72% perchloric ac with 45.7 parts of 100% perchloric ac. As it is very hygroscopic, it must be sealed in capillaries or otherwise protected from moisture (Ref 27); Q_f −19.7kcal/mole (Ref 20). It is stable up to 6 months at room temp (Ref 28), and is thermally stable up to 100–10° (Ref 36)

A Dihydrate, $HClO_4.2H_2O$, or $H_3O^+ClO_4^-.H_2O$, mp −17.8° (Ref 22), d_4 1.71282g/cc at 25°, RI 1.42052 at 25° (Ref 8), Q_f −162.8 kcal/mole (Ref 20); CA Registry No 23335-84-4

It is prepd by the addn of 10% by wt of anhyd Mg perchlorate to coml 68–71% perchloric ac, and distn of the mixt at 0.1–1.5mm, yield 40% (Ref 35). It reacts with 99% H peroxide to form a mixed hydrate $HClO_4.2H_2O.H_2O_2$, mp −53° (Ref 37)

Other hydrates have been prepd which have not been as well characterized as the above (see Fig 1)

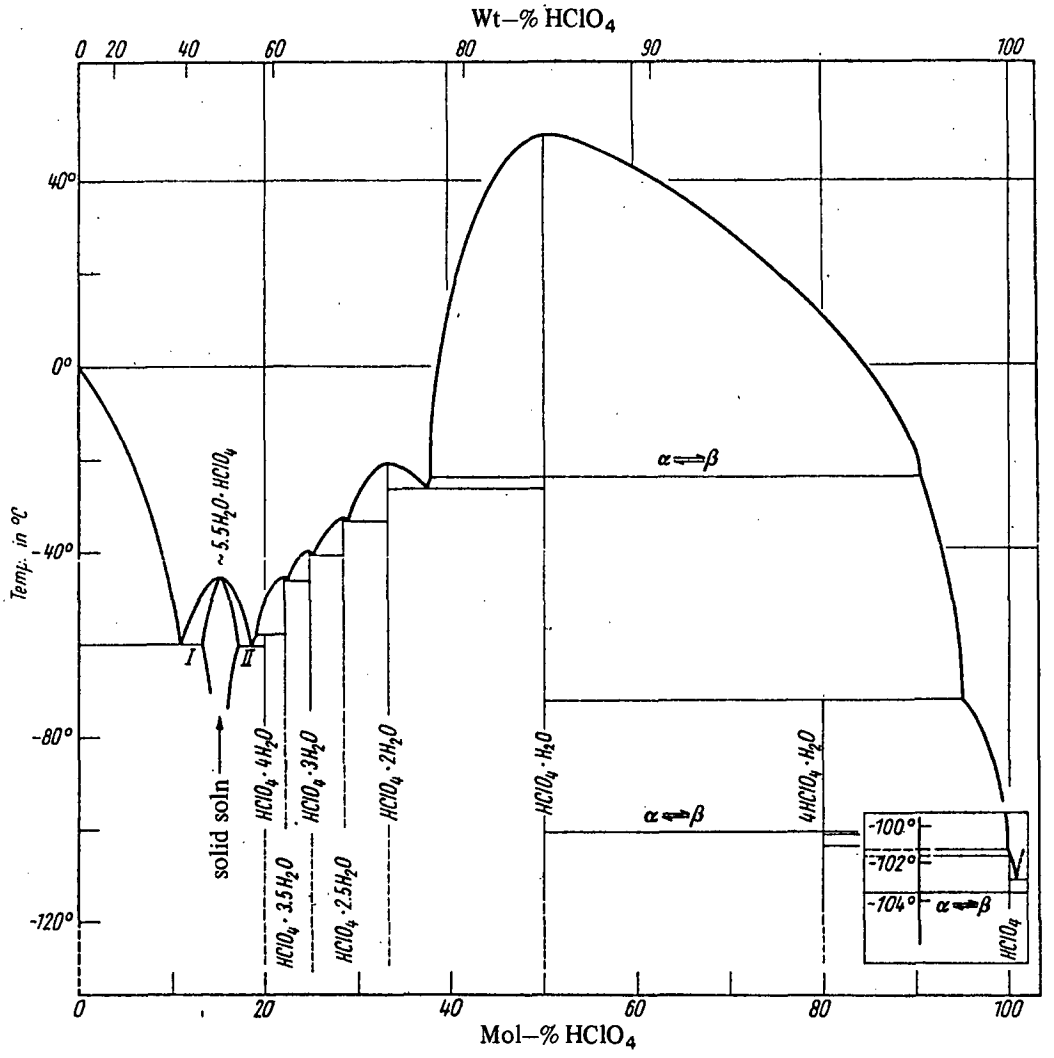


Fig 1 The System $HClO_4 - H_2O$

Ammonia (see also under ammonium perchlorate). Perchloric ac vapor and anhyd ammonia were reacted in a countercurrent flow reactor with the object of obtaining a stable flame. The vapors were found to react vigorously with the formn of gaseous prods and copious deposits of amm chloride, but a stable flame could not be established (Ref 39)

Antimony and Bismuth. In attempting to dissolve alloys of these metals in hot 72% perchloric ac, a coating was formed which was very sensitive and expl. The chem nature of the deposits was not ascertained (Ref 9)

Metals. It reacts with electropositive metals to evolve H and form metal perchlorates. These reactions must be carried out cautiously as they may proceed with expl violence (Ref 1)

Nitric Acid. Anhyd perchloric ac reacts with 100% nitric ac to form nitronium perchlorate ($O_2N^+ClO_4^-$) (see below) and hydronium perchlorate (see above under hydrates) (Ref 16)

Ozone. Anhyd perchloric ac reacts with ozone when irradiated with light of wavelength 254mμ to give $HOOClO_3$, which is unstable and decomps to O and chloric ac (Ref 25)

Phosphoric Acid. The two anhyd acids react to form a cryst solid which is formulated as $(HO)_4P^+ClO_4^-$ (Ref 19)

Explosive Properties. Aq solns of perchloric ac are insensitive and nonexpl up to their boiling

points (Ref 12)

Mixtures which are Unstable or Explosive
Dimethyl Sulfoxide. A violent expln occurs when a drop of 70% perchloric ac is added to 10ml of dimethylsulfoxide (Ref 40)
Ethanol. A mixt of 65 parts of perchloric ac, 35 parts of w, & 11.7 parts of et alc has been reported to be a liq expl with a crit diam of 3mm and a deton vel of 100m/sec (Ref 14)
Hydrogen. Vapors of perchloric ac form expl mixts with H, hence, in the presence of metals hot perchloric ac can form expl vapor mixts (Ref 12)
Hydrogen Chloride. Attempts to prep a complex betw anhyd HCl and anhyd perchloric ac resulted in severe explns (Ref 6)
Methane. The vapors of boiling 72% perchloric ac have been found to support the combustion of methane and other organic gases (Ref 39a). This work has been carried forward in a series of papers in "Combustion and Flame" by G.S. Pearson et al (Vols **8**, 199; **11**, 89, 97, 103 & 471; **12**, 54)
Sodium Hypophosphite. One g of Na hypophosphite and 10 drops of 72% perchloric ac expld violently when heated in a procelain crucible (Ref 22)
Sulfur Trioxide. An equimolar mixt of S trioxide and perchloric ac, either neat or in chlf, forms 2 layers which can deton without warning (Ref 23)
Trichloroethylene. Mixts of anhyd perchloric ac with trichloroethylene react with expl violence (Ref 42, p 648)

Explosive Incidents. Incidents which have involved mixts with perchloric ac which are normally safe, but which have expld as a result of unusual circumstances or mishandling:
Acetic Acid and Acetic Anhydride. Mixts of perchloric ac with these compds are widely used in the metal plating and finishing inds (see below under uses) (Ref 15). Fig 2 shows the triangular phase diagram for perchloric ac/Ac_2O/w (Ref 32), with indications as to those percentages where ign or deton might be expected to occur. One of the most violent ind explns occurred in Los Angeles, Calif on 20 Feb 1947 when an electropolishing bath contg 150gal of 72% perchloric ac and 70gal of Ac_2O detonated. Results: a large mushroom cloud rose over the city (causing rumors of an atomic attack); 17 persons killed, many injured; 116 buildings destroyed, and ca $2 million in damage. Investigation revealed that 1) the cooling coils around the vat had been malfunctioning causing acet ac and Ac_2O to evap, thus enriching the soln in perchloric ac; and 2) a cellulose acetate rack was accidentally introduced into the vat of hot acids, whose oxidn was the immediate cause of the blast (Ref 32)
Ferrous Sulfate. A mixt with 72% perchloric ac expld violently on strong and rapid heating. Slow and gentle heating of such mixts is recommended (Ref 42, p 646)
Methylene Chloride. On one occasion, in the prepn of anhyd perchloric ac in mete chloride, the soln turned yellow and then expld. It was thought that the expln was caused by too rapid mixing of 72% perchloric ac with the P pentoxide dehydrating agent (Ref 41)
Nitric Acid and Organic Substances. Mixts of perchloric and nitric ac are frequently used to digest (render w sol) organic materials such as animal and vegetable oils, milk, homogenized animal tissues, etc. If the mixts are heated too rapidly, explns may occur (Ref 42, p 646)
Thallium Salts. Although the same prepn had been carried out many times, a violent expln occurred during the evapn of a soln of ethylbenzene, Tl triacetate, and perchloric ac in acetic ac. No satisfactory explanation for the expln was found (Ref 40)
Wood. Over many years the wooden supports of a fume hood had become satd with spillage of chemicals, including perchloric ac and perchlorates. Upon contact with a bunsen burner flame, they expld with great violence (Ref 13)

In summary, **ANY** mixt of perchloric ac with reducible materials should be regarded as potentially expl and should be handled on the smallest practical scale and behind adequate shielding

Uses
For reviews see Refs 1 & 30. Its primary use in the expls industry is for the prepn of AP and other perchlorates for use in expls, proplnts, and pyrots (see below under individual perchlorates)
As an Electrolyte. As it is a strong ac and many metal salts are w sol, perchloric ac and solns of perchloric ac in both org and inorg solvs find

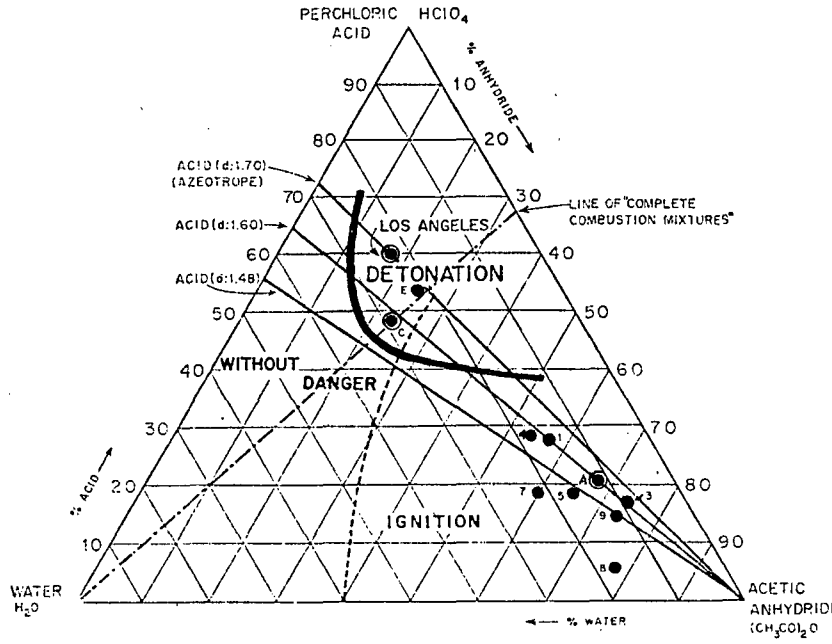


Fig 2 Properties of perchloric acid-acetic anhydride-acetic acid mixtures (from Ref 32)

many uses in electroplating, electrofinishing, and electropolishing (Ref 30). Even reactive metals, such as Al and Al alloys, may be cleaned, polished, and plated in perchloric ac solns (Ref 30)

In Digestions. Mixts of perchloric and nitric ac are used to digest org materials. For example, in the detn of metals in such materials, they are first refluxed with a mixt of perchloric and nitric ac to oxidize the organic material to C dioxide, oxides of N, and w. The soln is then evapd to dryness and the metal analysis carried out on the residue. An app is described in Ref 24 for carrying out these digestions in a safe manner. The reaction is first carried out under reflux with dilute ac, then when the reaction has subsided, distillate is removed giving a more concd ac which further oxidizes the material

Other Uses. It has also been used as a solv, a catalyst, and as a reagent for the isolation and characterization of org bases by forming insol salts. For details of these uses see Ref 30 and below under perchlorate salts

Toxicity. Being a strong ac, concd solns are corrosive to the skin and vapors & mists are lung irritants (Refs 31 & 43)

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INORGANIC PERCHLORATES

Aluminum Perchlorate [Aluminium Perchlorate (Brit)]. $Al(ClO_4)_3$, mw 325.37, OB to Al_2O_3 & HCl +29.5%; white delq cryst, mp decomps ca 300° (Ref 7), d 2.209g/cc (Ref 6) (for d of hydrates see below); CA Registry No 14452-39-2

Preparation. The anhyd salt is best prepd by the interaction of anhyd Al chloride and Ag perchlorate in an inert solv thus: Ag perchlorate is heated to reflux in anhyd Me alc in a 3-necked flask protected from w, and anhyd Al chloride in Me alc added dropwise. The pptd Ag chloride is filtered off and the solv stripped at 150° to give an almost quant yield of anhyd Al perchlorate. Benz or toluene may also be used as solvs (Ref 8). For prepn of hydrates see below. The anhyd salt cannot be prepd by removal of w from hydrates as decompn begins before all the w has been driven off (Ref 7)

Properties. It is v sol in w, and aq solns are acidic (reddens litmus paper). Its soly in w is given as 121.6g at 0°, 131.0g at 14.3°, and 148.9g/100ml at 96° (Ref 3). It is also sol in Me & Et alc

Hydrates. Hydrates of Al perchlorate contain 1, 3, 5, 6, 9, 12, & 15 moles of w; but only those contg 3, 6, 9, & 15 moles of w are of any importance:

$Al(ClO_4)_3.3H_2O$. Mp decomps, d 2.145g/cc. Prepd by heating higher hydrates **in vacuo**, and is the lowest hydrate which can be prepd this way (Ref 5)

$Al(ClO_4)_3.6H_2O$. Delq plates, mp 120.8°, d 2.020g/cc (Ref 5). Weinland & Ensgraber give the structure as $Al(H_2O_6(ClO_4)_3$ (Ref 4). It is prepd by dissolving the nonahydrate in boiling 70% perchloric ac and concentrating the soln (Ref 5)

$Al(ClO_4)_3.9H_2O$. Hygr crysts which require special care in handling, mp 85.3°, d 1.924g/cc. It is prepd by dissolving Al hydroxide, or better, Al metal, in an excess of 70% perchloric ac on a w bath, cooling the soln to give a gel to which more 70% perchloric ac is added. This breaks the gel and ppts the nonahydrate (Ref 5). DTA shows a strong dehydration endotherm at *ca* 220° (Ref 9)

$Al(ClO_4)_3.15H_2O$. Thin, slightly hygr needles, mp 76.2°, d 1.764g/cc. It is prepd by slowly

dissolving an excess of Al hydroxide in 30% perchloric ac on a w bath, cooling the soln to −15°, and filtering off the pptd crysts (Ref 5)

Other Complexes. Any Al perchlorate hydrate is placed in a large excess of dimethylsulfoxide, the solvs stripped under the vacuum of a w jet, the pptd $Al(ClO_4)_3.6Me_2SO$ filtered off, and dried by extn with benz. The product is a useful expl or expl ingredient (Ref 11)

A series of complexes of the general formula $MAl(ClO_4)_4$ have been reported either as anhyd salts or as hydrates. The following have been prepd:

$M = NH_4^+$. Mw 424.87, OB to Al_2O_3 & HCl +52.4%. It is prepd by the interaction of AP and Al perchlorate in liq S dioxide, followed by evapn of the solv. It is recovered as a white solid, stable up to 50° (Ref 10)

$M = Na^+$. Prepd by Weinland & Ensgraber (Ref 4) who added Na perchlorate to a soln of Al oxide in aq perchloric ac; no phys props are given (Ref 4). More recently workers in the USSR have reported complexes in which M = Rb and Cs, which were obtained as dihydrates by similar procedures (Ref 12). Workers at Callery Chem Co also prepd a complex in which $M = NO_2^+$, mw 506.78, OB to Al_2O_3 & HCl +58.4%. It is prepd by a similar procedure as that used for the ammonium salt using nitronium perchlorate, and has similar props (Ref 10)

Uses. (see under Perchlorate Explosives and Propellants)

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Ammonium Perchlorate [AP, Perchlorate d'Ammonium (Fr), Ammoniumperchlorat (Ger), Perclorato di Ammonio (It), Amonio Perclorato (Sp), Perkhlorata Ammoniya (Russ)]. NH_4ClO_4, mw 117.49, OB +27.2%; white rhmb crysts which change to a cubic form at 240° (Ref 15) and decomp at 269° with evolution of oxides of N and H chloride (Ref 15) (for further info on the effects of heat on AP see below); d at 25° 1.9518 ± 0.0001g/cc (Ref 7); CA Registry No 7790-98-9

Preparation. AP was first prepd in 1831 by Sérullas who neutralized aq perchloric ac with ammonia and evapd the soln until crysts formed (Ref 2). The next year it was prepd by Mitscherlich by mixing aq perchloric ac with an aq soln of diammonium hexafluorophosphate, the pptd dipotassium hexafluorophosphate filtered off, and the filtrate evapd (Ref 3). Later in the 19th century, AP was prepd by mixing equimolar aq solns of Ba perchlorate and Amm sulfate, the solid Ba sulfate filtered off, and the filtrate evapd (Ref 4). At present AP is best prepd in the lab by careful neutralization of aq perchloric ac with gaseous ammonia, the crysts filtered off, recrystd from w, and dried at 110° to const wt (Ref 6). On the coml scale AP is prepd by the interaction of Amm chloride and Na perchlorate. The less-sol AP ppts and is filtered off, leaving the NaCl in soln which may be recovered (Ref 19). Flow sheets for the manuf of AP from ammonia, HCl, and Na perchlorate are given in Refs 19 & 25. The process described in Ref 19 is continuous and capable of producing ca 5000 lbs/hr. The same process is described in a patent (Ref 18). In this process anhyd ammonia, 22°Bé aq HCl, 56% aq Na perchlorate, and recycled mother liquor from the NaCl crystallizer are metered continuously into a 1000gal glass-lined reactor heated with steam to 90°. The pH of the exit stream from this reactor is monitored and the info fed back to control the addn of HCl soln to keep the pH of the reaction close to 7. The exit stream goes to a crystallizer where the

temp is lowered to 35° by vac evaporative cooling, recycled mother liquor added, the mixt passed thru a vaporizer which gives a supersatd soln, and then thru a bed of AP crysts where the excess crystallizes. The AP slurry is fed to a centrifuge where the mother liquor is removed and recycled to the AP crystallizer. The AP crysts are washed, dumped into a satd soln of AP which removes last traces of chloride, recentrifuged, and dried in a bldg removed from the mfg operation. The mother liquor and washings from this operation are pumped to the NaCl crystallizer where w is removed in a vacuum evaporator, the pptd NaCl centrifuged off, and the mother liquor recycled to the AP reactor. Fig 1 is a flow sheet of the operation. Economics of the process dictate that a minimum of w be handled thruout the process (Ref 19). Particle size is controlled by rate of crystn or by subsequent processing to produce extremely fine particle AP

Ultrafine Ammonium Perchlorate (UFAP). For high burning rate proplnts a fine particle size AP is required and is produced by 3 processes:

a) In a jet mill. Coml AP is fed into a Model 0202 Jet-O-Mizer at a rate of 8 lbs/hr using either N or He at 180°F as the working fluid. The powd prod is collected in trichloroethylene. Best aresults are obtained with He which gave a prod whose particle size was 5μ or smaller (Ref 47)

b) By slurry grinding. A slurry of 85 parts of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), 15 of AP, and 0.15 of XD-7604 surfactant is ground in a Sweco Vibro-Energy mill for 160 hours to give a prod which, when dried, has a particle size of 1.72μ (Ref 48)

c) By freeze-drying. A concd emulsion is made of AP in w plus 1% Nopogen 16-0 emulsifier and 0.1% Johnson's Wax. The emulsion is freeze-dried in a vac sublimator to give a prod with a residual moisture content of 0.036% and a particle size of 0.37μ (Ref 48). Several variations of this formulation are given in this Ref. Expts were carried out at TCC (Huntsville) to find a coating mat which would prevent cryst regrowth in UFAP. Forty-one compds were examined and best results were obtained with methyl 2-cyanoacrylate (Eastman 910), Johnson's Paste Wax, and several HX emulsifiers (Ref 48, p 3)

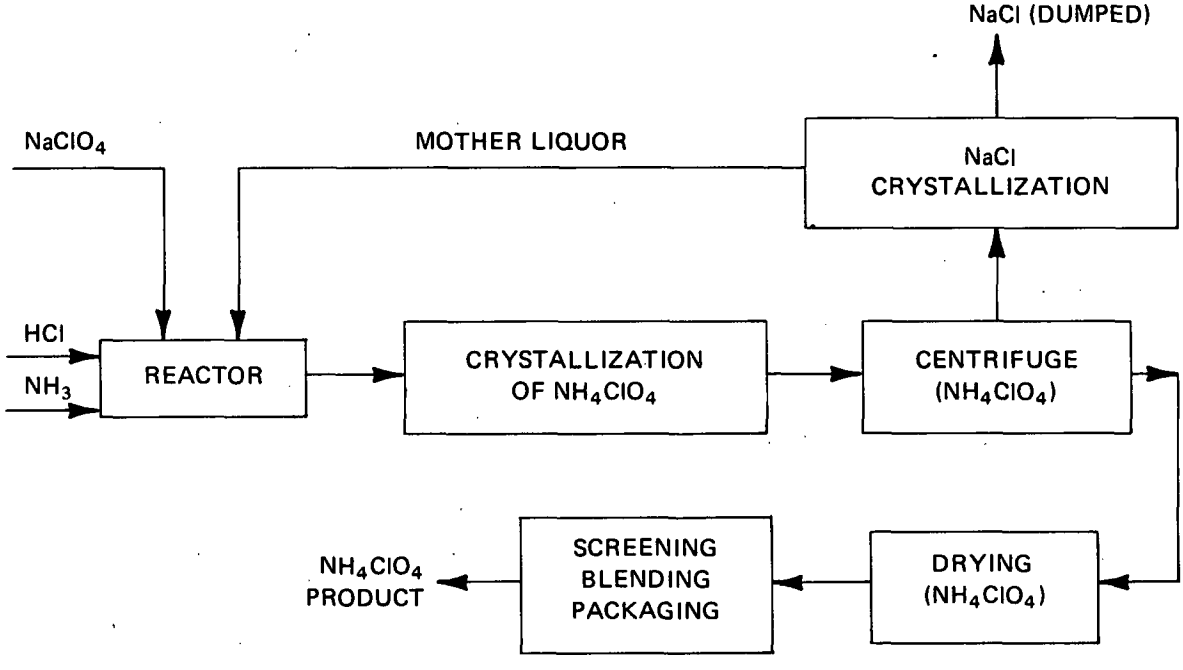


Fig 1 Schematic Flow Diagram for the Manufacture of Ammonium Perchlorate

Ammonium Perchlorate Analysis.

Assay Methods. A Na carbonate fusion prod is currently used for assay of mil grade AP (see below under Specifications), but recently attempts have been made to replace it with a method which is faster and simpler to carry out. Two procs have been proposed:

a) *Titanous Chloride Titration.* A measured excess of Ti trichloride is added to a known weight of AP which reacts according to the equation:

$$NH_4ClO_4 + 8HCl + 8TiCl_3 \rightarrow NH_4Cl + 8TiCl_4 + 4H_2O$$

The excess Ti trichloride is then back-titrated with a std ferric ammsulfate soln to a thiocyanate end-point. A blank is run concurrently on the Ti trichloride soln. The % AP in the sample is calcd by the formula:

$$\% AP = \frac{1.4687\ N(B-S)}{W}$$

where: N = normality of the ferric amm sulfate soln
B = vol used in titration of blank
S = vol used in titration of sample
W = weight of sample (Refs 11 & 34)

This proc, while fairly simple and accurate, has the disadvantage that the reagents are unstable, as well as air and moisture sensitive so the titration must be run in a closed system in a C dioxide atm. For a diagram of the set-up see Ref 46, p 465

b) *Titration in a Nonaqueous Solvent.* This proc is based on the enhanced acidity of the Amm ion in iso-Pr alc/dimethylformamide, so it can be titrated with a KOH soln according to the equation:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

using the blue-green end point of thymol blue/phenolphthalein.

Procedure: A 0.05N soln of KOH in iso-Pr alc is prepd and standardized with primary std benzoic ac. A 0.4g sample is weighed to the nearest 0.1mg into a 250ml erlenmeyer flask. 75ml of a 50/50 mixt by vol of iso-Pr alc & dimethylformamide added, the flask swept with N, 1ml of the indicator soln added, and the soln titrated with KOH soln to a blue-green end point. The % AP is then calcd by the equation:

$$\% AP = \frac{11.75VN}{W}$$

where: N = normality of KOH soln
V = vol of soln used
W = weight of sample (Ref 34, p 17)

This method is quick and fairly easy, but for good results air must be excluded.

Particle Size Analysis. A review of the techniques which have been used to detn the size distribution of fine powds is given in Ref 36:

Andreason Pipette. A sample is dispersed in a liq in a tall column, 10ml samples of the dispersion are withdrawn from a fixed position below the surface at fixed intervals of time, the liq evapd, and the weight of the solids detd. From the height and the fall time, the size distribution can be calcd using Stoke's Law

Coulter Counter. The vol of particles suspended in an electrolyte is detd by the change in resistance as the suspension streams past two closely placed electrodes. The vol is then converted to a particle size distribution

Fisher Sub-Sieve Sizer. Dry air is passed thru a packed bed of the mat and the pressure drop measured. Using curves supplied with the instrument, the surface area is detd and then converted into a particle size distribution

Flying Spot Particle Size Resolver. A moving beam of light scans the sample, the % light transmitted recorded electronically, and the info fed into the instrument which converts it into a particle size distribution curve

Micromerograph. The particles are dispersed and injected into the top of a column with compressed N. The wt settling as a function of time is recorded on an automatic balance and converted to a particle size distribution with templates based on Stoke's Law

Mine Safety Appliances Particle Size Analyzer. A dispersion of the sample is placed on top of a liq of greater density. The rate of sedimentation is detd by measuring the sediment vol at fixed time intervals. The results are converted to a size distribution by Stoke's Law

Nitrogen Adsorption. The amt of N adsorbed on a sample is detd by carefully measuring the press change of a known vol of N exposed to a known wt of dry mat at constant temp. The info is used to detn the surface area which is converted to a particle size distribution

Turbidometric Methods. The absorption of a beam of light passing thru a suspended sample in a suitable liq is measured as a function of time.

The info is converted to a size distribution using Stoke's Law

The most commonly used methods for detn of the particle size distribution of fine AP are the Micromerograph and Turbidometric Methods. For coarser AP samples standard sieves are used (see below under Specifications)

Surface Area Measurements. For a discussion of procs used see above under Fisher Sub-Siever and Nitrogen Adsorption. For AP, the Fisher Sub-Siever is most suitable for samples having surface areas from 0.05 to 0.46sqm/g, and the Nitrogen Adsorption method for finer mat, up to 30000 sqcm/cc (Ref 49)

Water Analysis

Nuclear Magnetic Resonance. The sample is dissolved in anhyd (0.02% w) dimethylformamide and the NH_4^+ peak width at half-height measured at 7.38 τ and compared with a graph prepd from samples of AP contg known amts of w. The method is accurate up to 7% w (Ref 44)

Karl Fischer Method. See below under Specifications

Specifications. For mil use, specs have been published for Ammonium Perchlorate (**MIL-A-23442A**, 8 Sept 1966); Ammonium Perchlorate, Technical (**MIL-A-192B**, 2 Sept 1965); Ammonium Perchlorate for Solid Propellant Grains Mark 75 & Mark 76 (**MIL-A-23946**, 19 Aug 1964); and Ammonium Perchlorate, Special, Coarse for Solid Propellant Grains Mark 75 & Mark 76 (**MIL-A-23948**, 19 Aug 1964). The requirements of the first two specs are:

	MIL-A-23442A	MIL-A-192B
Assay	99.3%	99.0%
Total moisture	0.050	0.08
Surface moisture	0.020	–
Bromates, as $NaBrO_3$	0.004	–
Chloride, as NH_4Cl	0.030	0.15
Chlorates, as $NaClO_3$	0.020	0.02
Chromates, as K_2CrO_4	0.015	–
Iron, as Fe	0.001	–
Iron, as Fe_2O_3	–	0.0036
Ash, sulfated	0.300	0.25
Total water	0.050	–
Total volatiles	0.040	–
Particle size	betw 190 & 210μ	–

The last two specs are primarily concerned with particle size. **MIL-A-23946** requires 100% to pass thru a 20 mesh sieve and 70% to be retained on a 100 mesh sieve. **MIL-A-23948** requires 97% to pass thru a 30 mesh sieve, 35–55% to be retained on a 40 mesh sieve, 90–100% to be retained on a 50 mesh sieve, and 98% to be retained on a 70 mesh sieve

Ammonium Perchlorate Properties

Brisance by Sand Crushing Test. A 0.4g sample, when initiated by 0.25g of Tetryl, crushed 6g of sand (TNT 48g) (Ref 11)

Card Gap Test. Freeze dried UFAP, 0 cards; jet milled UFAP, 0–4 cards; and slurry ground UFAP, 8–10 cards (Ref 48, p 56)

Critical Diameter (which will propagate a detonation). The min diam for dry AP, wet with acet, and wet with et alc, was found to be under 2 inches when confined, and under 4 inches when unconfined (Ref 24)

Critical Height at which a Deflagration-to-Detonation Transition will Occur. Description of test: The mat to be tested is loaded into a 2-inch diameter pipe capped at the lower end. The charge is then ignited at the confined end and any deflagration-to-deton or -expln transition noted. For AP the minimum height for an expln transition was found to be 12 inches, and over 24 inches for a deton transition (Ref 24)

Detonation Sensitivity. It was found that a No H blasting cap is the min size which will deton AP (Ref 24). Slurry ground and freeze dried UFAP can be detond by a No 8 blasting cap, but jet milled UFAP failed to deton in 5 tries (Ref 48, p 56)

Detonation Velocity. Dry AP, 3400m/sec; AP wet with et alc, 4200m/sec; and AP wet with acet, 4500m/sec (Ref 24)

Effect of Heat. (see *Thermal Decomposition*)

Electrostatic Sensitivity. An electrostatic discharge of over 5 joules is required to initiate AP (NG 3 joules) (Ref 24, p 46)

Explosion Temperature. 10sec at 435° (Ref 11)

Flammability. The flammability of AP, as measured by the min weight of a primer which will ignite it, was found to lie betw Xylyl (a Russian expl) and TNT (Ref 38)

Friction Sensitivity. By friction pendulum, it snaps when tested with a steel shoe (Ref 11). With an ABL-designed sliding friction machine, AP required a sliding dist of 16cm for 50% explns (NC 15cm) (Ref 24, p 20)

Hygroscopicity. When exposed for 192 hours at 21.1 ± 0.1°, AP weight gain was 0.03% at 52%

RH, 0.04% at 75.5% RH, and 0.18% at 90% RH (Ref 12)

Impact Sensitivity. With BM app, 91cm for 50% explns, and with PA app, 24 inches for 50% explns, both using a 2kg weight (Ref 11). In Ref 16 the impact sensy of AP is given as 17 inches for 1 expln out of 10 tries with a 2kg weight. By using an "up-and-down" technique, workers at NOL obtained a height of 107cm for 50% explns (Ref 18). The impact sensy of AP doped with various substances was also measured by these workers. Results:

Mixture	50% expl height, cm
AP/Amm dichromate, 99/1	95
AP/Magnetic Fe oxide, 99/1	90
AP/Mn dioxide, 99/1	88
AP/sugar/Amm dichromate, 98/1/1	71
AP/sugar/magnetic Fe oxide, 98/1/1	77
AP/sugar/Mn dioxide, 98/1/1	65
AP/sugar/magnetic Fe oxide, 97/1/2	64
AP/sugar/magnetic Fe oxide, 95/1/4	61
AP/sugar/magnetic Fe oxide, 93/1/6	84 (Ref 16)

Heat Capacity. At 36.6° it is 0.264cal/g/°C (Ref 25, p 552)

Heat of Formation. −70.74 ± 0.32kcal/mole (Ref 27)

Heat Test, 75°. All UFAP samples failed to expld after 48 hours at 75° (Ref 48, p 56)

Heat Test, 100°. Betw 0 and 48 hours, 1% weight loss; betw 48 and 96 hours, 0.6% weight loss; no explns after 100 hours (Ref 10)

Ignition and Unconfined Burning Test. All UFAP samples ignited and burned without expln (Ref 48, p 56)

Power by Ballistic Mortar. 100% of TNT (3 tries) (Ref 9)

Power by Lead Cylinder Compression Test. 58% of TNT (Ref 8)

Power by Lead Block Expansion Test. 46% of PA (Ref 5)

Solubilities. In w the soly at 0° is 10.92 (d 1.059g/cc), and at 107° (bp of soln) 48.5g in 100g of satd soln (d 1.221g/cc) (Ref 31). In org solvs the soly in g/100g of solv are: me alc 6.862, acet 2.260, et alc 1.907, pr alc 0.387, iso-Bu alc 0.127, et acetate 0.032, and bu alc 0.017. It is insol in eth (Ref 6)

Toxicity. The toxicity is similar to other perchlorates (see general introduction on Perchlorates)

Thermal Stability and Effects of Heat. The thermal stability and thermal decompn of AP have been extensively studied as a starting point for investigations into the decompn and combustn of AP-contg expls and proplnts. Work up to 1968 has been reviewed in Ref 42. In general, the uncatalyzed decompn can be divided into 3 phases: a) A low temp decompn occurring betw 200 and 300° at atm press. The decompn stops before all the AP is consumed. b) A high temp decompn occurring betw 350 and 400°. c) A deflagration or rapid combstn which starts ca 450°. The stoichiometry of the low temp decompn has been concluded to be:

$$4NH_4ClO_4 \rightarrow 2Cl_2+8H_2O+2N_2O+3O_2$$ (Ref 32)

Small amts of H chloride, N monoxide, N, and other prods which have been found in the decompn of AP are accounted for by secondary reactions and/or higher temp decompns (Ref 42, p 5). Kinetic work on the decompn of AP has been hampered by side reactions and the profound effect which small amts of impurities, especially metal salts, have on the decompn (see below)

At high temps the decompn is believed to be:

$$2NH_4ClO_4 \rightarrow 4H_2O+O_2+Cl_2+2NO$$ (Ref 42, p 8)

More recently the thermal decompn of single large crysts of AP has been studied on a hot-stage microscope. It was found that the low temp decompn started on a cryst face as a dark spot which rapidly expanded into a hole which then spread thruout the cryst. The crysts were not consumed, but a residue of finely powd AP was always left (Ref 45)

Factors which Catalyze the Decomposition of Ammonium Perchlorate. Irradiation of AP with X-rays or gamma radiation causes it to decomp at a lower temp, presumably by the formn of "holes" or active sites in the cryst (Ref 36). Metal salts have been found to lower the decompn point of AP by as much as 80° (Ref 39), and to lower the induction period for its expln at 233° by 21 minutes (Ref 41). Inorg salts which have been found to catalyze the decompn of AP are listed below:

Compound	Ref
Al_2O_3	22
CdO	36
$Cd(ClO_4)_2$	37
$CoCl_2$	30
Co oxalate	30
$CrCl_3$	30
Cr_2O_3	29
$Cr_2O_3 + Cr_3O_4$	23
CuCl	29
Cu_2O	29
$CuCO_3$	30
$CuCl_2$	30
Cu Chromite	29
CuO	29
$Cu(ClO_4)_2$	41
Fe Oxalate	30
$FeCl_3$	30
Fe_2O_3	28
$Hg(ClO_4)_2$	36
MgO	36
$Mg(ClO_4)_2$	37
MnO_2	22
$HMnO_2$	22
$MnCl_3$	30
Mn_2O_3	22
Mn_3O_4	22
$NiCO_3.Ni(OH)_2$	30
$NiCl_2$	30
Ni Oxalate	30
NiO	29
Ni_2O_3	23
V_2O_5	30
ZnO	29
$Zn(ClO_4)_2$	37

Uses. (See also under Perchlorate Explosives)
Combustible Cartridge Cases. Cotton cloth is impregnated with a slurry of AP and a monomer in methyl ethyl ketone, the solv evapd, and the monomer cured on a mold to give a combustible cartridge case (Ref 35)
Flares. An AP-contg flare is described in Ref 13 which produces little smoke and an intensity of 10000 candlepower
Igniters. A mixt of 3kg of NC, 3.5kg of NG, and 400g of Centralite is homogenized with 100g of dioctyl phthalate, 200g of dye, and 2.98kg of AP (particle size below 60μ), and the mixt pressed into strands 1.5mm in diam which can be used as an ign cord for rocket motors (Ref 43). A Zr/AP mixt (compn unspecified) has the following props: autoign time, 5 sec at 521°F; Q_f 1704cal/g; threshold ign energy, 1.85cal/sqcm and d when compressed to 1000psi 2.03g/cc (Ref 40)
Incendiaries. AP has been added to Napalm-type flame agents to raise the flame temp and increase the burning intensity (Ref 17). Graphite, 30 parts; 20 of AP; 13 of polyester; 37 of styrene, 2 of methyl ethyl ketone peroxide, and 0.5 of Co naphthenate are mixed together and cured to give a conductable, flammable plastic with a resistivity of ca 0.7ohm-cm (Ref 21)
Smoke Generating Compositions. A soln of 3 parts of chloronaphthalene in trichloroethylene is slurried with 23 parts of powd Zn and 4 parts of kieselguhr, the solv evapd, the granulated prod mixed with 50 parts of AP and 20 parts of Amm chloride, and the mixt pressed in a mold to give a waterproof smoke generator (Ref 14). A mixt of 50–80 parts of sulfamic ac and 50–20 parts of AP evolves copious amts of smoke on ign (Ref 20). A similar mixt of 390 parts of Zn oxide, 375 parts of hexachloroethane, and 190 parts of AP is slurried in a soln of 40 parts of polyvinyl acetate in 200 parts of mete chloride. The mixt is packed into cylinders, the solv evapd, and ignited to give copious amts of white smoke with a burning time of 68 secs (Ref 26)
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Barium Perchlorate. $Ba(ClO_4)_2$, mw 336.27, OB to BaO & HCl +19.0%; colorl hex crysts (called alpha) which change to a cubic form (beta) at 284° (Ref 3) and to a second cubic form (gamma) at 360° (Ref 11), mp 505° with decompn and evolution of O (Ref 14), d 3.681g/cc at 25° (Ref 9); CA Registry No 13465-95-7

Preparation. The anhyd salt is prepd in good yield by heating a mixt of solid Ba chloride and nitrosyl perchlorate (Ref 15), by heating an intimate mixt of AP and Ba carbonate (Ref 8), or by dehydration of the trihydrate in a vacuum at 140–70° (Ref 5)

Properties. Solubilities. At 25° the soly of Ba

perchlorate in g/100 ml of Me alc is 217.1, Et alc is 124.6, Pr alc is 75.7, isobutyl alc is 56.2, acet is 124.7, and Et acetate is 113.0. It is insol in eth (Ref 4). It is v sol in w; at 0° a satd soln contains 67.3g/100ml of soln, d 1.782g/cc; and at 140° it contains 88.3g/100ml of soln, d 2.230 g/cc (Ref 6)

Other Properties. Heat of Formation. −185.06 ± 0.26kcal/mole (Ref 18)

Thermal Decomposition. Differential thermal analysis shows phase transitions at 295° and 370° (see above) and a sharp decompn exotherm at 485–500° (Ref 20). G.F. Smith claims that it is unchanged after heating to 400° for long periods of time (Ref 5). Workers in the USSR further investigated the thermal decompn and found that decompn took place betw 320 and 465° with formn of Ba oxide, Ba chloride, and evolution of O. No Cl was evolved below 520–50° (Ref 14)

Hydrates. $Ba(ClO_4)_2.H_2O$ is prepd by dehydration of the trihydrate at room temp over P pentoxide (Ref 7)

$Ba(ClO_4)_2.3H_2O$ is pptd when solns of Ba perchlorate are crystd, as in its prepn by the action of perchloric ac on Ba carbonate, hydroxide (Ref 2), or chloride (Ref 4); or by the action of a satd soln of AP on Ba hydroxide (Ref 5)

Other Complexes. Complexes are known which contain 1 and 4 moles of ethylenediamine. The complex with 4 moles was found to decomp slowly over a broad temp range, but the one with 1 mole expld shortly after decompn started (Ref 12). A complex is formed with dioxane which is reported to be $Ba(ClO_4)_2.2C_4H_8O_2$. It forms colorl crysts which lose dioxane on slow heating, but explds violently when heated rapidly to higher temps (Ref 14a)

Uses. (see also under Perchlorate Propellants and Explosives) Ba perchlorate is a strong oxidizing agent and burns with a green flame, hence it is used as an oxidizing colorant in green flares (Refs 19 & 21). A procedure is described in Ref 16 for coating Ba perchlorate with Al metal and for the use of the coated mat in pyrots. A mixt of 70% Ba perchlorate and 30% Al was examined by workers at PicArsn as a possible high altitude photoflash compn. Of the alkaline earth perchlorates tested, Ca perchlorate gave the best results. The mixt of Ba perchlorate and Al had an impact sensy of 13 inches (PicArsn app); and a friction pendulum test: detond by a steel shoe, unaffected by a fiber shoe (Ref 13). Fifty g of anhyd Ba perchlorate was dissolved in 100ml of Me alc, and 4.6g of Carbopol 940 gelling agent added to form a gel. Approx 5g of this gel was placed in a burner and upon ign it burned for 5 mins with an intense green flame (Ref 19). The anhyd salt is an efficient drying agent for gases and is sold under the trade name "Desichlora" (Ref 17). It should not be used for drying org compds as there is danger of expln

Refs: 1) Gmelin, System No 30 (1932), 218 & Supp (1960), 373 2) G.S. Sérullas, AnnChimPhys **46** (2), 304 (1831) 3) D. Vorländer & E. Kaascht, Ber **56**, 1157 (1923) 4) H.H. Willard & G.F. Smith, JACS **45**, 294 (1923) 5) G.F. Smith, IEC **19**, 411 (1927) 6) Anon, ICT **3** (1928), 105 7) P. Ephraim & C. Zapata, Helv **17**, 296 (1934) & CA **28**, 4326 (1934) 8) G.F. Smith & V.R. Hardy, ZAnorgAllgemChem **223**, 1 (1935) & CA **29**, 5033 (1935) 9) G.F. Smith & E.G. Koch, ZAnorgAllgemChem **223**, 17 (1935) & CA **29**, 5035 (1935) 10) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 11) A.A. Zinov'ev et al, ZhurNeorgKhim **1**, 1850 (1956) & CA **51**, 2371 (1957) 12) H. Diehl & H.W. Wharton, JInorgNuclChem **17**, 120 (1961) & CA **62**, 2492 (1965) 13) S. Lopatin, "Sea-Level and High-Altitude Performance of Experimental Photoflash Compositions", **PA FRL-TR 29** (1961), 28, AD 266213 & CA **60**, 7606 (1964) 14) L.I. Chudinova, IzvVysshikhZavedenii,KhimIKhimTekhnol **5**, 357 (1962) & CA **58**, 1114 (1963) 14a) E. Giesbrecht et al, JInorgNuclChem **24**, 381 (1962) & CA **58**, 3419 (1963) 15) M.M. Markowitz & P.F. Winternitz, USP 3110558 (1963) & CA **60**, 6519 (1964) 16) A.D. Coates & E.O. Baicy, USP 3120459 (1964) & CA **60**, 9094 (1964) 17) Kirk & Othmer **7** (1965), 395 18) A.F. Vorobev et al, VestnMoskUnivSerII **22** (6), 3 (1967) & CA **68**, 108673 (1968) 19) R.J. Fay & P.J. Keitel, USP 3461006 (1969) & CA **71**, 126734 (1969) 20) P.W.M. Jacobs et al, CombFlame **17**, 125 (1971) 21) J.E. Tanner, Jr et al, "Effect of Barium and Calcium on Illuminating Flare Performance", **NAD RDTR 281** (1974), AD 923559 (USGO)

Beryllium Perchlorate. $Be(ClO_4)_2$, mw 207.91, OB to BeO and HCl +30.8%; a white hygr powd, mp decomps (Ref 2); CA Registry No 13597-95-0
Preparation. It was first prepd by the action of perchloric ac on Be oxide (Ref 2), and more recently by heating a mixt of Be nitrate and excess 70% perchloric ac until fumes appear, cooling, and filtering off the pptd crysts (Ref 3)
Properties. Its Q_f was calcd to be −105kcal/mole (Ref 4). It forms a complex $Be(ClO_4)_2 \cdot 4H_2O.4$(dioxane); colorl crysts which lose dioxane on slow heating, but expld on rapid heating (Ref 3)
Refs: 1) Gmelin, System No 26 (1930), 121 2) C. Marignac, AnnChimPhys **30** (4), 54 (1873) 3) E. Geisbrecht et al, JInorgNuclChem **24**, 381 (1962) & CA **58**, 3419 (1963) 4) D.E. Wilcox & L.A. Bromley, IEC **55**, 32 (1963)

Cadmium Perchlorate. $Cd(ClO_4)_2$, mw 311.30, OB to CdO & HCl +20.6%; white delq crysts, mp 290° with decompn (Ref 2); CA Registry No 13760-37-7
Preparation. The anhyd salt can be prepd by the solvolysis of Cd nitrate with anhyd perchloric ac in abs nitric ac (Ref 9); by the action of anhyd perchloric ac on a soln of Cd ions in trifluoroacetic ac (Ref 11); or by the slow dehydration of the hydrates in vacuum (Refs 8 & 15)
Properties. Its Q_f is −49.24 ± 0.42kcal/mole (Ref 15). Its soly in w at 25° is 4.0 and 50° is 4.8 moles/ℓ (Ref 10)
Complexes. *$Cd(ClO_4)_2.2H_2O$.* Prepd by the dehydration of the hexahydrate at 90°, then at 130°, at a press of 1mm (Ref 15)
$Cd(ClO_4)_2.4H_2O$. Prepd by dehydration of the hexahydrate (Ref 2)
$Cd(ClO_4)_2.6H_2O$. Mp 105°, prepd by evapn of Cd oxide (Ref 2) or Cd carbonate (Ref 15) dissolved in excess 70% perchloric ac, recrystd from 79% perchloric ac (Ref 15)
$Cd(ClO_4)_2.4NH_3$. Prepd by allowing the hexaammoniate to stand in air. Effect of heat: begins to lose ammonia at 150°; mp ca 200°; decomps violently above 350°; explds at 400° in a sealed tube (Ref 3)
$Cd(ClO_4)_2.6NH_3$. Prepd by the action of an excess of ammonia on Cd perchlorate (Ref 3). Its expl props are: expln temp 270°; impact sensy (1 kg wt) 53cm (MF 20cm); in Trauzl Pb block expansion test, 1 g on deton produced a cavity of 12.6cc (TNT 21.5cc) (Ref 5). It is readily detond by a No 8 blasting cap contg 0.01g of LA (Ref 4)
$Cd(ClO_4)_2.6H_2O.5$(dioxane). Colorl crysts, loses dioxane on slow heating, explds on rapid heating (Ref 12)
$Cd(ClO_4)_2.Cd(OH)_2.3N_2H_4$. Prepd by mixing a soln of 28.6g of Cd perchlorate hexahydrate in 20ml of w with a soln of 50g of hydrazine hydrate in 5ml of w (Ref 6). Its expl props are: expln temp 235°; impact sensy (1 kg wt) 36cm (MF 20cm); in the Trauzl Pb block expansion test 1 g on deton produced a cavity of 11.8cc (TNT 21.5cc) (Ref 7)
Uses. Cd perchlorate is an efficient catalyst for the decompn and expln of AP (Ref 14). The presence of as little as 0.3% Cd perchlorate in AP lowers its ign temp by 80°, and a 4% mixt will expld at 257° (Ref 13)
Refs: 1) Gmelin, System No 33 (1925), 513 & Supp (1959), 92 2) G.G. Sérullas, AnnChimPhys **46** (2), 304 (1831) 3) R. Salvadori, Gazz **42 (I)**, 458 (1912) & CA **6**, 2216 (1912) 4) W. Friederich & P. Vervoorst, SS **21**, 67 (1926) & CA **21**, 1184 (1927) 5) W. Friederich & P. Vervoorst, SS **21**, 95 (1926) & CA **21**, 1184 (1927) 6) Ibid, SS **21**, 103 (1926) & CA **21**, 1184 (1927) 7) Ibid, SS **21**, 123 (1926) & CA **21**, 1184 (1927) 8) A.L. Chaney & C.H. Mann, JPhysChem **35**, 2291 (1935) 9) G. Jander & H. Wendt, ZAnorgChem **258**, 1 (1949) & CA **43**, 6495 (1949) 10) L.S. Lilich & B.F. Dzhurinskii, ZhObshchKhim **26**, 1549 (1956) & CA **51**, 4798 (1957) 11) G.S. Fujioka & G.H. Cady, JACS **79**, 2451 (1957) 12) E. Geisbrecht et al, JInorgNuclChem **24**, 381 (1962) & CA **58**, 3419 (1963) 13) F. Solymosi & K. Fónagy, "Effect of Cadmium Oxide and Cadmium Perchlorate on the Decomposition and Ignition of Ammonium Perchlorate", in Eleventh Symposium (International) on Combustion (Aug 14–20, 1966), The Combustion Institute, Pittsburgh, Pa (1967), 429 14) F. Solymosi, MagyKemFoly **73**, 366 (1967) & CA **68**, 6735 (1968)
15) V.Ya. Rosolovskii & N.V. Krivstsov, ZhNeorgKhim **13**, 36 (1968) & CA **68**, 99320 (1968)

Calcium Perchlorate. $Ca(ClO_4)_2$, mw 238.98, OB to CaO & HCl +26.8%, colorl, delq crysts, mp 220° with decompn (Ref 5); CA Registry No 13477-36-6

Preparation. The anhyd salt is prepd by heating an intimate mixt of one mole of Ca carbonate and 2 moles of AP. Amm carbonate is evolved leaving pure Ca perchlorate (Ref 4). It is also prepd by heating the tetrahydrate to melting at 100°, gradually increasing the temp until all the w is expelled, and finally drying to constant wt at 250° (Ref 3)

Properties. The Q_f of the anhyd salt was calcd to be −179kcal/mole (Ref 8), and of the aq soln to be −173.94kcal/mole (Ref 6). Effect of heat: Marvin & Woolaver found by thermogravimetric analysis that Ca perchlorate starts to decomp at 220° and decomps rapidly at 400° to give Ca oxide, Ca chloride, and perchloric ac (Ref 5). Chudinov in the USSR states that it decomps betw 320 and 455° with the formn of Ca oxide, Ca chloride, Cl, and O (Ref 7). Solubility: it is sol in w and most org solvs except eth (Ref 3)

$Ca(ClO_4)_2.4H_2O$. Colorl crysts, obtained by evapn of the soln prepd by dissolving Ca oxide or carbonate in aq perchloric ac (Ref 5)

Uses. Incendiary flare compns contg Ca perchlorate are reported in Ref 9

Refs: 1) Gmelin, System No 28, Supp (1957), 578 2) G.S. Sérullas, AnnChimPhys (2) **46**, 304 (1831) 3) H.H. Willard & G.F. Smith, JACS **45**, 286 (1923) 4) G.F. Smith & V.R. Hardy, ZAnorgAllgemChem **223**, 1 (1935) & CA **29**, 5033 (1935) 5) G.C.Marvin & L.B. Woolaver, IEC,AnalEd **17**, 474 (1945) 6) A.F. Vorobev et al, DoklAkadN **135**, 1388 (1960) & CA **55**, 13033 (1961) 7) L.I. Chudinov, IzvVysshikhUchebnZavedenii,KhimIkhimTeknol **5**, 357 (1962) & CA **58**, 1114 (1963) 8) D.E. Wilcox & L.A. Bromley, IEC **55** (7), 32 (1963) 9) C.D. McKinney, Jr & R. Pleasant, "Feasibility Study of a High-Output Gasless Heat Source", Technidyne, Inc Report **RR-68-39** (Oct 1968), AD 393460L (DOD only)

Cesium Perchlorate. $CsClO_4$, mw 232.26, OB to Cs_2O & HCl +13.8%; rhombic crysts which change to a cubic form at 219°; mp 250° with decompn; d 3.327g/cc (Ref 7). Gordon & Campbell say that they found by differential thermal analysis that the phase transition point is 224°, the mp is 575°, and that decompn occurs at 628–30° (Ref 2); CA Registry No 13454-84-7

Preparation. By treatment of chem pure Cs chloride with dil perchloric ac followed by evapn of the soln (Ref 5)

Properties. Its Q_f is −103.86kcal/mole (Ref 3). Its soly in w is 2g/100ml (Ref 5). Its soly in org solvs are given in Ref 7

Uses. Stoichiometric mixts of Cs perchlorate and Al are proposed as incendiary compns. Strands were prepd and found to burn at a press of 10000psi, but not at 125000psi. The burning temps was 3826°K at 14.7psi and 4943° at 1000psi. The burning rate was 0.2ips at 10000psi and 0.09ips at 125000psi (Ref 4). The flame spectra of burning Al/Cs perchlorate mixts has also been studied (Ref 6)

Refs: 1) Gmelin, System No 25 (1938), 168 2) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 3) R.D. Stewart, "Alkali Metal, Ammonium, and Alkaline Earth Perchlorates" in J.C. Schumacher "Perchlorates, their Properties, Manufacture, and Uses", ACS Monograph **146**, Reinhold, NY (1960), 30 6) L.W. Fagg, JQuantSpectryRadiativeTransfer **5**, 321 (1965) & CA **63**, 6430 (1965) 7) ChemRubHdb, 56th Ed (1975–76), B-85

Chromic Perchlorate. $Cr(ClO_4)_3$, mw 350.30, OB to CrO & HCl +28.5%; only the hexahydrate has been prepd as blue-green delq crysts, mp 94° (Refs 1, 5 & 6); CA Registry No 13537-21-8

Preparation. By dissolving hydrated chromic oxide in 20% perchloric ac followed by evapn of the soln (Ref 4)

Effect of Heat. In 1910, R. Roth reported that the blue-green hexahydrate turns green on heating. At 110° w is lost, then perchloric ac, followed by decompn at 210° into chromyl chloride and chromic ac (Ref 3)

It forms a complex with 6 moles of dimethyl sulfoxide which is stable to 195°, but explds betw 200 and 235° (Ref 8)

Chromyl Perchlorate. $CrO_2(ClO_4)_2$, mw 282.89, OB to CrO & HCl +25.5%; a red liq, bp 36° under high vac (Refs 2 & 7). It darkens on cooling to dry ice temp and is stable for about a

month at this temp. It decomps at room temp, explosively in the presence of light; and flames in the presence of org mat (Ref 7)

Refs: 1) Gmelin, System No 52, Part B (1962), 260 2) Ibid, 279 3) R. Roth, "Zur Kenntnis der Perchlorate", München, (1910), thru Mellor, 1st Ed **2** (1922), 403 4) R.F. Weinland & F. Ensgraber, ZAnorgChem **84**, 368 (1913) & CA **8**, 878 (1914) 5) V. Biber et al, JGenChemUSSR **7**, 2658 (1937) & CA **32**, 2044 (1938) 6) I. Neiman, JGenChemUSSR **10**, 723 (1940) & CA **35**, 24334 (1941) 7) M. Schmeisser, AngewChem **67**, 493 (1955) & CA **49**, 15509 (1955) 8) M. Glavas & T. Skerlak, GlasHejTechnolBosneHercegovine, **15**, 41 (1967) & CA **69**, 64250 (1968)

Cobalt Perchlorate (Cobaltous Perchlorate). $Co(ClO_4)_2$, mw 257.83, OB to CoO and HCl +24.8%; red needles, d 3.327g/cc (Ref 28); CA Registry No 13455-31-7

Preparation. The anhyd salt can be prepd by treating the hexahydrate with a large excess of 2,2-dimethoxypropane; and the excess reagent, acet, and Me alc distd off to give two liq phases. The lower phase solidifies to a complex of Co perchlorate with Me alc which can be desolvated by careful heating (Ref 27). *Caution:* prepn of anhyd perchlorates by this procedure has been reported to result in violent explns if the mixts are heated above 65° (Ref 26). An etherate is obtained by the reaction of anhyd Co bromide with Ag perchlorate in eth (Ref 16)

Complexes

Hydrates. $Co(ClO_4)_2.4H_2O$. A violet solid, prepd by dehydration of the hexahydrate at 180°. It decomps rapidly above 180° with the evolution of O, Cl, and H chloride (Ref 4)

$Co(ClO_4)_2.6H_2O$. Long red hexagonal prisms, mp above 100° with decompn (Ref 4). It is prepd by dissolving Co carbonate or oxide in aq perchloric ac followed by evapn of the soln (Ref 10). It detons on percussion and deflgr on rapid heating (Ref 3)

$Co(NH_3)_4(ClO_4)_2$. Violet crysts, prepd by heating the hexa-ammoniate to 80°. It decomps at 170°, rapidly at 220°, and explds at ca 256° (Ref 21)

$Co(NH_3)_6(ClO_4)_2$. Light brown cubic crysts (Refs 9 & 24), prepd by dehydration of the hexahydrate with 2,2-dimethoxypropane followed by the addn of anhyd ammonia to the soln (Ref 24), or by the addn of aq ammonia to a soln of Co perchlorate in O-free w contg an excess of perchloric ac (Ref 9). Expln temp 275°; impact sensy with 1 kg wt, 55cm for 50% explns (MF 20cm); power by Trauzl Pb block expansion test: 1 g, upon deton, made a cavity of 18.6cc (TNT 21.5cc) (Ref 6)

$Co(N_2H_4)_x(ClO_4)_2$. Expln temp 215°; impact sensy for 50% explns with 1 kg wt, 20cm (MF 20cm) (Ref 7)

Uses. At a level of 1%, anhyd Co perchlorate was found to increase the burning rate of a propint formulation from 0.07 to 0.12 inches/sec at 1000psi (Ref 20)

Cobaltic Perchlorate. $Co(ClO_4)_3$. It is known only in the form of complex salts (see below)

$Co(NH_3)_5(ClO_4)_3$. It has been reported to have a high impact sensy and to expld at 320° (Ref 29)

$Co(NH_3)_6(ClO_4)_3$. Yellow cubic crysts (Refs 9 & 12); prepd by the action of perchloric ac on Co hexammino trinitrate in abs nitric ac (Ref 12). Q_f −307kcal/mole (Ref 2); expln temp 360°; impact sensy with 2kg wt, 18cm for 50% explns (LA 10cm); power by sand test: 1 g, when initiated with 0.25g of MF, crushed 39.2g of sand (TNT 42.0g) (Ref 11)

$CoCl(NH_3)_5(ClO_4)_3$. Carmine red lustrous cryst powd (Ref 17); prepd by soln of Co aquopenta-ammino perchlorate in N-hydrochloric ac, evapn of the soln, and recrystn of the solid obtained from dil perchloric ac (Ref 17); or, by treatment of Co chloropenta-ammino dichloride with concd perchloric ac, the soln cooled in ice, the crysts filtd, and dried (Ref 25). Q_f −252.8 kcal/mole (Ref 18, p 428); expln temp 320°; impact sensy with 2kg wt for 50% explns, 21cm (LA 10cm); power by sand test: 1 g, when initiated with 0.25g of MF, crushed 30.6g of sand (TNT 42.0g) (Ref 11)

$CoPH_2(NH_3)_5(ClO_4)_3$. A sample of the dry mat was reported to have expld when touched with a hot Pt wire (Ref 29, p 673)

$CoSCN(NH_3)_5(ClO_4)_2$. Deep rose red needles; prepd by the addn of aq Na perchlorate to an ice cold soln of Co thiocyanato penta-ammino dithiocyanate, the pink solid filtered, and dried (Ref 19); by the addn of aq Na perchlorate to the sulfate (Ref 15); or by the addn of Na thiocyanate to Co aquopenta-ammino diperchlorate

(Ref 23). Expln temp 375°; impact sensy with 2kg wt, 55cm for 50% explns (LA 10cm); power by sand test: 1 g, when initiated with 0.2g of MF, crushed 20.1g of sand (TNT 42.0g) (Ref 11)

$CoH_2O(NH_3)_5(ClO_4)_3$. Deep red cubic crysts (Ref 8); prepd by the action of perchloric ac on Co aquopenta-ammino dichloride (Ref 5). Impact sensy with 2kg wt, 21cm for 50% explns. The expln is described as strong with a visible flame and loud report (Ref 25)

$CoCl_2(NH_3)_4ClO_4$. Impact sensy with 2kg wt, 20cm for 50% explns (RDX 25cm) (Ref 25)

$Co(NO_2)_2(NH_3)_4ClO_4$. Brownish yellow crysts; prepd by the action of perchloric ac on Co dinitrotetra-ammino nitrate in w (Ref 5). Impact sensy with 2kg wt for 50% explns, cis-isomer, 36cm; trans-isomer, 59cm (AP 22cm). The expln is described as strong with a visible flame and loud report (Ref 18)

$Co(SCN)_2(NH_3)_4ClO_4$. Expln temp 335°; impact sensy with 2kg wt, 35cm for 50% explns (LA 10cm); power by sand test: 1 g, when initiated with 0.2g of MF, crushed 13.9g of sand (TNT 42.0g) (Ref 11)

$Co(H_2O)_2(NH_3)_4(ClO_4)_3$. Brownish red octahedral crysts (Ref 13); prepd by the action of aq perchloric ac on Co carbonato tetra-ammino nitrate (Ref 22). Impact sensy with 2kg wt for 50% explns, 24cm. The expln is described as strong with a visible flame and loud report (Ref 25)

Refs: 1) Gmelin, System No 58, Part A (1932), 301 & Supp Part A (1961), 581 2) Gmelin, System No 58, Part B Supp Vol **2** (1964), 331 3) R. Salvadori, Gazz **40 II**, 9 (1910) & CA **5**, 1568 (1911) 4) R. Salvadori, Gazz **42 I**, 458 (1912) & CA **6**, 2216 (1912) 5) F. Ephraim, Ber **56**, 1541 (1923) 6) W. Friederich & P. Vervoorst, SS **21**, 65 (1926) & CA **21**, 1184 (1927) 7) W. Friederich & P. Vervoorst, SS **21**, 123 (1926) & CA **21**, 1184 (1927) 8) O. Hassel & G.B. Naess, ZAnorgAllgemChem **174**, 24 (1928) & CA **22**, 4077 (1928) 9) O. Hassel & H. Kringstad, ZAnorgAllgemChem **209**, 281 (1932) & CA **27**, 2618 (1933) 10) A. Benrath et al, JPraktChem **143**, 298 (1935) & CA **30**, 366 (1936) 11) W.R. Tomlinson et al, JACS **71**, 375 (1949) 12) H. Wendt & G. Jander, ZAnorgChem **259**, 309 (1949) & CA **44**, 5262 (1950) 13) M. Linhard & M. Weigel, ZAnorgChem **260**, 65 (1949) & CA **44** 5753 (1950) 14) C.E.H. Bawn & A.G. White, JCS **1951**, 331 15) A.W. Adams & R.G. Wilkins, JACS **76**, 3380 (1954) 16) G. Monnier, AnnChim **13S**, 45 (1957) & CA **51**, 12734 (1957) 17) M. Linhard & M. Weigel, ZPhysikChem(Frankfurt) **11**, 308 (1957) & CA **51**, 12650 (1957) 18) T.B. Joyner, "Study of Explosive Sensitivity of Cobalt Ammine Complexes", **NOTS 1864, Navord 5639** (Oct 1957), AD 201554 (19) R.L. Carlin & J.O. Edwards, JInorgNuclChem **6**, 217 (1958) & CA **52**, 18054 (1958) 20) R.W. Lawrence & G.A. Zimmerman, USP 3000716 (1961) & CA **56**, 2627 (1962) 21) A.A. Zinov'ev & V.I. Naumova, ZhNeorgKhim **7**, 52 (1962) & CA **56**, 12519 (1962) 22) K.D. Kopple & R.R. Miller, InorgChem **2**, 1204 (1963) 23) K. Schug et al, InorgChem **6**, 2180 (1967) 24) B.B. Wayland & W.L. Rice, InorgChem **6**, 2270 (1967) 25) T.B. Joyner, CanJChem **47**, 2729 (1969) 26) R.C. Dickinson et al, ChemEngNews **48** (28), 6 (1970) 27) R.E. Elson & J.E. Stuckey, JInorgNuclChem **35**, 1029 (1973) & CA **78**, 118607 (1973) 28) ChemRubHdb (1975–76), B-88 29) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 689

Copper Perchlorate (Cupric Perchlorate). $Cu(ClO_4)_2$, mw 262.43, OB to CuO and HCl +24.4%; green monoclinic crysts, mp 82.3° (Ref 21), bp subl under high vac (Ref 13), d at 23° 2.225g/cc (Ref 21), Q_f −19kcal/mole (Ref 9); CA Registry No 13770-18-8

Preparation. The anhyd salt is prepd by heating in vac at 200° a mixt of nitrosyl perchlorate ($NOClO_4$) and either Cu monoxide, dichloride, nitrate, or perchlorate dihydrate. Lower temps favor the formn of mixts of Cu nitrate and perchlorate. The last traces of nitrate can be removed by fractional subln (Ref 13). It is also prepd by the action of nitrosyl perchlorate on powd Cu in org solvs (Ref 14)

Complexes

Hydrates. *$Cu(ClO_4)_2.7H_2O$*. Prepd by the action of perchloric ac on Cu carbonate followed by evapn of the soln (Ref 6); d at 20°, 1.955g/cc (Ref 3)

$Cu(ClO_4)_2.6H_2O$. Light blue delq triclinic crysts, mp 82° (Ref 21). It is prepd by dis-

solving Cu monoxide in aq perchloric ac followed by evapn of the soln (Ref 2), or by allowing the heptahydrate to stand over P pentoxide (Ref 6). It soly in w is 54.3g/100ml of soln (Ref 6), and it is sol in et alc and eth (Ref 21). It is also very sol in dimethylformamide and its UV and visible spectra have been measured in this solv (Ref 10). Its thermal decompn by differential thermal analysis has been studied and shows that the dehydration occurs in two steps at 93 and 282° followed immediately by a strong exotherm at 300–400° (Ref 11)

$Cu(NH_3)_4(ClO_4)_2$. Blue-violet to violet crysts (Ref 7); d at 25°, 1.952g/cc (Ref 6). It is prepd by dehydration of the hexahydrate in an excess of 2,2-dimethoxypropane followed by addn of anhyd ammonia to the soln (Ref 16)

Explosive Properties

Burning Rate. Samples were compressed into Plexiglas tubes 7mm in diam and the burning rate vs press measured. At 1 atm it was found to be ca 1g/sqcm-sec and at 100atm 27g/sqcm-sec (Refs 19 & 20)

Explosion Temperature. 260° (Ref 4), 269.5° (Ref 8)

Impact Sensitivity. 50cm for 50% explns with 1 kg wt (MF 20cm) (Ref 4)

Power by Trauzl Lead Block Expansion Test. 1 g, when initiated by a No 8 blasting cap, formed a cavity of 14.2cc (TNT 21.5cc) (Ref 4)

Sensitivity to Initiation. It is readily initiated by 0.01g of LA (Ref 4)

$Cu(N_2H_4)_2(ClO_4)_2$. A sens solid, expln temp ca 35° (Ref 5)

Uses: Addn of 1 mole % of anhyd Cu perchlorate lowers the decompn point of K perchlorate from 618 to 525° (Ref 15). Addn of 0.015 mole % to AP lowers the induction period for its decompn at 233° from 27 ± 4 to 6 ± 2 mins (Ref 17). Cu perchlorate has been patented as a burning rate modifier in solid proplnts (Ref 12)

Refs: 1) Gmelin, System No 60, Part B-1 (1958), 337 2) G.S. Sérullas, AnnChimPhys (2) **46**, 306 (1831) 3) ICT Vol **1** Index No 943 (1926), 122 4) W. Friederich & P. Vervoorst, SS **21**, 65 (1926) & CA **21**, 1184 (1927) 5) W. Friederich & P. Vervoorst, SS **21**, 123 (1926) & CA **21**, 1184 (1927) 6) R. Portillo & L. Albertola, AnalesSocEspanFisQuim **28**, 1117 (1930) & CA **25**, 261 (1931) 7) F. Rosenblatt, ZAnorgAllgemChem **204**, 351 (1932) & CA **26**, 2933 (1932) 8) J. Amiel, CR **200**, 672 (1935) & CA **29**, 2470 (1935) 9) F.D. Rossini, "Selected Values of Chemical Thermodynamic Properties", NBS Circular 500 (1 Feb 1952), 209 10) R.D. Pflaum & A.I. Popov, AnalChimActa **13**, 165 (1955) 11) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 12) R.W. Lawrence & G.A. Zimmerman, USP 3000716 (1955) & CA **56**, 2627 (1962) 13) B.J. Hathaway, ProcChemSoc **1958**, 344 14) B.J. Hathaway & A.E. Underhill, JCS **1960**, 3705 15) D.A. Anderson & E.S. Freeman, JInorgNuclChem **7**, 1471 (1965) & CA **63**, 5225 (1965) 16) B.B. Wayland & W.L. Rice, InorgChem **6**, 2270 (1967) 17) Yu.P. Savintsev et al, KinetKatal **9**, 542 (1968) & CA **69**, 61887 (1968) 18) N.V. Kirvtsov & V.Ya. Rosolovskii, ZhNeorgKhim **13**, 317 (1968) & CA **68**, 99323 (1968) 19) V.V. Gorbunov et al, FizGoreniyaVzryva **7**, 607 (1971) & CA **77**, 77440 (1972) 20) V.V. Gorbunov & L.F. Shmagin, FizGoreniyaVzryva **8**, 523 (1972) & CA **78**, 89293 (1973) 21) ChemRubHdb (1975–76), B-92

Fluorammonium Perchlorate (Fluoroammonium Perchlorate). FNH_3ClO_4, mw 135.48, OB +35.4%; white hygr solid, mp 104–5° with decompn; sol in esters, nitriles, nitroalkanes, and tetrahydrofuran, insol in hydrocarbons and halocarbons; impact sensy similar to RDX. Prepd by the hydrolysis of et or iso-Pr N-fluorocarbamate in a soln of anhyd perchloric ac in chlf

Refs: 1) Gmelin, not found 2) V. Grakauskas et al, JACS **90**, 3839 (1968)

Fluorine Perchlorate. (Supplements article in Vol **6**, F135-R). From hydrolysis data the Q_f was calcd to be +37.6 ± 9.0kcal/mole (Ref 2); CA Registry No 10049-03-3

Refs: 1) Gmelin, System No 6, Part B-2 (1969), 587 2) J.D. Brezeale & R.O. McLaren, "Thermochemistry of Oxygen-Fluorine Bonding", United Technology Corp **UTC 2002-FR** (1963), AD 402889

Hydrazine Perchlorate. (See in Vol **7**, H200-R); CA Registry No 13762-80-6

Hydrazine Diperchlorate (Hydrazinium Diperchlorate; in Gmelin it is called **Hydrazonium Hydroperchlorate, HDP).** $N_2H_4.2HClO_4$, mw 232.97, OB +34.3%; white crysts, mp 191°, d 2.21g/cc (Ref 4); CA Registry No 13812-39-0

Preparation. HDP was first prepd by the interaction of equimolar amts of aq Ba perchlorate and hydrazine sulfate, the pptd Ba sulfate filtered off, and the filtrate evapd on a w bath until crystn occurs (Ref 2). It has also been prepd by the interaction of 2 moles of aq perchloric ac and 1 mole of hydrazine hydrate followed by evapn of the w or its azeotropic removal by distn with trichloroethylene (Ref 6), or by sweeping hydrazine vapors into 70% perchloric ac with dry N (Ref 7)

Properties

Heat of Formation. −70 ± 1kcal/mole (Ref 3)

Impact Sensitivity. Explds with a hammer blow (Ref 2)

Thermal Stability. Impure prepns turn yellow on standing at RT (Ref 2). When heated it shows a slow press increase starting at 120° due to evolution of 1 mole of perchloric ac followed by an extremely sharp press rise due to the decompn of the monoperchlorate (Ref 5)

Uses. It has been proposed as a high energy proplnt ingredient, but high cost and hygroscopicity have precluded general acceptance (Ref 4)

Refs: 1) Gmelin, System No 23 (1936), 557 2) J.W. Turrentine, JACS **37**, 1122 (1915) 3) R. Caruso et al, JPhysChem **69**, 1716 (1965) 4) J.B. Levy & G. vonElbe, "Research on Deflagration of High-Energy Solid Oxidizers", ARC Final Tech Report (1965), AD 628035 5) C.J. Grelecki & W. Cruice, "Thermal Decomposition of Hydrazinium Monoperchlorate and Hydrazinium Diperchlorate", in "Advanced Propellant Chemistry", ACS Advances in Chemistry No **54**, ACS, Wash, DC (1966), 73 6) J.E. Paustian et al, BritP 1122422 (1968) & CA **69**, 78858 (1968) 7) E.K. Weinberg & F.J. Loprest, BritP 1122852 (1968) & CA **69**, 78861 (1968)

Hydroxylamine Perchlorate (Hydroxylammonium Perchlorate, HAP). (See Vol **7**, H245-R); CA Registry No 15588-62-2

Iron Perchlorate (Ferrous Perchlorate). $Fe(ClO_4)_2$, mw 254.75, OB to FeO and HCl +25.1%. It is only known in the form of hydrates, the most well known being the hexahydrate, $Fe(ClO_4)_2.6H_2O$; long green crysts, stable in air (Ref 2), Q_f calcd to be −56kcal/mole (Ref 5); CA Registry No 13933-23-8

Preparation. It is prepd by the action of 70% perchloric ac on Fe sulfide (Ref 2), or sulfate (Ref 7) followed by evapn of the soln. *Caution:* strong heating of the mixt of perchloric ac and Fe sulfate was reported to result in a violent expln; gentle heating is recommended (Ref 7). An etherate was prepd by the interaction of Ag perchlorate and Ag dibromide in eth (Ref 3)

Uses. The addn of 0.03 to 0.29 mole % of the hexahydrate lowers the decompn point of AP to 100° (Ref 6). It has been patented as a burning rate accelerator in solid proplnts (Ref 4)

Refs: 1) Gmelin, System No 59, Part B (1930), 320 2) F. Lindstrand, ZAnorgAllgemChem **230**, 187 (1936) & CA **31**, 2115 (1937) 3) G. Monnier, AnnChim(Paris) **13S**, 45 (1957) & CA **51**, 12734 (1957) 4) R.W. Lawrence & G.A. Zimmerman, USP 3000716 (1955) & CA **56**, 2627 (1962) 5) D.E. Wilcox & L.A. Bromley, IEC **55** (7), 32 (1963) 6) Yu.P. Savintsev et al, KinetKatal **9**, 542 (1968) & CA **69**, 61887 (1968) 7) R.L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 646

Lead Perchlorate. $Pb(ClO_4)_2$, mw 406.09, OB to PbO & HCl +15.8%. The anhyd salt is a white solid which is extremely hygr and can only be handled in the dry atm of a glove box (Ref 3), mp 270–5° with decompn (Ref 3); d_4 at 25°, 4.84g/cc (Ref 1); CA Registry No 13637-76-8

Preparation. The anhyd salt is prepd by drying the trihydrate over P pentoxide in a vacuum at 65° for 19 hours, then at 100° for 10 hours, and finally at 120° for 14 hours (Ref 3). More recently workers in the USSR have reported a similar proc in which the hydrate is dried at 2–4mm as the temp is raised slowly from 10 to 200–20° (Ref 4)

Effect of Heat. Anhyd Pb perchlorate is stable up to 200°, begins to decomp at ca 250° with the evolution of Cl and O, and decomps completely above 275° (Ref 3). The Russian workers

found that the decompn prods are Pb monoxide, Pb dichloride, Cl, and O (Ref 4)
$Pb(ClO_4)_2.3H_2O$. White rhombic crysts (Ref 6), mp 83–4° (Ref 3); bp, decomps ca 100°; d 2.6 g/cc (Ref 6). It is prepd by dissolving Pb carbonate in aq perchloric ac followed by evapn of the soln until crysts appear (Ref 2), or by allowing the anhyd salt to stand in a moist atm (Ref 3). It is very sol in w and alcs (Ref 6). An almost satd soln in me alc was reported to have expld violently upon manipulation. Care in handling such solns is recommended (Ref 3)
Refs: 1) Gmelin, System No 47, Part C-1 (1969), 340 2) G.S. Sérullas, AnnChimPhys(2) **46**, 306 (1831) 3) H.H. Willard & J.L. Kassner, JACS **52**, 2391 (1930) 4) A.A. Zinov'ev & N.V. Krivtsov, ZhNeorgKhim **5**, 1418 (1960) & CA **56**, 4345 (1962) 5) D.A. Anderson & E.S. Freeman, JInorgNuclChem **27**, 1471 (1965) & CA **63**, 5225 (1965) 6) ChemRubHdb (1975–76), B-105

Lithium Perchlorate (updates article in Vol **7**, L45). OB to Li_2O and HCl +60.0%; CA Registry No 7791-03-9
Preparation. The anhyd salt is prepd by dehydration at 300° of the trihydrate, which is prepd by evapn of solns prepd by the interaction of Li sulfate and Ba perchlorate (Ref 4), or by the action of aq perchloric ac on an excess of Li carbonate (Ref 2). Both the anhyd salt and the trihydrate are coml compds, and their manuf has been reviewed (Ref 5). Workers in the USSR have prepd it by the electrolysis of aq Li perchlorate using Pt electrodes (Ref 3)
Uses. Addnl refs to the use of Li perchlorate in oxygen producing compns (oxygen candles) are in Refs 6 & 7. These compns have been proposed as substitutes for compressed or liq oxygen in enclosed spaces such as spacecraft cabins and submarines (Ref 6). A mixt of 35g of amor Si and 65g of Li perchlorate was compressed into a cylinder at 2000psi and ignited with an Ignitacord fuse to give a dense white smoke whose obscuring power was 5000cu ft/lb (Ref 8); a similar mixt of 6 parts of powd B and 4 parts of Li perchlorate also is a smoke generating compn (Ref 9).
Refs: 1) Gmelin, System No 20 (1927), 166, Supp (1960), 404 2) G. Scatchard et al, JACS **56**, 805 (1934) 3) N.A. Izgaryshev & M.G. Khachaturyan, DoklAkadN **59**, 1125 (1948) & CA **42**,7165 (1948) 4) T.E. Moore et al, JPhysChem **59**, 90 (1955) 5) J.E. Reynolds & T.W. Clapper, ChemEngrgProg **57** (12), 94 (1961) 6) D.A. Keating, "A Study of the Application of Lithium Chemicals to Air Regeneration Techniques in Manned, Sealed Environments", Foote Mineral Co Tech Documentary Rept **AMRL-64-1** (Feb 1964), AD 435815 7) P.R. Gustafson & R.R. Miller, USP 3174936 (1965) & CA **62**,12960 (1965) 8) G.A. Lane & W.A. Smith, USP 3471345 (1969) & CA **72**, 4848 (1970) 9) G.A. Lane et al, USP 3475237 (1969) & CA **72**, 57363 (1970)

Magnesium Perchlorate. $Mg(ClO_4)_2$, mw 223.21, OB to MgO & HCl +28.7%; white delq crysts, melts with decompn over a wide temp range betw 244 & 520° (Ref 10); d at 18° 2.21g/cc (Ref 15); Q_f −140.6kcal/mole (Ref 9); CA Registry No 10034-81-8
Preparation. The anhyd salt is best prepd by drying the hexahydrate first in a stream of dry air at 170°, then in a vacuum over P pentoxide at 250° to remove the last traces of w (Ref 2). It may also be prepd by heating an intimate mixt of AP and Mg carbonate at 200° and 1–10mm (Ref 5)
Effect of Heat. The anhyd salt was found to decomp betw 320 & 450°. The decompn is autocatalyzed by the O evolved, and the prods are Mg oxide, Mg chloride, O and Cl (Ref 12). The addn of 1.75 mole % to AP raises its decompn rate at 273° from 1.8 to 5.9 x 10^{-4}g/min; and a 20 mole % mixt decomps at 7.9 x 10^{-2} g/min (Ref 13)
Hydrates. The only important hydrate is the *hexahydrate*, $Mg(H_2O)_6(ClO_4)_2$, long rhombic needles, mp 185–90° (Ref 15), d at 25°, 1.970 g/cc (Ref 4); prepd by dissolving pure Mg oxide in dil perchloric ac, evapg the soln until fumes appear, and cooling. The solid crysts are filtered off and recrystd from w (Ref 2)
Impact Sensitivity. On the ERL machine the anhyd salt had a 50% expln height of 254cm with sandpaper and over 320cm without sandpaper. A mixt with 2% sugar had 50% expln heights of 135cm and over 320cm respectively (Ref 11)

Solubilities. The anhyd salt is very sol in w, me alc, et alc, pr alc, Bu alc, acet, and et acetate; but only sl sol in eth (Ref 3)

Uses. Anhyd Mg perchlorate has found widespread use as a drying agent under the trade names Anhydrone and Dehydrite. This use has been reviewed in a book by G.F. Smith (Ref 6). It has an advantage over many other drying agents as it can be readily regenerated by dehydration at 250–300° (Ref 12). It is especially useful in packing drying towers for drying gases. Extreme care must be taken, however, in drying org compds as explns can results. For example; contact of anhyd Mg perchlorate with a hydrocarbon gas contaminated with Bu fluoride caused a purple discoloration of the solid, followed almost immediately by an expln (Ref 7). Upon attempted regeneration of a sample of Mg perchlorate which had been used to dry olefins, it expld when the temp reached 220° (Ref 8). On another occasion, upon addn of tri-methyl phosphite to anhyd Mg perchlorate, the mixt expld with injury to the operator (Ref 12a). Anhyd Mg perchlorate was added to a mixt of Bu acrylate and acrylonitrile, and the mixt polymerized in a 2.75 inch mold to give an illuminating flare of 2 million CP (Ref 14)

Refs: 1) Gmelin, System No 27, Part B (1937), 154 2) H. H. Willard & G.F. Smith, JACS **44**, 2255 (1922) 3) H.H. Willard & G.F. Smith, JACS **45**,295 (1923) 4) ICT Vol **1** (1926), 141 5) G.F. Smith & V.R. Hardy, JAnorgAllgemChem **223**, 1 (1935) & CA **29**, 5033 (1935) 6) G.F. Smith, "Dehydration Studies Using Anhydrous Magnesium Perchlorate", G.F. Smith Chem Co, Columbus, O (1935) & CA **29**, 6132 7) M.J. Stross & G.B. Zimmerman, IECNewsEd **17**, 30 (1939) & CA **33**, 1940 (1939) 8) P.M. Heertjes & J.P.W. Houtman, ChemWeekblad **38**, 85 (1941) & CA **36**, 5359 (1942) 9) F.D. Rossini et al, "Selected Values of Chemical Thermodynamic Properties", NBS Circular 500 (Feb 1952), 376 10) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 11) G. Svadeba & S. Duck, "Sensitivity of Explosives to Impact, Period 1 July 1953 to 1 November 1954", NOL **NAVORD 3955** (Nov 1955), 5, AD 068500 12) L.I. Chudinova, IzvVysshikhUchebnZavedenii,KhimIKhimTeknol **5**, 357 (1962) & CA **58**, 1114 (1963) 12a) L.M. Jercinovic & D.L. Rost, JChemEd **45**, 750 (1968) 13) R.J. Acheson & P.W.M. Jacobs, JPhysChem **74**, 281 (1970) 14) G.S. Handler & D. Sbrocca, "Castable Illumination Flares", **NWC-TN-4543-03-72** (Mar 1972), AD 902089 15) ChemRubHdb (1975–76), B-109

Manganese Perchlorate (Manganous Perchlorate). $Mn(ClO_4)_2$, mw 253.84, OB to MnO & HCl +25.2%; the hexahydrate is obtained as pale rose needles (Ref 2); Q_f calcd to be –90kcal/mole (Ref 5); CA Registry No 13770-16-6

Preparation. The *hexahydrate,* $Mn(H_2O)_6(ClO_4)_2$, has been prepd by dissolving Mn hydroxide or carbonate in dil perchloric ac followed by evapn of the soln until crysts appear (Ref 2). Attempts to dehydrate it by heating with an excess of 2,2-dimethoxypropane resulted in severe explns when the temp was raised above 65° (Ref 6)

Effect of Heat. The hexahydrate loses 2 moles of w at 115° to form a tetrahydrate which decomps with formn of Mn dioxide at 145–50°. Around 195° it explds (Ref 3)

Uses. A Mn perchlorate (degree of hydration unspecified) has been patented as a burning rate accelerator for solid proplnts (Ref 4)

Refs: 1) Gmelin – not found 2) G.S. Sérullas, AnnChimPhys (2) **46**, 304 (1831) 3) N.V. Sidgwick, "Chemical Elements and their Compounds", Vol **2**, Clarendon Press, Oxford (1950), 1285 4) R.W. Lawrence & G.A. Zimmerman, USP 3000716 (1955) & CA **56**, 2627 (1962) 5) D.E. Wilcox & L.A. Bromley, IEC **55** (7), 32 (1963) 6) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1970), 457

Mercury Perchlorate (Mercuric Perchlorate). $Hg(ClO_4)_2$, mw 399.49, OB to HgO & HCl +16.0%; white microcryst solid (Ref 2); Q_f –17kcal/mole (Ref 4); CA Registry No 7616-83-3

Preparation. The anhyd salt is prepd by the addn of a soln of perchloric ac in trifluoroacetic ac to that of a Hg salt in the same solv, followed by careful evapn of the solv until crysts form (Ref 2)

Uses. It has been reported to be an efficient

catalyst for the decompn and expln of AP (Ref 3)
Refs: 1) Gmelin, System No 34, Part B02 (1967), 705 2) G.S. Fugioka & G.H. Cady, JACS **79**, 2451 (1957) 3) F. Solymosi, MagyKemFoly **73**, 366 (1967) & CA **68**, 6735 (1968) 4) N.V. Krivstov & V.Ya. Rosolovski, ZhNeorgKhim **13**, 317 (1968) & CA **68**, 99323 (1968)

Nickel Perchlorate (Nickelous Perchlorate). $Ni(ClO_4)_2$, mw 257.61, OB to NiO & HCl +24.8%; a yellow solid, d 3.4g/cc (Ref 20); CA Registry No 13637-71-3
Preparation. The anhyd salt is prepd by treating the hexahydrate with a large excess of 2,2-dimethoxypropane. Two phases are obtained with most of the Ni perchlorate in the lower phase. After several hours a solid seps from this phase which is filtered off and dried to give Ni perchlorate contg ca 0.5% w (Ref 20).
Caution: On one occasion, in the use of this proc, a violent expln occurred when the mixt was heated above 65° (Ref 18). It has also been prepd by dissolving Ni oxide or carbonate in anhyd trifluoroacetic ac followed by addn of anhyd perchloric ac. The pptd solid is filtered off and dried in a vacuum to remove trifluoroacetic ac (Ref 12)
Complexes. Hydrates with 9, 7, 6, 5, 4, & 2 moles of w are known, but only the *hexahydrate*, $Ni(H_2O)_6(ClO_4)_2$ is of any importance. It is obtained as long green hexagonal needles, mp 209° (Ref 8), by the action of Ni sulfate on Ba perchlorate; or by dissolving Ni hydroxide (Ref 14), nitrate, or carbonate (Ref 13) in dil perchloric ac followed by evapn of the soln, filtering, and drying the crysts formed. It is very sol in dimethylformamide, and its visible spectrum has been measured in this solv (Ref 10)
$Ni(NH_3)_6(ClO_4)_2$. Lavender crysts, prepd as follows: to a soln of 23.8g of Ni dichloride and 5.4g of Amm chloride in 125ml of w is added 14.0g of Na perchlorate in 50ml of w, followed by the slow addn with stirring of 60ml of concd aq ammonia. The mixt is chilled for 4 hours in an ice bath and the solid filtered to give 48% of the hexaammoniate which is free of chloride (Ref 11). It also can be prepd by treatment of an O-free aq soln of Ni perchlorate contg an excess of perchloric ac with aq ammonia, filtering off the crysts, and drying (Ref 15); or by the dehydration of Ni perchlorate hexahydrate with an excess of 2,2-dimethoxypropane and adding anhyd ammonia to this soln (Ref 16). The compd is very insol in w and can be used for the quant detn of Ni (Ref 9)
Explosive Properties.
Burning Rate. 1.90g/sqcm/sec at 60atm. The rate is almost independent of press betw 1 and 100atm (Ref 19)
Detonation Sensitivity. It is readily detond by a No 8 blasting cap contg 0.01g of LA (Ref 3)
Detonation Velocity. 5303m/sec (Ref 4)
Explosion Temperature. 275° (Ref 3)
Heat of Combustion. 260kcal/mole (Ref 19)
Impact Sensitivity. With a 1 kg wt, 55cm for 50% explns (MF 20cm) (Ref 3); with a 2kg wt, 9 inches for 50% explns (Ref 11)
Power by Trauzl Lead Block Expansion Test. A 1 g sample, on deton, formed a cavity of 19.7cc (TNT 21.5cc) (Ref 3)
Thermal Decomposition. Betw 80 & 140° a reversible deamination occurs with the loss of 4 moles of ammonia, and betw 240 & 280° an irreversible exothermic reaction occurs resulting finally in an expln at ca 280°. A residue of Ni oxide contg some chloride is left (Ref 17)
Hydrazine Complex. A complex with the empirical compn $Ni(ClO_4)_2.Ni(OH)ClO_4.5N_2H_4.H_2O$ has been reported to be a pale blue solid (Ref 5) with the following expl props:
Effectiveness as a Detonator. Wts of the subs which will initiate the following expls are: Tetryl 0.10g, TNT 0.15g, & TNAns 0.45g (Ref 7)
Explosion Temperature. 175° (Ref 6)
Impact Sensitivity. With a 1 kg wt, 19cm for 50% explns (MF 20cm) (Ref 6)
Power by Trauzl Lead Block Expansion Test. A 1 g sample formed a cavity of 19.5cc on deton (TNT 21.5cc) (Ref 6)
Refs: 1) Gmelin, System No 57, Part B-2 (1966), 596 2) P. Groth, PoggAnn **133**, 213 (1868) 3) W. Friederich & P. Vervoorst, SS **21**, 65 (1926) & CA **21**, 1184 (1927) 4) Ibid, SS **21**, 84, (1926) & CA **21**, 1184 (1927) 5) Ibid, SS **21**, 103 (1926) & CA **21**, 1184 (1927) 6) Ibid, SS **21** 123 (1926) & CA **21**, 1184 (1927) 7) Ibid, SS **21**, 143 (1926) & CA **21**, 1184 (1927) 8) A. Benrath et al, JPraktChem **143**, 298 (1935) & CA **30**, 367 (1936)

9) F. Ephraim, "Inorganic Chemistry", 6th ed revised by P.C.L. Thorne & E.R. Roberts, Interscience, NY (1954), 403 10) R.T. Pflaum & A.I. Popov, AnalChimActa **13**, 165 (1955) 11) Anon, RHC(H) Report No **P-54-20**, "Quarterly Progress Report on Organic Chemistry", Contr No W-01-021-ORD-334, (25 Jan 1955), 30 12) G.S. Fujioka & G.H. Cady, JACS **79**, 2451 (1957) 13) H. Freund & C.R. Schneider, JACS **81**, 4780 (1959) 14) S.D. Ross, SpectrochimActa **18**, 228 (1962) 15) A.A. Zinov'ev & V.I. Naumova, ZhNeorgKhim **7**, 52 (1962) & CA **56**, 12519 (1962) 16) B.B. Wayland & W.L. Rice, InorgChem **6**, 2270 (1967) 17) R.A.F. Sherriff & A.K. Galway, JCS A **1967**, 1705

Nitrosyl Perchlorate. $NOClO_4$, mw 120.46, OB +36.5%; white hygr orthorhombic crysts (Ref 3), d 2.162g/cc (Ref 4); CA Registry No 15605-28-4

Preparation. It was first prepd by passing a mixt of N monoxide and N dioxide into 72% perchloric ac, the mixt evapd until the temp rose to 140° and dense white fumes were evolved, and cooled. The solid which sepd was found to be a monohydrate of nitrosyl perchlorate which was dried in a vacuum over P pentoxide to give the anhyd salt (Ref 2). More recently it was obtained by the action of an excess of liq dinitrogen tetroxide on anhyd Mg perchlorate (Ref 5)

Properties

Reactions. It reacts with w to form N oxides, with me alc to form NMe, and explds on contact with dry eth or amines (Ref 2)

Thermal Decomposition. Workers at the Hebrew Univ, Israel found that the thermal decompn of nitrosyl perchlorate at 100–140° results in an equilibrium being established with nitryl perchlorate and the decompn prods of both compds (nitronium). N dioxide, Cl dioxide, and O were found to be the final decompn prods isolated (Ref 6)

Refs: 1) Gmelin, System No 6, Part B-2 (1969), 533 2) K.H. Hofmann & G.A. Zedtwitz, Ber **42**, 2031 (1909) 3) L.J. Klinkenberg, Rec **56**, 749 (1937) & CA **31**, 7307 (1937) 4) K. Cruse et al, ZAnorgChem **259**, 154 (1949) & CA **44**, 5251 (1950) 5) J.D. Archambault et al, JInorgNuclChem **17**, 130 (1961) & CA **55**, 21950 (1961) 6) A. Glasner et al, JInorgNuclChem **31**, 3395 (1969) & CA **72**, 6587 (1970)

Nitryl Perchlorate (Nitroxyl Perchlorate, Nitronium Perchlorate). NO_2ClO_4, mw 161.45, OB +29.7%; colorl monoclinic hygr crysts; mp decomps above 135° without explg; CA Registry No 17495-81-7

Structure. Earlier workers considered it to be the mixed anhydride of nitric and perchloric acids (O_2NOClO_4) (Ref 3), but later, as a result of X-ray (Ref 5) and Raman spectrographic work (Ref 8), it was shown to be an ionic salt with distinct NO_2^+ and ClO_4^- ions present in the cryst lattice

Preparation. It was first prepd in an impure form by Hantzsch who isolated a cryst solid when anhyd nitric and perchloric acids were mixed. He reported the solid to be $ON(OH)_2^+.ClO_4^-$ (Ref 2), but later work by Goddard and coworkers showed this solid to be a mixt of nitronium perchlorate and perchloric ac monohydrate (Ref 4). It is best prepd by distilling anhyd perchloric ac onto an excess of dry dinitrogen pentoxide at –80°, the mixt allowed to warm to room temp, and the mixt pumped under vacuum for 2 days to remove volatiles. The residue was shown by analysis to be a mixt of 89 mole % nitronium perchlorate and 11 mole % perchloric ac hydrate. Pure nitronium perchlorate was obtained by repeating the expt in NMe and using a large excess of dinitrogen pentoxide (Ref 6)

Properties. It is very sol in nitric ac and may be recrystd from this solv (Ref 7). It is a strong oxidizing and nitrating agent, and flames or explds on contact with org compds. In soln in NMe it is less reactive and can be used in this solv as a nitrating agent. Benz, for example, is instantly nitrated to NB on contact with a NMe soln of nitronium perchlorate, but further nitration takes place very slowly (Ref 7)

Uses. Attempts have been made to use nitronium perchlorate as a high energy propInt ingredient, but incompatibility with other ingredients and hygroscopicity have combined to hinder such use (Ref 9)

Refs: 1) Gmelin, System No 6, Part B-2 (1969), 536 2) A. Hantzsch, Ber **58B**, 941 (1925)

3) W.E. Gordon & J.W.T. Spinks, CanJRes B **18**, 358 (1940) & CA **35**, 1336 (1941)
4) D.R. Goddard et al, Nature **158**, 480 (1946)
5) E.G. Cox et al, Nature **162**, 259 (1948)
6) D.R. Goddard et al, JCS **1950**, 2550
7) R.D. Stewart, "Miscellaneous Perchlorates" in J.C. Schumacher, ed, "Perchlorates, their Properties, Manufacture, and Uses", ACS Monograph **146**, Reinhold, NY (1960), 61 8) J.W. Nebgen et al, InorgChem **4**, 1796 (1965)
9) C.R. Guibert et al, "Studies of Complex Perchlorates", Callery Chem Co Final Report (1966), p 2, AD 634105

Potassium Perchlorate. $KClO_4$, mw 138.55, OB to K_2O & HCl +46.2%; white rhomb cryst solid which is transformed to a cubic form at 300° and melts at 588° with decompn (Ref 16); d at 0°, 2.53574 ± 0.0001g/cc (Ref 11); Q_f −111.29kcal/mole (Ref 14); CA Registry No 7778-74-7

Preparation. The early history of the prepn of K perchlorate by the action of acids on K chlorate is reviewed in Ref 3. These authors found that treatment of 2–5g of K chlorate with 50ml of concd sulfuric ac gave an 11% yield of K perchlorate. The sulfuric ac must be added slowly with cooling to the K chlorate, or explns may result. Similarly, nitric ac gave a yield of 15–30%, 85% phosphoric ac gave a yield of 15%, and Cr trioxide gave a yield of 12–15%. Org acids failed to yield any perchlorate when heated with K chlorate (Ref 3). It can also be prepd by heating a mixt of solid K chloride with nitrosyl perchlorate ($ONClO_4$). Nitrosyl chloride is evolved and a residue of K perchlorate is left (Ref 26). On a coml scale, K perchlorate is prepd by mixing hot aq solns of Na perchlorate and K chloride. Upon cooling, Na chloride is pptd and filtered off. Upon further cooling, the K perchlorate seps and is recrystd from hot w (Ref 18). The manuf has been reviewed (Ref 21). Prior to 1958 prodn was betw 784 and 4370 tons/yr at a cost of 18.5–20 cents/lb (Ref 19, p 87)

Impact Sensitivity. K perchlorate and mixts of it with 1% ferric oxide, Mn dioxide, sugar, Amm dichromate, and a 50/50 mixt with Amm nitrate were all insensitive to impact (over 320cm) with a 2.5kg wt (Ref 13)

Solubility. In w at 0° it is 0.75; at 100°, 18.2; and at 265°, 70g/100ml of satd soln. These values are smoothed data from several earlier sources (Ref 27, p 178). Solys in org solvs are given in Ref 27, p 187

Effect of Heat. The thermal decompn is said to be sharp at 510° to give K chloride and O (Ref 7). Bircumshaw & Phillips, however, state that the decompn is complicated and irreproducible in a vacuum, with Cl as well as O and K chloride being formed (Ref 8)

Explosion Temperature. The expln temp of 80/20 mixts of K perchlorate with org compds was found to be: ethylene glycol, 240°; polyester resin, 290°; and cotton linters, 245°. The addn of 1% K chloride, Li chloride, or Li bromide failed to change these temps (Ref 15)

Uses (see also under Perchlorate Propellants and Explosives):

Delay Compositions (comps used in fuses and other timing devices and which have an exactly predetd burning rate). A mixt of 54.5% Ba chromate, 30.5% powd W, 10% K perchlorate, and 5% Si dioxide has a Q_r of 358cal/g, and burning rates of 29.7sec/inch at 15psi and 18.7 sec/inch at 1200psi (Ref 4). Similar mixts of 44.5–49.5% Ba chromate, 35–9% powd W, 10% K perchlorate, 5% diatomaceous earth, and 1.0–1.5% Ba or Zn stearate have burning rates of 11.8768–12.8962sec/inch at −65°F, and 12.5313–13.1420sec/inch at 71°F (Ref 34). Compns of 54% Zr/Ni alloy, 31% Ba chromate, and 15% K perchlorate have burning rates which can be varied by using alloys of 70/30, 50/50, or 30/70 Zr/Ni. The burning rates are ca 1:2:3 respectively (Ref 22, p 283). Specs for mil W delays are in **MIL-T-23132** (1961). A similar series of fuse powder contg mixts of Zr/Ni and Ti/Ni alloys, Ba chromate, and K perchlorate are described in Ref 31. The burning rates can be varied betw 2 and 25sec/inch by changing the compn

Flares, Signaling Devices, and other Pyrotechnics. A large number of formulations contg K perchlorate have been reported. Some devices which use these are: red RR signal flares (Refs 2 & 22, p 275); parachute flares (Ref 6); "stars" for use in signaling pistols (Very pistols) (Refs 5 & 22, p 275); variously colored flares (Refs 19, pp 197–8 & 22, p 275); "stars" and other components of display fireworks (Refs 16 & 32);

and "whistlers" (Ref 22, p 280)

Combustible Cartridge Cases. Cotton gauze is impregnated with a mixt of 70% K perchlorate, 14.5% et cellulose, 9.6% Neolyn 23 curing agent, and 6.2% plasticizer; the impregnated cloth is formed into cartridge cases, and cured to give combustible cartridge cases (Ref 29)

Igniters. A pellet composed of 26.5% K perchlorate, 16.6% Ba nitrate, 53.9% 50/50 Zr/Ni alloy, and 3.0% et cellulose can be used to ignite solid proplnt grains (Ref 25). A series of mixts of K perchlorate with powd metals and other oxidizable mat were examined as substitutes for BlkPdr as a gun primer. Most of the mixts tested were found to be satisfactory and to be compatible with brass and other metals (Ref 9)

Incendiary Compositions. Stoichiometric mixts of K perchlorate with metals and oxidizable mat have been proposed as incendiaries of the Thermit type and have heats of reaction as follows: Al dust 2504, powd Mg 2429, red P 1477, powd S 705 and powd C (lampblack) 1118cal/g (Ref 4). A mixt of 12.5% K perchlorate, 75% powd Zr, and 12.5% of a 50/50 Al/Mg alloy is reported to be a readily-ignited incendiary (Ref 20). Mixts of powd Al and/or powd Fe with K perchlorate with 1.5–2% NC as a binder are also good incendiaries (Ref 35). A mixt of 35% Ca silicide, 35% powd Sb, 30% K perchlorate, and 5% NC is listed as a fire starter mixt (Ref 22, p 282). A mixt of 40 parts of powd Al, 60 parts of K perchlorate, and 4 parts of chlorinated rubber were placed in a hole drilled in concrete and ignited, resulting in the concrete being shattered without any expln (Ref 33)

Photoflash Compositions. Workers at PicArsn have investigated a series of mixts of K perchlorate with powd metals for use as photoflash compns. Info on candlepower, time to peak luminosity, and duration of flash, as well as performance at sea level and 1 x 10^5 feet, are given for each compn (Ref 23). A standard mil photoflash compn is given as 40% atomized Al, 30% Ba nitrate, and 30% K perchlorate (Ref 22, p 274)

Smoke Generating Compositions. A series of mixts of K perchlorate with powd Zn, hexachloroethane, and/or C black is reported in Ref 12. Temp stability info is also included in this Ref. A compn of 42.7% K perchlorate, 22.3% powd Al, 18.1% hexachloroethane, and 16.9% Li carbonate forms a dense smoke on ignition which is hygroscopic, giving a denser smoke cloud in moist air (Ref 28). Another somewhat different compn of 50–80 parts of sulfamic ac and 20–50 parts of K perchlorate is claimed to produce dense smoke on combustion (Ref 17)

Tracers. To a mixt of 34 parts of Laminac resin, 4 of benzyl alc, 2 of Co naphthenate, and 4 of me et ketone peroxide is added an equal wt of a mixt of 1 part of powd Mg and 2 of K perchlorate. The mixt is formed and cured to give a tracer for following visibly the path of rockets (Ref 24). In Ref 16, p 275 are given formulations for mixts contg K perchlorate which is used in tracer ammo for automatic small arms. Tracer compns contg powd Zr which are suitable for modern HV small arms are discussed in Ref 30

Specification. The requirements for mil grade material are covered in Mil Spec MIL-P-217A, Amendment 1 (1966). Two grades are listed, Grade A and Grade B; their chemical requirements are detailed in Table 1

Table 1
Potassium Perchlorate—Chemical Requirements

	Percent by Weight	
	Grade A	Grade B
Moisture, max	0.02	0.04
Chlorides (as KCl), max	0.10	0.10
Chlorates (as $KClO_3$), max	0.10	0.086
Hypochlorites	None	None
Bromates (as $KBrO_3$), max	0.02	0.004
Sodium (as $NaClO_4$), max	0.20	0.20
Calcium and Magnesium salts (as oxides), max	0.20	0.080
Grit and Water insoluble material, max	0.02	0.02
Iron (as Fe_2O_3), max	–	0.0004
pH of water solution	7.0 ± 1.5	7.0 ± 1.5
Assay $KClO_4$, min	99.0	99.0

Five classes of $KClO_4$ are given based on particle size. These are: Class I – 99.9% by wt passing US Standard Sieve No 40 (420 micron); Class 2 – 99.9% by wt passing US Standard Sieve No 100 (149 micron); Class 3 – 99% by wt min passing US Standard Sieve No 80 (177

micron), and 80–90% by wt passing US Standard Sieve No 200 (74 micron); Class 4 – Average particle diameter 20 ± 5 microns by Fisher Sub-Sieve Sizer; Class 5 – Average particle diameter 70 ± 30 microns by Fisher Sub-Sieve Sizer

Refs: 1) Gmelin, System No 22 (1936), 502 2) L.S. Ross, USP 1094596 (1914) & CA **8**, 2227 (1914) 3) V. Lenher et al, JACS **44**, 143 (1922) 4) A. Stettbacher, Protar **10**, 158 (1944) & CA **39**, 2203 (1945) 5) L.H. Ericksen & O.E. Sheffield, "Substitutes for Potassium Perchlorate in Pyrotechnic Compositions", PATR **1408** (1944), AD 496017 6) L.H. Ericksen & O.E. Sheffield, "Substitutes for Potassium Perchlorate in Pyrotechnic Compositions", PATR **1426** (1944), AD 496018 7) G.G. Marvin & L.B. Woolaver, IECAnalEd **17**, 474 (1945) 8) L.L. Bircumshaw & T.R. Phillips, JCS **1953**, 703 9) R.D. Cool & L.F. Gowen, "Case Gun Propellant Ignition", NOL **NAVORD 2839** (1953), AD 019292 10) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 11) J.I. Fernandez-Alonso & L. Gasco, AnalesRealSocEspanFizYQuim **51B**, 5 (1955) & CA **49**, 7910 (1955) 12) S. Gordon & C. Campbell, "Pre-Ignition and Ignition Reactions of the Pyrotechnic System Zn-C_6Cl_6-$KClO_4$" in 5th Symp Combstn (1955) 227 13) G. Svadeba & S. Duck, "Sensitivity of Explosives to Impact, Period 1 July 1953 to 1 November 1954", NOL **NAVORD 3955** (1955), AD 068500, p 4 14) P. Tavernier, MP **38**, 267 (1956) & CA **51**, 15952 (1957) 15) J. Grodzinski, JApplChem **8**, 523 (1958) 16) R.G. Hall, USP 2841481 (1958) & CA **52**, 17716 (1958) 17) S.J. Magrum, USP 2842502 (1958) & CA **52**, 17717 (1958) 18) T.W. Clapper et al, "Manufacture of Perchloric Acid and Perchlorates" in J.C. Schumacher "Perchlorates, their Properties, Manufacture, and Use", ACS Monograph **146**, Reinhold, NY (1960), 89 19) F.A. Warren et al, "Chlorates and Perchlorates, their Manufacture, Properties, and Use", SRI **NAVORD 7147**, Vol **1** (1960), AD 242192 20) T. Stevenson, USP 2951752 (1960) & CA **55**, 2108 (1961) 21) J.E. Reynolds & T.W. Clapper, ChemEngrgProg **57** (12), 94 (1961) 22) H. Ellern, "Modern Pyrotechnics", Chemical Pub Co, NY (1961) 23) S. Lopatin, Sea-Level and High-Altitude Performance of Experimental Photoflash Compositions", PA **FRL-TR-29** (1961), AD 266213 24) E. Rolle & J.Q. Tabor Jr, USP 2984558 (1961) & CA **55**, 25257 (1961) 25) E.J. Walden, USP 2990683 (1961) & CA **55**, 25258 (1961) 26) M.M. Markowitz & P.R. Winternitz, USP 3110558 (1963) & CA **60**, 6519 (1964) 27) A. Seidel, "Solubilities of Inorganic and Metal-Organic Compounds", 4th ed revised by W.F. Linke, Vol **II**, ACS, Wash DC (1965) 28) L.A. Burkhardt & W.G. Finnegan, USP 3274035 (1966) & CA **65**, 18420 (1966) 29) W.S. Baker, USP 3282146 (1966) & CA **66**, 29709 (1967) 30) W.W. Cavell et al, Ordn **52** (283), 66 (1967) 31) R. Zimmer-Galler, "The Combustion of Tungsten and Manganese Delay Powders", Paper No 68-19 presented at the 1968 Fall meeting, Western States Section, The Combustion Institute, at Menlo Park, Calif 32) K.H. Ide et al, Explosivst **18**, 56 (1970) & CA **73**, 89716 (1970) 33) M. Kamasaki & N. Nakashima, GerOffenP 1906487 (1970) & CA **73**, 133772 (1970) 34) J.E. Rose & R. Zimmer-Galler, USP 3726730 & CA **79**, 7573 (1973) 35) W.F. Beckert & O.H. Dengel, USP 4000022 (1976)

Addnl Refs (limited distribution): 1) K.S. Warren, "Explosive Characteristics of the R23H Tracer Composition", PATR **1354** (1943), AD 492990 2) M. Gilford et al, "The Anticipatory Effect, a Study of the Burning Mechanism of Delay-Relay Columns", PATR **3047** (1964), AD 432537 3) J.E. Rose, "Effect of Potassium Perchlorate on Flame Propagation in Modified Tungsten Delay Compositions" NOS **IHTR 322** (1970), AD 875812

Rubidium Perchlorate. $RbClO_4$, mw 184.92, OB to Rb_2O and HCl +34.6%; white rhmb crysts which change to a cubic form at 281° and melt at 606° with decompn (Ref 2); d at 25°, 2.80 g/cc; RI at 25°, 1.4701 (Ref 6); CA Registry No 13510-42-4

Preparation. It is prepd by dissolving Rb carbonate in dil aq perchloric ac, evapg the soln until crysts appear, filtering, and drying the crysts at 120° (Ref 3). Workers in the USSR have reported its large scale prodn by a similar process (Ref 5)

Effect of Heat. Differential thermal analysis shows an exotherm above the mp at 625–35°

(Ref 2). The addn of 10 mole % of Mn dioxide lowers this decompn point to ca 550° (Ref 4)
Refs: 1) Gmelin, System No 24 (1937), 160 2) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 3) M.M. Markowitz et al, JPhChem **65**, 261 (1961) 4) M.M. Markowitz & D.A. Boryta, JPhChem **69**, 1114 (1965) 5) I.V. Vinarov et al, KhimProm,InformNaukTekhnZh **1965** (1), 30 & CA **63**, 2604 (1965) 6) ChemRubHdb (1975–6), B-133

Silver Perchlorate. $AgClO_4$, mw 207.32, OB to Ag_2O and HCl +30.9%; white delq rhmb crysts, mp 486° with decompn; d at 25°, 2.806g/cc (Ref 15); Q_f –7.44kcal/mole (Ref 13); CA Registry No 7783-93-9
Preparation. It was first prepd by dissolving Ag oxide in aq perchloric ac followed by evapn of the soln until crysts form (Ref 3). More recent procedures for the prepn of the anhyd salt are by the addn of anhyd perchloric ac to the soln of a Ag salt in trifluoroacetic ac (Ref 9); by the interaction of solid nitrosyl perchlorate and Ag bromide (Ref 10); or by the addn of the monohydrate to et bz. Two phases are formed, the upper phase contg only et bz and Ag perchlorate. This phase is treated with a satd hydrocarbon to give anhyd Ag perchlorate (Ref 13). Last traces of w can be removed by azeotropic distn with bz (Ref 11)
Solubilities. A remarkable prop of Ag perchlorate is its extremely high soly in w and org solvs. For example, 557g will dissolve in 100ml of w at 25°, d of the soln 2.8478g/cc (Ref 4). Some solys in org solvs are: aniline 5.3, pyridine 26.4, toluene 101 (Ref 5), and eth 19.2g/100ml (Ref 7). It is also sol in glycerol, acetic ac, nitromethane, nitrobenzene, and chlorobenzene; but insol in chlf and C tetrachloride (Ref 5)
Explosion Temperature. 800° (Ref 2)
Impact Sensitivity. After recrystn from eth, a sample expld violently on crushing in a mortar. It was assumed that either an etherate or occluded eth caused the expln (Ref 8). A similar incident occurred, however, where there was no evidence of the presence of org subs (Ref 16)
Uses. Ag perchlorate has been patented as a burning rate accelerator for solid proplnts (Ref 6). Solid Ag perchlorate has been used as a catalyst for the ign of hydrazine as a monoproplnt (Ref 12)
Refs: 1) Gmelin, System No 61, Part B-1 (1971), 508 2) A.E. Hill, JACS **43**, 254 (1921) 3) M. Gomberg, JACS **45**, 400 (1923) 4) G.F. Smith & F. Ring, JACS **59**, 1889 (1937) 5) N.V. Sidgwick, "The Chemical Elements and their Compounds", Vol **II**, Clarendon Press, Oxford (1950), 1233 6) R.W. Lawrence & G.A. Zimmerman, USP 3000716 (1955) & CA **56**, 2627 (1962) 7) G. Monnier, AnnChim(Paris) **13S**, 45 (1957) & CA **51**, 12734 (1957) 8) F. Hein, ChemTech **9**, 97 (1957) & CA **51**, 10061 (1957) 9) G.S. Fujioka & G.H. Cady, JACS **79**, 2451 (1957) 10) M.M. Markowitz et al, JInorgNuclChem **16**, 159 (1960) & CA **55**, 5212 (1961) 11) J. Radell et al, JACS **83**, 3958 (1961) 12) D.N. Griffin & D.R. Feller, USP 3021667 (1962) & CA **57**, 10098 (1962) 13) S. Buffagni & I.M. Vezzosi, Gazz **97**, 1258 (1967) & CA **67**, 113277 (1967) 14) D.D. Wagman et al, "Selected Values of Chemical Thermodynamic Properties", NBS Tech Note **270-4** (1969), 31 15) ChemRubHdb (1975–6), B-138

Sodium Perchlorate. $NaClO_4$, mw 122.44, OB to Na_2O & HCl +52.3%; white rhmb crysts which change to the cubic form at 313°, melt at 473°, and decomp at 480° (Ref 8) into Na chloride and O (Ref 7); d 2.5298g/cc (Ref 10); Q_f –91.48 ± 0.22kcal/mole (Ref 12); CA Registry No 7601-89-0

The anhyd salt is obtained when samples are recrystd from w above 53°; below this temp a monohydrate is obtained (see below). The pure salt is best obtained on a lab scale by dissolving pure Na carbonate in a slight excess of dil aq perchloric ac, the soln partly evapd, cooled to 50°, the solid centrifuged off, and dried in a current of air at 250°. Similar results were obtained starting with pure Na chloride (Ref 2). On a coml scale it is prepd by the electrolysis of Na chlorate (see Vol **2**, C197-R). Processing details and economics of the prepn are given in Refs 5 & 11. Concd solns are used, and modern plants use continuous electrolytic cells. In 1960 prodn was estimated to be ca 10000 tons/year at a cost of 17.56¢/lb (Ref 11, p 87)
Hydrates. Monhydrate, $NaClO_4.H_2O$, hygr crysts, mp 130° with loss of w. It is obtained

when concd aq solns are recrystd below 50° (Ref 1). A sesquihydrate, $2NaClO_4.H_2O$, and a trihydrate have also been reported (Ref 1)

Impact Sensitivity. Pure Na perchlorate and mixts with 1–2% of various subs were found to be insensitive to impact (over 320cm) (Ref 9)

Solubilities. In g/100g of solv the solys are: w 209.6, me alc 51.4, acet 51.7, et alc 14.7, pr alc 4.89, bu alc 1.86, et acetate 9.65 and iso-Bu alc 0.786. It is insol in eth (Ref 3)

Toxicity. Injection of aq Na perchlorate into rabbits caused no long term toxic effects. It behaved as a mild muscular poison, and large doses caused liver damage and diarrhea. Goldfish will live indefinitely in a 0.1% soln, but a 1% soln will cause asphyxia (Ref 4)

Uses. The primary use for Na perchlorate is in the mfg of other perchlorates and most of the prodn is used captively by the same plant which made it (Ref 11, p 87). Other uses which have been reported follow:

Flares. A flare compn is described in Refs 15 & 16 contg powd Mg, Na perchlorate, and a binder which can be cast and cured, and which has a luminous intensity of 50,500 candle-secs/g

Incendiaries. A mixt of 100g of Na perchlorate and 58.7g of powd Al has a Q_r of 2751cal/g and can be used as a filler for incendiary bombs (Ref 6). A proc is described in Ref 14 for coating Na perchlorate with Al, and the use of the coated material in incendiaries

Photoflash Compositions. Mixts of 80% Ca metal and 20% Na perchlorate; and 80% Ca, 10% Na perchlorate, and 10% Na nitrate have been examined as expl photoflash compns for both sea level and high altitude use (Ref 13)

Refs: 1) Gmelin, System No 21 (1928), 408 & Supp Part 1 (1964), 180 2) H.H. Willard & G.F. Smith, JACS **44**, 2816 (1922) 3) H.H. Willard & G.F. Smith, JACS **45**, 293 (1923) 4) E. Kahne, BullSocChimBiol **18**, 352 (1936) & CA **30**, 3882 (1936) 5) J.C. Schumacher, ChemMetEng **51** (12), 108 (1944) & CA **39**, 2031 (1945) 6) A. Stettbacher, Protar **10**, 158 (1944) & CA **39**, 2203 (1945) 7) G.C. Marvin & L.B. Woolaver, IECAnalEd **17**, 474 (1945) 8) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 9) G. Svadeba & S. Duck, "Sensitivity of Explosives to Impact, Period 1 July 1953 to 1 November 1954", NOL **NAVORD 3955** (Nov 1955), AD 068500, p 5 10) R.D. Stewart, "Alkali Metal, Ammonium And Alkaline Earth Perchlorates" in J.C. Schumacher, Ed, "Perchlorates, their Properties, Manufacture, and Uses", ACS Monograph **146**, Reinhold, NY (1960), 29 11) F.A. Warren et al, "Chlorates and Perchlorates, their Manufacture, Properties and Uses", SRI **NAVORD 7147**, Vol **1** (May 1960), AD 242192, p 53 12) A.A. Gilliland & W.H. Johnson, JRNBS **65A**, 67 (1961) & CA **55**, 12020 (1964) 13) S. Lopatin, "Sea-Level and High-Altitude Performance of Experimental Photoflash Compositions", PA **FRL-TR-29** (Oct 1961), AD 266213, p 17 14) A.D. Coates & E.O. Baicy, USP 3120459 (1964) & CA **60**, 9094 (1964) 15) H.R. Waite & Y. Arikawa, "Binder Study-Visual Cast Flares", Ord Res, Inc **RDTR 92** (Mar 1967), AD 655821 16) Y. Arikawa & H.R. Waite, USP 3462325 (1969) & CA **71**, 93223 (1969)

Strontium Perchlorate. $Sr(ClO_4)_2$, mw 286.52, OB to SrO & HCl +22.3%; white delq rhmb crysts; decomps vigorously at 477° (Ref 6); d_4 at 25°, 2.973g/cc (Ref 5); Q_f (calcd) –187kcal/mole (Ref 9); CA Registry No 13450-97-0

Preparation. It is prepd by dissolving pure Sr nitrate in an excess of perchloric ac, the excess ac neutralized with Sr carbonate, all solids centrifuged off, and the soln chilled until crysts appear (Ref 2). The anhyd salt can also be prepd by drying the hydrate at 250°, yield 50% (Ref 3); or the addn of anhyd perchloric ac to a soln of Sr ion in anhyd trifluoroacetic ac, the pptd solid filtered, and the excess acid removed in a vacuum (Ref 7)

Solubilities. Soly in g/100g of solv are: w 309.7, me alc 221.0, et alc 180.7, pr alc 140.4, bu alc 113.5, iso-Bu alc 77.9, acet 140.1, and et acetate 136.9. It is insol in eth (Ref 2)

Uses. (see also under Perchlorate Propellants and Explosives). It is used in pyrotechnics to impart a bright red color to flames (Ref 3). A gel was made from 50g of Sr perchlorate, 100g of me alc, and 4.6g of Carbopol 940 gelling agent. Five g of this gel burned for 10 mins with an intense red flame (Ref 11). A 66/34 mixt of Sr perchlorate/powd Al was tested as a photoflash compn for both sea level and high altitude use (Ref 8). Another mixt of 50ml of me

methacrylate, 165g of Sr perchlorate, and 3 drops of cumene hydroperoxide was polymerized in a mold to give a candle which burned for 30 secs with a bright red flame 24 inches high (Ref 10)

Refs: 1) Gmelin, System No 29 (1931), 145 & Supp (1960), 222 2) H.H. Willard & G.F. Smith, JACS *45*, 286 (1923) 3) G.F. Smith, USP 1824101 (1931) & CA **26**, 265 (1932) 4) F. Ephraim & C. Zapata, Helv **17**, 296 (1934) & CA **28**, 4326 (1934) 5) G.F. Smith & E.G. Koch, ZAnorgChem **223**, 17 (1935) & CA **29**, 5035 (1935) 6) S. Gordon & C. Campbell, AnalChem **27**, 1102 (1955) 7) G.S. Fujioka & G.H. Cady, JACS **79**, 2451 (1957) 8) S. Lopatin, "Sea-Level and High-Altitude Performance of Experimental Photoflash Compositions", PA **FRL-TR-29** (Oct 1961), AD 266213, p 15 9) D.E. Wilcox & L.A. Bromley, IEC **55** (7), 32 (1963) 10) B.E. Douda, USP 3258373 (1966) & CA **65**, 13450 (1966) 11) R.J. Fay & P.J. Keitel, USP 3461006 (1969) & CA **71**, 126735 (1969)

Titanium Perchlorates

Titanyl Perchlorate. $OTi(ClO_4)_2$, mw 262.80, OB to TiO & HCl +27.4%; colorl hex tablets contg an undetd number of moles of w (Ref 1). Later work indicates that the compd is probably a mixt of penta and tetra hydrates (Ref 2)

Preparation. By dissolving 1 mole of anhyd Ti tetrachloride in 2 moles of anhyd perchloric ac, and the viscous yellow soln evapd in a vacuum at 30–40° to give colorl crysts (Refs 1 & 2)

It forms an expl compd with dioxane

Titanium Tetraperchlorate. $Ti(ClO_4)_4$, mw 445.70, OB to TiO & HCl +30.5%; CA Registry No 13498-15-2

Preparation. Anhyd perchloric ac and Ti tetrachloride were combined in a mole ratio of 8:1 at −10° to give a cryst solid whose purity by analysis was 97–8% (Ref 3)

Properties. It can be stored at low temps in the absence of air or w, and is described as a powerful oxidant which is insensitive to shock, but explds on contact with eth, and flames on contact with formamide or dimethyl formamide (Ref 3)

An excess of dinitrogen tetroxide is condensed onto Ti tetraperchlorate at liq N temp and the excess removed by vacuum distn to give a complex $Ti(ClO_4)_4.N_2O_4$ (Ref 4), which is described as very hygr and as being a useful dessicant, nitrating agent, and oxidizing agent (Ref 5)

Refs: 1) Gmelin, System No 41 (1951), 323 2) V. Krishman & C.C. Patel, IndianJChem **2**, 425 (1964) & CA **62**, 4940 (1965) 3) R.J. Laran, USP 3157464 (1964) & CA **62**, 2530 (1965) 4) G.C. Robinson, USP 3224833 (1965) & CA **64**, 6155 (1965) 5) F.W. Frey & R.J. Laran, USP 3224834 (1965) & CA **64**, 6155 (1965)

Uranyl Perchlorate. $UO_2(ClO_4)_2$, mw 469.0, OB to UO_2 & HCl +15.4%. The hexahydrate is obtained as monoclinic crysts, mp 90° (Ref 1); CA Registry No 13093-00-0

Preparation. U trioxide is dissolved in 40% aq perchloric ac, the soln concd on a w bath, and chilled to give yellow crysts of the hexahydrate (Ref 3). Attempted recrystn of this salt from et alc resulted in an expln (Ref 2)

Refs: 1) Gmelin, System No 55 (1936) 2) O. Erämetsä, SuomenKemist **15B**, 1 (1942) & L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 685 3) G. Vincentini et al, Ber **94**, 1963 (1961)

Zinc Perchlorate [Zink Perchlorat (Ger)]. $Zn(ClO_4)_2$, mw 264.27, OB to ZnO & HCl +24.2%; Q_f −37.42kcal/mole (Ref 11); CA Registry No 13637-61-1

Preparation. The anhyd salt has only recently been prepd by heating a mixt of Zn oxide and nitrosyl perchlorate in a vacuum at ca 180° (Ref 11)

Complexes.

Hexahydrate. $Zn(ClO_4)_2.6H_2O$, white rhmb crysts, mp 106°, decomps at 200°, d 2.252 ± 0.01g/cc (Ref 12). It was first prepd by interacting aq solns of Zn sulfate and Ba perchlorate, filtering off the pptd Ba sulfate, and evapng the soln until crysts appear (Ref 2). It has also been prepd by dissolving Zn oxide or carbonate in aq perchloric ac and evapng the soln until crysts appear (Ref 4). The hexahydrate loses 2 moles of w at its mp to form a tetrahydrate which on further heating decomps at 260° (Ref 4)

Solubilities of Hexahydrate. In w at 20°, the soly is 32.4moles/ℓ (Ref 8); in cellosolve, 130g is sol in 100cc of soln; and in furfural, 100g will dissolve in 100cc of soln (Ref 7). It is also sol in et alc (Ref 4)

Tetra-ammoniate. $Zn(ClO_4)_2.4NH_3$, small tetrahedral crysts, mp 220°, decomps rapidly ca 250°, explds on rapid heating (Ref 3). It is prepd by the addn of an aq soln of AP to the soln of a Zn salt in aq ammonia (Ref 3); or by the dehydration of the hexahydrate with a large excess of 2,2-dimethoxypropane, followed by the addn of anhyd ammonia to the soln. The ppt is filtered off and dried (Ref 9)

Explosive Properties of Tetra-ammoniate.

Explosion Temperature. 305° (Ref 5)

Impact Sensitivity. With a 1 kg wt, 70cm for 50% explns (MF 20cm) (Ref 5)

Power by Trauzl Lead Block Expansion Test. 1 g, on ign, formed a vol of 15.1cc (TNT 21.5cc) (Ref 5)

A **hydrazinate** has been prepd which could not be analyzed because of extreme sensy (Ref 6)

Uses. Anhyd Zn perchlorate is a good catalyst for the decompn and expln of AP (Ref 10)

Refs: 1) Gmelin, System No 32, Supp (1956), 883 2) G.S. Sérullas, AnnChimPhys(2) **46**, 304 (1831) 3) R. Salvadori, Gazz **40 II**, 19 (1910) & CA **5**, 1717 (1911) 4) R. Salvadori, Gazz **42 I**, 458 (1912) & CA **6**, 2216 (1912) 5) W. Frederich & P. Vervoorst, SS **21**, 65 (1926) & CA **21**, 1184 (1927) 6) W. Frederich & P. Vervoorst, SS **21**, 103 (1926) & CA **21**, 1184 (1927) 7) A.L. Chaney & C.A. Mann, JPhysChem **35**, 2289 (1931) & CA **25**, 5099 (1931) 8) K. Schwabe, ZElectroChem **39**, 791 (1933) & CA **28**, 47 (1934) 9) B.B. Wayland & W.L. Rice, InorgChem **6**, 2270 (1967) 10) F. Solymosi, MagyKemFoly **73**, 366 (1967) & CA **68**, 6731 (1968) 11) V.Ya. Rosolovskii & N.V. Krivtsov, ZhNeorgKhim **13**, 36 (1968) & CA **68**, 99320 (1968) 12) ChemRubHdb (1975–6), B-158

Inorganic Perchlorate Explosives. Expls contg one of the inorganic perchlorates (primarily K or Amm perchlorate) or perchloric acid as one of the principal ingredients

Alfred Nobel first proposed using inorganic perchlorates in expls, and in 1885 patented some proplnts contg them. They were not successful. However, when used in blasting expls (in lieu of chlorates), it was found that they were very suitable ingredients. With the introduction of electrolytic methods of manuf of the perchlorates in the 1890's, the extensive use of these compds in both commercial and military expls was inaugurated. Sweden and Switzerland were the first to use blasting expls contg perchlorates extensively

Certain advantages of perchlorates over Dynamite or other NG expls for a number of specific applications were soon recognized. One of the outstanding features of perchlorate expls is their greater safety due to being much less sensitive to shock, particularly at lower temps where freezing seriously affects the safe handling of NG expls. Also, in warm climates, perchlorates are free from exudation tendencies, and they are relatively nontoxic compared with Dynamite. In general, their expl action is slower than that of NG, but they are capable of producing a relatively greater expl effect. Their adaptability covers quite a wide range. For example, by using mixts of K and Amm perchlorate in varying ratio, by adding Na nitrate, or by incorporating other types of expl materials such as nitroorganic compds, the expl action may be adjusted to suit the particular material to be blasted. Either hard or soft rock can be shattered into small pieces, or only broken into large blocks as in the case of the quarrying of building stone. Dynamite, on the other hand, exerts a more nearly constant effect which tends toward the shattering side. The action of perchlorate expls seems to extend laterally more than in the case of Dynamite, which is more local in its action (Ref 17)

Following is a listing of past and present inorganic perchlorate expls which are detailed thruout the Encycl:

Ajax Powder, Alcalsits (Alkalsits), Alvisi Explosive; Berges, Corbin et Cie Explosifs A, B, I, II and III; Blastine, Burrows Explosive, Carbonites, Cheddites (Perchlorate), Cremonita, Dynobel, Explosif P, Frazer Explosive (for clearing mine fields), Gesteinspermonit, Gesteinspersalit, Herculite, Kaipinites, Kratits, Lheure Explosives, Manlianite, M.B. Powder, Neonals, Nisser Powder, O'Brien Explosive, Ophorite,

Peragon (Paragon), Perammon (Parammon), Perchloratits, Perchlorits, Perdit, Perilit, Perkoronit, Permonite, Pernitral, Persalit, Petrofracteurs, Polarite, Rosslin Giant Powder, Schultz and Gehre Explosives, Silberrad Explosive, Super-Rippite No 2, Swale Powder, Symmon Adde Explosive, Tarnowski Explosive, Territ, Wetterperchlorits, and Yonckites (Jonckites).

Although perchlorates are still more expensive than chlorates, their use can be justified by the following advantages: 1) perchlorates contain more available oxygen per unit weight than the corresponding chlorates, and are more stable; 2) they are less sensitive to mechanical action, and for this reason it is not necessary that each particle be encapsulated in resilient material to diminish the sensitivity, as is the case with chlorate expls; and 3) as an additional advantage, Amm perchlorate produces only gaseous products, but these unfortunately include the toxic hydrogen chloride. These gases are not objectionable when expls are used in bombs, mortar shells or in open pit mining; but are objectionable when used in confined spaces. However, they can be rendered harmless if nitrates (10 to 20%) are incorporated, as was done in some German Perchlorits, Swedish Territ, English Blastine and Belgian Yonckite. The incorporation of MnO_2 (up to 18%) also acts as an inhibitor of HCl formation

Although perchlorate expls are fairly insensitive to mechanical action, they are, nevertheless, too sensitive for some applications. Incorporation of materials such as paraffin (as was done in the French Perammon and the English Blastine) or of castor oil (as was done in some Swiss expls), renders them quite plastic and insensitive to shock and friction. This addition might make these expls too insensitive to an initiating agent. In order to counteract this defect, small quantities of NG (as low as 4%) may be incorporated, as was done in some Perchloratits. The addition of NG not only makes the mixt more readily detonatable but it also helps to plasticize the expl, especially if aromatic nitrocompds, such as DNT, TNT, etc, are also present

When perchlorate expls are used in gaseous mines, a cooling agent must be incorporated. For example, Wetterperchlorit and Yonckite 10 bis, have Na chloride incorporated; some Perchlorits, Permonits, Telsits, etc, contain AN; and Ajax Powder, Herculite, Neonals, etc, have Amm oxalate as a cooling agent

It should be noted that the incorporation of substances such as TNT increased the sensitivity to initiation, and the addition of AN increased the quantity of expln gases, while at the same time diminishing the sensitivity of the perchlorate expl to open flame

Refs: See below under Inorganic Perchlorate Military Explosives

Inorganic Perchlorate Military Explosives. Due to the shortage of aromatic nitrocompds such as TNT, several European countries, during WWI and even during WWII, used expls contg K or Amm perchlorate

According to Stettbacher (Ref 11, Vol 1) the Germans during WWI used a mixt (called "Deutscher gesichiessbarer Minensprengstoff") consisting of K perchlorate 56, DNB 32 and DNN 12%, which was cast-loaded in trench mortar shells, land mines and various bombs, while the French used 'Perammon" (qv) for loading aerial bombs

Marshall (Ref 1, Vol 3) states that the British used a mild but hot expl, "Ophorite" (qv), during WWI as an opening charge for incendiary shells and smoke bombs

According to Davis (Ref 12), during WWI the Germans used an expl called "Perdit" (qv) in their trench mortar shells. Its compn was identical to that given by Stettbacher for "Deutscher geschiessbarer Minensprengstoff" above. Davis also relates that the French used a mixt consisting of Amm perchlorate 86 and paraffin 14% for loading their 75mm shells

Both Davis (Ref 12) and Naoûm (Ref 8) affirm that the following compn was used by the French during WWI for loading 58mm trench mortar shells; Amm perchlorate 74.5, paraffin 17, and Al powder 8.5%

According to Stettbacher (Ref 11, Vol 2), an expl contg Amm perchlorate 90 and paraffin 10%, was used for military purposes under the name "Parammon" (qv). This seems to be the same expl as "Perammon", used by the French during WWI

A rather unusual application for a military perchlorate expl is covered by a US patent issued to Frazer et al (Ref 16) on producing

surface explns over large areas. This is intended primarily as a means of clearing fields of land mines. The area is first sprayed with a mixt of concd perchloric acid and a miscible organic liq of low volatility, such as ethylene glycol monoethyl ether. The sprayed film is then detonated by suitable means, such as a grenade, in order to expld the mines in the area

Refs: 1) Marshall **1**, 383–7 (1917) & **3**, 113–14 (1932) 2) Perchlorate Safety Explosive, Ltd, SwedP42115 (1917) & CA **11**, 2154 (1917) (Expls prepd by mixing alkali or Amm perchlorates with finely divided metallic Zn and combustible non-nitrogenous compds that are not reduced by Zn) 3) Colver (1918), 286, 680, 684 & 689 4) Barnett (1919), 112–13 5) B. Mühlefeld, SS **16**, 113–5 (1921) & CA **16**, 496 (1922) (The term "chlorate explosives" is applied to expls contg either chlorates or perchlorates. Among expls contg perchlorates are cited some contg K perchlorate and Amm perchlorate, varying from 10 to 55%, plus nitrocompds, carbonaceous materials, AN, etc) 6) E. Spitalsky & E. Krause, SS **20**, 121 (1925) & CA **20**, 1141 (1926) (A Moscow University study of the influence of the increasing density of various chlorate and perchlorate expls on their brisance, as well as the effect of variations in the nature of the combustible ingredient on the expl strength at the optimum loading density. These expls were designated as "Almatrites" (qv). As for perchlorate expls, they recommended a mixt contg Amm perchlorate 89 and organic matter 11% (consisting of rosin 65, paraffin 27 & vaseline 7%). Its brisance at a density of 1.17g/cc was 16.2mm using the Pb block compression test) 7) Ullmann **4** (1926), 789–90 8) Naoúm, Expls (1927), 126–37 9) Naoúm, NG (1928), 430–32 10) Vennin, Burlot & Lécorché (1932), 544 11) Stettbacher **1** (1933), 315–16 & **2** (1948), 91 12) Davis (1943), 364–66 13) A. Pérez Ara (1945), 218–19 14) Vivas, Feigenspan & Ladreda **2** (1946), 347–50 15) Thorpe **4** (1949), 464 16) J.H. Frazer, J.W. Perry & W.R. Johnson, USP 2504119 (1950) & CA **44**, 6130 (1950) 17) J.C. Schumacher, "Perchlorates, Their Properties, Manufacture and Uses", ACS Monograph **146**, Reinhold, NY (1960), 133–55 18) R.T. Holzmann, "Chemical Rockets and Flame and Explosives Technology", Marcel Dekker, NY (1969), 78–9 & 212–13

Perchlorit (Perchlorites). A type of Ger perchlorate mining expl used prior to and during WWI. Two typical formulations are shown in Table 1:

Table 1

Ingredients and properties	Composition, %	
	1	2
K perchlorate	35	34
Amm nitrate	42	48
DNT*	10	10
DNN	4	0
Wood meal	5	6
Coal powder	–	2
NG	4	–
Oxygen Balance, %	+1.7	+1.7
Trauzl Test, cc	340	340

*DNT was prepd by the nitration of m-MNT

Refs: 1) Naoúm, NG (1928), 133 2) PATR **2510** (1958), Ger 129-R

Perchlorocellulose, Perchloronitrocellulose, Perchloroglycerin and Perchloronitroglycerin. A series of expls prepd by Alvisi (BelgP 141582 of 1899) by treating cellulose or glycerin with either perchloric acid alone, or with mixts of perchloric and nitric acids

Ref: Daniel (1902), 606

Perchromic and Perpolyperchromic Acids and Their Salts

Monoperchromic or Permonochromic Acid, $HCrO_5$, or **Monoperchromates,** $MeCrO_5$ or $R.CrO_5$, where Me stands for a metal and R for an organic radical. The acid has not been isolated, but some of its salts were prepd by O. Wiede in 1897 (Ref 3). Its K salt can be obtained by treating a cold sulfuric acid soln of $K_2Cr_2O_7$ with an excess of H_2O_2. It is a violet, unstable product to which the structural formula $(KO.O)CrO_3$ was assigned. Wiede, Riesenfeld

and others prepd the following organic salts and additive compds of monoperchromic acid:
Tetramethylammonium Monoperchromate. $N(CH_3)_4.CrO_5$. Violet prisms; can be kept in the cold for several days; dissolves in w with a brown coloration
Pyridine Monoperchromate. $C_5H_5N.HCrO_5$. Blue, rhombic plates, fairly stable when dry. It detonates when heated, or on contact with concd sulfuric acid

Diperchromic Acid. H_3CrO_7 or $(HO.O)_2CrO_2$-(OH) and **Diperchromates**, $R.H_2CrO_7$, also called "Blue Perchromates". The compds were discovered by Wiede (Ref 3), and were also obtained by Hofmann et al (Ref 4) and Riesenfeld et al (Ref 5). The latter investigators prepd the blue perchromates by the action of 30% hydrogen peroxide on an acidic soln of a chromate
Ammonium Diperchromate. $(NH_4)H_2CrO_7$. Bluish-black or violet crysts. When dry, it can be kept for several days at RT, dissolves in ice cold w, forming a violet-brown liq which gives a neutral reaction. When heated rapidly the salt burns with a hissing noise
Potassium Diperchromate. KH_2CrO_7. Exists in the form of red and dark violet modifications. The dark violet powder detonates at slightly above 0°

In general, all diperchromates are less stable than triperchromates, which are described below

Triperchromic or Hypermonoperchromic Acid, H_3CrO_8 or $(HO.O)_3CrO_2$ and **Triperchromates**, $R_3.CrO_8$, also called "Red Perchromates", were first prepd by Riesenfeld et al (Refs 1, 5 & 6). The alkaline salts can be obtained by treating an alkaline soln of chromic acid with 30% hydrogen peroxide. The K salts can be obtained by slowly adding a K dichromate soln in concd sulfuric acid to aq hydrogen peroxide
Ammonium Triperchromate. $(NH_4)_3CrO_8$ or $(NH_4O.O)_3CrO_2$. Reddish-brown octahedral crysts; explds when heated to about 50° or above. Sl sol in w; insol in alc and eth. It decomps rapidly at 40°. When dry it can be kept for several days without decompn
Potassium Triperchromate. K_3CrO_8. Dark red prisms which can be kept for a month when dry without decompn. Sl sol in w; insol in alc and eth. It decomps explosively at about 178°, or when in contact with concd sulfuric acid. The impure salt is more expl
Sodium Triperchromate. Na_3CrO_8. Reddish-yellow plates which cannot be completely dried. Sl sol in cold w; insol in alc and eth. Decomps explosively at 115°
Refs: 1) Mellor **11** (1931), 353–61 2) L. Barreswil, AnnChimPhys (3), **20**, 364 (1848) 3) O. Wiede, Ber **30**, 2178 (1897); Ibid **31**, 516, 3139 (1898) 4) K.A. Hofmann et al, Ber **37**, 1663 (1904); Ibid **38**, 3059, 3066 (1905) 5) E. Riesenfeld et al, Ber **38**, 1885 (1905) 6) E. Riesenfeld, "Zur Kenntoriss der Ueberchromsäuren", Freiburg (1906) 7) K.A. Hofmann & K. Büchner, Ber **42**, 2773 (1909) 8) E. Riesenfeld, ZAnorgChem **74**, 48 (1912) 9) A. Glasner, JCS **1950**, 2795–98 10) W.P. Griffith, JCS **1962**, 3948; Ibid, JCS **1964**, 5248

Percoronit (Percoronite). A blasting expl which replaced Coronit in stone quarries and ore mines: K perchlorate 65, NG 5, aromatic nitrocompds 25, and vegetable meal 5% (See also Perkoronit)
Refs: 1) Bebie (1943), 116 2) PATR **2510** (1958), Ger 129-R 3) F.A. Warren et al, "Chlorates and Perchlorates, Their Manufacture, Properties and Uses", NavOrdRept **7147**, Vol 1 (1960), 205

Percussion. The act of striking one body against another with a sharp blow. As some expls, such as MF or LSt are very sensitive to such a blow (shock or impact), they may be expld (or ignited) by such action. In this case, the term "percussion" can be applied to initiation or priming by such action, as well as to the expln (or deflagration or ignition) caused by percussion

Percussion or Explosive Bullet. A bullet provided with a percussion cap which, on impact, explds a powder charge inside the bullet

Percussion Cap. (See under Cups, Percussion or Primer; and Caps in Vol **3**, C577; and Anvil of a Percussion Primer in Vol **1**, A473-L)

Percussion Fuze. See Vol **4**, D882-R

Percussion Gun. See under Percussion Principle in Vol **4**, D755-L

Percussion Lock. A firearm mechanism in which a cap loaded with a detonating mixt is fitted over a pierced nipple and exploded by the blow of the falling hammer. The flash of the exploding cap is carried to the charge. Its development followed that of the flintlock (See Vol **6**, F107-R), and its use was widespread by the middle of the nineteenth century. The US Army adopted percussion rifles and muskets in 1841–42, and by 1842 all British Brown Bess muskets were converted to percussion fire. Also see under History of Development of Military Detonators, Igniters, Primers and Other Initiating Devices in Vol **4**, D753-R to D756-R
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 345

Percussion Powder. Any compd or mixt which can be easily fired by percussion. The first mixts of this type were invented by a Scotch clergyman, A. Forsyth. See Vol **4**, D755-R and Vol **6**, F232-R

Percussion Primer. See under Primer, Percussion in this Vol

Percussive Effect or Force (Relative). A term coined by Clark (Ref 2) for the numerical value obtained by dividing the compression of a Pb cylinder produced by firing an expl to that produced by the same quantity of TNT under the same conditions

For example, when 50g of an expl (d 0.75 g/cc) was detonated unconfined atop a steel plate, placed on a Pb cylinder (40.0mm diam, 65.0mm height), the following values were obtained:

	TNT	PA	Tetryl	Pentryl
Compression of Pb cylinder in mm	14.8	16.4	16.6	18.5
Relative percussion effect (TNT=1.00)	1.00	1.11	1.12	1.25

The test was conducted in the same manner as described bv Munroe & Tiffany (Ref 1)
Note: Earlier investigators such as Kast, Hess, Vennin, Burlot and Lécorché regarded this test as being indicative of relative brisance
Refs: 1) C.E. Munroe & J.E. Tiffany, USBur-Mines Bull **346** (1931) 2) LeRoy V. Clark, IEC **25**, 1389 (1933)

Perdit (Perdite). Ger perchlorate expls of varying compn, introduced during WWI as replacements for the Corps of Engineers Explosive (Pioneer-munition), Donarit (see Vol **5**, D1531). A compn contg K perchlorate 56, DNB 32 and DNN 12% was used in trench mortar shells and mines. Stettbacher (Ref 2) referred to it as "Deutscher Geissbarer Minensprengstoffe" (Ger castable mine expl)

A Compn contg AN 72, K perchlorate 10, wood meal 3, and a eutectic mixt of DNT and TNT 15%, was used as a demolition charge and for loading bombs and trench mortar shells. Its d was 1.20–1.25g/cc; Trauzl test value, 370–380cc; sensitivity to initiation, required at least a No 3 cap for detonation
Refs: 1) Naoûm, Expls (1927), 132–3 2) Stettbacher (1933), 316 3) Pepin-Lehalleur (1935), 352 4) Davis (1943), 364 5) A. Pérez Ara (1945), 243 6) Urbański **3** (1967), 264

Perforated Grains (Propellants). See under Cannon Propellant or Cannon Powder in Vol **2**, C30 to C31

Performance of Explosives or Propellants. The best way to estimate their performance is to conduct "practical" tests by actual firings (see Performance Tests, Practical). As these tests are rather expensive and require large "Proving Grounds" for their execution, it is common to conduct preliminary testing by any of the following indirect methods:

Brisance (shattering power). Measured by a series of tests which determine the explosive's ability to crush sand, fragment steel pipe, or deform solid Pb cylinders. The results of these tests are recorded as the weight of sand crushed, the number and size of pipe fragments produced, or the distance the cylinder is deformed

Power. Is a measure of the max press developed by detonation and the rate at which this pressure is released. The Ballistic Pendulum used for testing expl power consists of a mortar (suspended as a pendulum from knife-edges) in which an expl sample is detonated to expel a heavy shot from the mortar and cause the suspended mortar to recoil. The recoil of the mortar is proportional to the propulsive force of the expl, and the arc of swing is registered in cm and compared with that obtained with a standard expl such as TNT

Detonation Velocity. The speed at which the detonation wave travels thru the expl, or the rate of chemical reaction of the detonation process. High-speed photographic testing has determined that this reaction is of the order of a few microseconds, showing that as the detonation wave progresses the area behind the wave undergoes a chemical change, while the area or material ahead of the detonation wave remains unchanged until the wave passes thru it. Detonation velocity can be measured with high-speed streak cameras, spectrometers, or electric counters which record the make-break cycle the detonation wave causes in an electric circuit

Sensitivity. Friction sensitivity, as detd by the Friction Pendulum app, consists of dropping a pendulum with a 20-kg steel- or fiber-faced shoe one meter so that it swings across a grooved anvil into which a sample of expl has been spread. The passing of the shoe over the sample is recorded by the number of snaps, cracklings, ignitions and explns that occur. The steel-faced shoe will often produce snaps, crackles, or detonations in expls that withstand the fiber-faced shoe

Impact sensitivity can be expressed by denoting the min height of drop at which a standard test wt (2 or 10kg) will detonate an expl sample

Shock sensitivity of an expl can be gaged by subjecting a sample to the impact of a rifle bullet. In this test the caliber and type of bullet and the manner in which the expl sample is contained or positioned during the test can be varied. Confinement generally enhances the probability that an expl will detonate in the rifle-bullet test

Detonation sensitivity determines if an expl possesses the sensitivity necessary for it to react predictably from the action of the initiating medium designed to produce detonation. To determine the detonation sensitivity of an expl, standard test detonators of graded strength ratings from 1/2 to 16 are utilized. Their strength ratings are controlled by varying the type and wt of charge, and equating the detonators to 90/10 MF/K chlorate or PETN/LA detonators which specify the following charges:

Test Detonator No.	Weight of Charge, 90/10 MF/K chlorate compn, g	Weight of Charge, PETN/LA
½	0.26	–
1	0.30	–
1½	0.35	–
2	0.40	–
2½	0.47	–
3	0.54	–
3½	0.59	–
4	0.65	–
5	0.80	–
6	1.00	–
7	1.50	–
8	2.00	–
12	–	1.20g PETN/0.35g LA ignition mixt
16	–	1.50g PETN/0.35g LA ignition mixt

Grades of commercial expls not cap-sensitive and most military expls which cannot be detonated with a No 6 commercial blasting cap must be tested with detonators of No 8–16 strength in order to detn their sensitivity. Less sensitive expls, ie, Nitrocarbonitrates (ANFO), expl slurries, and Nitrocarbonitrate slurries, necessitate the use of extremely large initiators of 3–10g for ANFO mixts, to 50g or larger for the less sensitive slurries in order to detn basic sensitivity. Normally, initiation test charges larger than 3g are made of Pentolite, Comp B, or other high-strength expls, which, in turn, are detonated by a blasting cap

To the above tests can be added: explosion,

or ignition temp; sensitivity to flame, temp developed on expln or combustion; thermal stability; mp; bp; loading d; "colorific power", etc

In terms of the application of these tests as yardsticks for specific expl useage, the following examples are given:

1) If an expl is intended as a bursting charge in general purpose shells, there would be required high brisance, high power, high detonation velocity, and low sensitivity to impact, friction and shock (TNT, PA, Comp B, Pentolite, etc would be suitable)

2) If an expl is to be used for APS (armor-piercing shell) application, the same requirements as above are pertinent, except that the impact sensitivity should be very low (Explosive D, TNT desensitized with wax, etc, would be suitable)

3) If an expl is to be used as a booster, the same requirements as in (1) are applicable, except that the impact sensitivity should be higher (Tetryl, PETN, RDX, cryst PA, Nitromannite, etc, would be suitable)

All of the above expls should also possess high thermal stability

4) If an expl is intended for use in primers, then its brisance and power may be lower than for groups (1), (2) and (3), but it should possess low sensitivity to impact and friction and should produce a hot flame in order to ignite a charge of proplnt or a delay train

5) In the case of initiating expls, the requirements are the same as in (4) except that a hot flame is not required, but rather that it produce a shock wave strong enough to detonate a HE such as Tetryl, PETN, RDX, PA, TNT, etc

6) In the case of blasting expls to be used in coal mining applications, brisance should be low (to avoid breaking the coal down too finely); power and detonation velocity should also be low, but the gas volume evolved on expln should be high so that the so-called "heaving power" will be great. If mines are gaseous, it is required that the temp developed on expln be sufficiently low so as not to cause ignition of firedamp

7) With regard to proplnts, brisance, power and detonation velocity are not tested. It is, however, necessary to determine the burning rate, press developed on burning, vol of gas evolved, calorific value, thermal stability, etc. If one is concerned with gun barrel life, the calorific power should be low

Ref: D.M. Considine, Ed, "Chemical and Process Technology Encyclopedia", McGraw-Hill, NY (1974), 455–465

Performance Tests, Practical. Any test based on the employment of an expl or ammo item under actual operating conditions may be included in this category. For example, a blasting expl can be tested by burying a weighed sample deep in the ground and then firing it. The effect caused by the expln of the sample is compared with that produced by an equal weight of standard expl fired under the same conditions. This is called the "Cratering Effect Test" (Refs 1 & 2)

In testing proplnts, several charges can be fired, varying the weight of charges, etc, until the desired performance is achieved

In the testing of demolition expls, eg, those intended for the destruction of rails, various charges can be detonated against an exptl rail until the minimum amount of charge required is established

In testing penetration of armor, etc, by various projectiles, they can be fired against armor plate of varying thickness and compn until the maximum depth of penetration is detd

In testing the performance of expls used for bursting charges, the so-called "fragmentation test" (see Vol **6**, F180–181) gives fairly accurate results. This test can also be used to determine the performance of metals used in the construction of various projectiles

Refs: 1) M. Meyer, "The Science of Explosives", Thomas Y. Crowell, NY (1943), 379–80
2) C.E. Gregory, "Explosives for North-American Engineers", Trans Tech Publications, Cleveland (1973), 157–60

Periodic Acid and Periodates

Periodic Acid. $HIO_4.2H_2O$, mw 227.96. monoclinic hygr crysts, loses $2H_2O$ at about 100°, mp 122°, decomps at 130–140°. Sol in w and alc; sl sol in eth (Refs 5 & 6). Prepd by electrolytic oxidation of iodic acid or from Ba periodate according to the equation

$Ba_3H_4(IO_6)_2+6HNO_3 \rightarrow 2H_5IO_6+3Ba(NO_3)_2$ (Ref 1). Periodic acid is highly toxic, and is dangerous in contact with organic materials (Ref 7). In periodic-dimethyl sulfoxide oxidizing systems, violent explns can occur if the concn of periodic acid is too strong. For example, in oxidizing glycopyranosides an expln took place at a 1.5N concn of the periodic acid (Refs 2, 3 & 4)

Refs: 1) J. Willard, InorgSynth **1**, 172 (1939) 2) Anon, C&EN **44** (15), 48 (1966) 3) R.J. Yu & C.T. Bishop, CanJChem **45**, 2195 (1967) 4) Ibid, JACS **90** (7), 1924 (1968) 5) Merck (1968), 799 6) CondChemDict (1971), 670 7) Sax (1975), 832

Ammonium Periodate (Ammonium meta-Periodate). NH_4IO_4, mw 208.96, colorl crysts, mp explds, d 3.056g/cc at 18/4°. Was prepd by C.F. Rammelsberg in 1868 and by T.V. Barker in 1908 (Refs 1 & 2) by neutralizing periodic acid with aq ammonia. Sax (Ref 6) lists it as an expl and advises great care in its storage and handling because a simple abrasion, or impact at ordinary temps, is sufficient to detonate it violently. A serious expln occurred on simply scooping the material from one container to another (Ref 3). Ellern (Ref 5) reports that the metaperiodates ($MeIO_4$) can decomp with expl violence when strongly heated, and Remy (Ref 4) states that ammonium periodate may expld even on gentle friction, eg, when touched with a spatula. If stored, it must be kept in a cool, isolated area away from fire hazards, excessive vibration and shock. It can be disposed of by dissolving in w

Refs: 1) T.V. Barker, JCS **93**, 17 (1908) 2) Mellor **2** (1922), 386–95 & 406–18 3) G.F. Smith, C&EN **29**, 1770 (1951) 4) H. Remy, "Treatise on Inorganic Chemistry", 2 Vols, Elsevier, NY (1956) 5) Ellern (1968), 288 6) Sax (1975), 394

Potassium Periodate. (Potassium meta-Periodate). KIO_4, mw 230.00, colorl tetragonal crysts, mp 582°, explds at 1076°F (Ref 3), bp $-O_2$ at 300°, d 3.618g/cc at 15/4°. Sl sol in w, v sl sol in KOH. Can be prepd by the oxidizing action of chlorine on a hot soln of K iodate and an excess of KOH, or by the electrolysis of K iodate. K periodate is highly toxic, a strong irritant to tissue, and a fire risk when in contact with organic materials

Refs: 1) Mellor **2** (1922), 386–95 & 406–18 2) CondChemDict (1971), 724-L 3) Sax (1975), 1051

Perkins Explosive. A primary mixt patented in Engl in 1870 contg amorph P, metallic sulfides (such as antimony sulfide), and K chlorate or nitrate

Ref: Daniel (1902), 609

Perkoronit. Ger perchlorate expls of varying compn, extensively used during and after WWI for blasting purposes (especially in ore mines and quarries).

According to Naoûm (Ref 1), the original Perkoronits were: 1) K perchlorate 77, m-DNT 10, woodmeal 3, powdered coal 1, paraffin 5 & NG 4%; OB to CO_2 +0.9% and Trauzl value 285cc; 2) K perchlorate 68, AN 10, DNT 16, woodmeal 1, naphthalene 1 & NG 4%; OB to CO_2 +11.1% and Trauzl value 265cc

After WWI, these expls were replaced by the following two, manufd by Dynamit A-G

Table 1
Post WWI Perkoronits

Components and Properties	1	2
K perchlorate	58	59
Amm nitrate	8	10
DNT+TNT+vegetable meal	30	31
NG (nitroglycerin)	4	–
Oxygen Balance to CO_2, %	+2.2	+1.8
Density, g/cc	1.58	1.52
Velocity of Deton, m/sec	5000	4400
Trauzl Test, cc	340	330
Pb Block Crushing, mm	20.0	18.0
Requires for initiation, min	No 3 cap	No 3 cap
Gap Test, cm	6.0	4.0
Heat of Explosion, kcal/kg	1170	1160
Temp of Explosion, °C	3145	3115

These expls were highly brisant, being about equal in that respect to the best chlorate expls. There were also some "Perkoronits" that did not contain AN

Refs: 1) Naoûm, Expls (1927), 133 2) Ibid, NG (1928), 430 3) Davis (1943), 364–5 4) PATR **2510** (1958), Ger 130

Perlit. A Ger perchlorate blasting expl contg K perchlorate 32, AN 10, K or Na nitrate 10, nitrobody (such as TNT) 12.5, wood or cereal meal 31, and NG 4.5%
Ref: Ullman **4** (2nd Ed) (1926), 788

PERMANGANATES

Ammonium Permanganate. NH_4MnO_4, mw 136.97, mp explds (see below), d 2.208g/cc at 10°. Long, reddish-purple needles; rhombic crysts (crysts become steel-grey in storage, presumably due to surface reactions). Sol in cold w, decompd by hot w. Was prepd by E. Mitscherlich in about 1824 (Refs 1 & 2) by treating $AgMnO_4$ with an equiv quantity of NH_4Cl, filtering the liq and evapg to crysts. H. Aschoff (Ref 3) used the same process, while R. Böttger (Ref 1) prepd it from $Ba(MnO_4)_2$ and NH_4SO_4. Christiansen (Ref 4) modified Böttger's method. Since NH_4MnO_4 decomps in hot w, as used in the Christiansen method, Bircumshaw and Taylor (Ref 7) proposed the following modification: $KMnO_4$ (40g) was dissolved in boiling w (400g), NH_4Cl (110g) added, and the hot soln immediately filtered thru a sintered glass funnel (to remove Mn oxides) into a container placed in a cooling mixt. The crysts were recrystd twice from hot w in the same manner

Although most handbooks give its expln temp as 60°, more recent work (Ref 7) has shown that when 0.02g samples of NH_4MnO_4 were heated in air, they expld at 96° only after heating (induction period) for 600–700 seconds, while at 117° it required from 80 to 110 seconds. No expln at 60° was reported. When small samples were heated under confinement (immersed in an inert oil), they expld at 99.5° after about 10 minutes, but required 250 mins to expld at 70°

Amm permanganate decomps slowly in storage even at ordinary temps, forming manganese oxides. After 3 month storage the sample was only 96% pure, and after 6 months it assumed the color of iodine and smelled strongly of nitrogen oxides (Ref 7)

Ref 8 states that dry Amm permanganate is expl at 60° and is likely to expld when rubbed. Kast (Ref 6) reports that mixts of K permanganate and AN can interact to form Amm permanganate. Sax (Ref 9) categorizes it as a moderate expln hazard when shocked or exposed to heat, and that when heated to decompn it emits toxic fumes

Amm permanganate has been used as an ingredient in some of the older expl compns, for example, see under "Pyrodialytes" (Ref 5)
Refs: 1) Mellor **12** (1932), 301 2) E. Mitscherlich, AnnPhysik **2**, 10 (1824); **25**, 300 (1832); **31**, 677 (1834); **32**, 8 (1834) 3) H. Aschoff, "Ueber die Uebermangansäure und die Ueberchromsäure", Berlin (1861) 4) O.T. Christensen, ZAnorgChem **24**, 203 (1900) 5) Daniel (1902), 663 6) H. Kast, SS **22**, 6–8 (1927) & CA **21**, 3745 (1927) 7) L.L. Bircumshaw & F.M. Taylor, JCS **1950**, 3674–78 8) Anon, "Rules for the Packing, Storage, and Labelling of Explosives for Carriage by Sea", Laboratory of the Government Chemist, Board of Trade, London (1965) 9) Sax (1975), 394

Potassium Permanganate. $KMnO_4$, mw 158.03; dark purple or bronze-like, odorless crysts; sweet with astringent taste; stable in air; mp, decomps at 240° with evolution of O_2; d 2.7032 g/cc. Sol in w, acet and methanol; decompd by alc. Can be prepd by (a) oxidation of the manganate in an alkaline electrolytic cell; (b) treating a hot soln of the manganate with CO_2; on cooling, the soln deposits crysts of the permanganate (Refs 6 & 7)
Hazards. K permanganate is a powerful oxidizing agent. It can expld in contact with organic materials, especially alc, ether, glycerin and combustible gases or with sulfuric acid

Bretherick (Ref 8) details the following incidents with original references:

Acetic acid or Acetic anhydride. Cooling is necessary to prevent possible expln from contact of K permanganate (or the Ca or Na salts) with acetic acid or its anhydride

Aluminum carbide. Incandescence on heating

Ammonia, Surfuric acid. Ammonia is oxidized with incandescence in contact with the per-

manganic acid formed in the mixt

Ammonium nitrate. A mixt of 0.5% K permanganate with an AN expl caused an expln 7 hours later. This was due to formation and exothermic decompn of Amm permanganate, leading to ignition

Antimony or Arsenic. Sb ignites on grinding in a mortar with the solid permanganate, while As explds

Glycerol. Contact of glycerol with solid K permanganate caused a vigorous fire

Hydrochloric acid. During prepn of chlorine by addition of the concd acid to solid permanganate, a sharp expln occurred on one occasion (contamination of the acid with sulfuric acid could have produced permanganic acid)

Hydrogen peroxide. Contact of H_2O_2 soln from a broken bottle with pervious packages of permanganate caused a violent reaction and fire

Hydrogen trisulfide. Contact with solid permanganate ignites the liq sulfide

Non-metals. A mixt of C and K permanganate is not friction sensitive, but burns vigorously on heating. Mixts with P or S react explosively on grinding and heating, respectively

Sulfuric acid, Water. Addition of concd sulfuric acid to the slightly damp permanganate caused an expln. This was attributed to formation of permanganic acid, dehydration to dimanganese heptoxide and expln of the latter, caused by heat liberated from interaction of sulfuric acid and moisture. A similar incident was reported previously, when a soln of K permanganate in sulfuric acid, prepd as a cleaning agent, expld violently

Titanium. A mixt of powdered metal and oxidant explds on heating

Wood. Contact between solid K permanganate and wood, either in the presence of moisture or of mechanical friction, may cause a fire

Ref 9 adds the following hazardous reactions without references:

Sulfur, Tin. Expln results on heating with K permanganate to 170° or higher

Ethanol plus Sulfuric acid. Ignition with flashing on contact with K permanganate

Acids plus concd Sulfuric acid. Ignition on contact with K permanganate

Iron. Combustion on percussion of mixt with K permanganate

Ether, Alcohol, Paper, Turpentine oil plus Sulfuric acid. Ignition on contact with K permanganate

Ref 10 adds hazardous reactions between K permanganate and Al carbide, As, dimethyl sulfoxide, hydroxylamine, and polypropylene, which are supported by references

Toxicity. Sax (Ref 11) lists K permanganate as being highly toxic by ingestion, inhalation, or as an irritant. Ref 4 gives a lethal dose 50% kill level (orally in rats) of 1090mg/kg, (subcutaneous in mice) of 500mg/kg

Uses. According to Daniel (Ref 2), K permanganate, as well as other permanganates were used as oxidizing agents in expl compns. However, there was no advantage over materials such as K nitrate, AN, K perchlorate, etc (also see Ref 3)

Davis (Ref 4) reports its use in pyrots as a "flash report" in the mixt 3p K permanganate/ 2p Al

Fielder (Ref 4) used it in a liq expl prepd by soaking a mixt of 70p K chlorate/30p K permanganate in a liq consisting of 80p NB/20p turpentine

Ellern (Ref 5) comments on its use in pyrot delay compns and heating devices

Specification. A US Military Specification (**MIL-P-11970B**, 23 Aug 1973) entitled, "Potassium Perchlorate, Technical Grade", covers Dept of Defense requirements. They state that the material shall be in the form of dark purple crystals and shall assay at not less than 97.0% K permanganate by titration into Na oxalate/ dil sulfuric acid soln

Refs: 1) Mellor **12** (1932), 303–31 2) Daniel (1902), 69 & 610 3) Marshall **1** (1917), 4 4) Davis (1943), 105 & 355 5) Ellern (1968), 49ff, 197, 203, 225 & 338 6) Merck (1968), 856 7) CondChemDict (1971), 724 8) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 843–45 9) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 436–7 10) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, Natl Fire Protection Assn, Boston (1975), **491M**, 346–7 11) Sax (1975), 1051

Silver Permanganate. $AgMnO_4$, mw 226.81; dark violet, monocl crysts; mp, deflagrates at about 135°; d 4.27g/cc; decomps in light. Sl sol in cold w, decompd by hot w or alc. Can be prepd by thoroughly mixing a 5% K permanganate soln with an equiv quantity of 5N Ag nitrate soln. The resulting ppt is filtered, washed with ice cold w, and dried in a vacuum desiccator over sulfuric acid. Purity of the product is 99.5–100%. Ref 3 terms it a dangerous expln risk which may detonate if shocked or heated

By adding concd aq ammonia to a 1M K permanganate soln in w at 10°, and adding one mole of Ag nitrate dissolved in 10 times its wt of w, T. Klobb (Ref 1) obtained

Silver Diamminopermanganate, $AgMnO_4 . 2NH_3$; violet rhombic plates; sparingly sol in cold w, more sol in hot w. It expld on percussion; decompd slowly on standing

Refs: 1) Mellor **12** (1932), 332–3 2) Merck (1968), 949 3) CondChemDict (1971), 788 4) Hackh's (1972), 613 5) Sax (1975), 1099

Sodium Permanganate. $NaMnO_4.3H_2O$, mw 194.98; purple to reddish-black crysts or powder; mp 170_9 decompn; d 2.47g/cc. Very sol in w, decomps in alc. Can be prepd by passing a current of chlorine or ozone thru an aq soln of Na manganate. The soln is then concd and crystd. Na permanganate is a strong oxidizing agent, highly toxic, and is a dangerous fire risk in contact with combustible materials

Refs: 1) Mellor **12** (1932), 302 2) Merck (1968), 963 3) CondChemDict (1971), 807 4) Hackh's (1972), 620 5) Sax (1975), 1115

Complex Explosive Salts of Permanganates.

In addition to Ag diamminopermanganate, described above under Ag permanganate, there are other expl ammino-compds, eg:

Cadmium Tetramminopermanganate. $Cd(MnO_4)_2.4NH_3$. It was prepd by T. Klobb by saturating a soln of K permanganate with ammonia, and adding a soln of a Cd salt. In a few days, the black crysts turned to a brown mass, which detonated on percussion

Cobaltic Hexamminopermanganate. $[Co(NH_3)_6](MnO_4)_3$. Black tetrahedryl crysts, sl sol in cold w, sol in hot w with decompn. Explds on heating or on being struck. It was prepd by T. Klobb and E. Wilke-Dörfurt by mixing a warm concd soln of one mole of cobaltic hexamminochloride with 12 moles of K permanganate

Cobaltic Hexamminodichloropermanganate. $[Co(NH_3)_6]Cl_2(MnO_4)$. Black crysts, appearing red or brown in transmitted light. Very unstable; decompd by w; detonates on rapid heating. Was prepd by treating a warm soln of 8 moles of cobaltic hexamminochloride with a soln of 1 mole of cobaltic hexamminopermanganate, then filtering rapidly and allowing to cool

Ref: Mellor **12** (1932), 335–6

Perfluorosuccinamide-Lithium Aluminum Hydride (Danger of Explosion). In an attempt to reduce perfluorosuccinamide to the corresponding diamine, it was added to an ether soln of lithium aluminum hydride in a nitrogen atm. Hydrolysis was then attempted, but as a second drop of w was added, a violent expln and ether fire resulted. It was shown that the diamide and the lithium aluminum hydride reacted to give an unstable complex which detonated at room temp

Ref: T.S. Reid & G.H. Smith, C&EN **29**, 3042 (1951) & CA **46**, 3279 (1952)

Perform. Another name for 3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]-nonane. See Vol **5**, E91-L

Performance vs Constitution of Explosives. The following discussion is taken from Ref 9, published under the title "Classification of Explosives":

Expls may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint we distinguish between chemical individual substances and mixts. The former are divided into: (1) nitro compds, (2) nitric esters, (3) nitramines, (4) derivatives of chloric and perchloric acids, (5) azides, and (6) various compds capable of producing an expln, for example fulminates, acetylides, nitrogen rich compds such as tetrazene, peroxides and ozonides, etc

Individual substances are expl if their mole-

cules contain groups which confer upon them expl props. The first attempt at a systematic approach to the relation between the expl props of a molecule and its structure was made by van't Hoff (Ref 1). He pointed out, that in the molecules of expl compds the following groups were present:

O – O in peroxides and ozone and ozonides
O – Cl in chlorates and perchlorates
N – Cl in nitrogen chloride
N = O in nitro compds, nitric acid esters and salts
N = N in diazo compds, hydrazoic acid, its salts and esters
N = C in fulminates and cyanogen
C ≡ C in acetylene and acetylides

A further effort to establish a relationship between expl props and structure has been made more recently by Pletz (Ref 7). He proposed a theory of "explosophores" and "auxoploses". According to Pletz the expl props of any substance depend upon the presence of definite structural groupings, called *explosophores*. The *auxoploses* fortify or modify the expl props conferred by the explosophore. Pletz divided all expls into eight classes containing the following groups as explosophores:

(1) $-NO_2$ and $-ONO_2$ in both inorganic and organic substances
(2) –N=N– and –N=N=N– in inorganic and organic azides
(3) $-NX_2$, for example in NCl_3 (X–a halogen)
(4) –N=C in fulminates
(5) $-OClO_2$ and $-OClO_3$ in inorganic and organic chlorates and perchlorates repectively
(6) –O–O– and –O–O–O– in inorganic and organic peroxides and ozonides respectively
(7) –C≡C– in acetylene and metal acetylides
(8) M–C metal bonded with carbon in some organometallic compds

Although this classification is in principle correct, the distinction between the terms "explosophore" and "auxoplose" is very vague and of little practical value

A further step in the classification of expls was made by Lothrop and Handrick (Ref 4). They collected and classified all the available information on the performance of expls and related it to four factors: oxygen balance, "plosophoric" groups, "auxoplosive" groups, and heat of expln

A *plosophore* has been defined as a group of atoms which is capable of forming an expl compd on introduction into a hydrocarbon. According to these authors there are two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence it is suggested tht these be called "primary" and "secondary" plosophores. Primary plosophores include nitrate esters, aromatic and aliphatic nitro groups and the nitramine group. The secondary plosophores that comprise the remainder include such groups as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc. If more than one type of these groups is present such a molecule may be named a *hybrid* according to Lothrop and Handrick. Groups which do not themselves produce expl props, but may influence them are called *auxoplosives* by these authors. We may quote hydroxyl, carboxyl, chlorine, sulfur, ether, oxygen, amine, etc. as examples of such groups

Although the classification of groups existing in expl molecules suggested by Lothrop and Handrick may be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of expls aroused strong criticism (Ref 6). It is known that the oxygen present, for example, in carbonyl or hydroxyl groups, has little effect on the performance of an expl. This is due to the high heat of formation of C–O and C–O–H bonds. On the contrary, the low (negative) heats of formation of N–O and C≡C bonds are of great significance in relation to the performance of expls

That is the reason why the performance of Picric Acid (trinitrophenol) is only very slightly higher than that of Trinitrobenzene and why the performance of Trinitroanisole is much the same as that of Trinitrotoluene

The low value of the expl power of oxygen atoms bonded with carbon and hydrogen atoms in such a group as COOH had already been stressed by Stettbacher (Ref 2), who also pointed out that an exception is provided by peroxides and ozonides which form exothermic bonds that considerably enhance expl performance

However, the slightly better performance of

Picric Acid compared with Trinitrobenzene is probably the result of the former's greater ability to detonate. The ease of detonation of Picric and Styphnic acids as compared with Trinitrobenzene is well known. D. Smoleński and W. Czuba (Ref 8) recently pointed out that Dinitrophenol detonates more readily than Dinitrobenzene

It is also well known from the classic work of L. Wöhler and Wenzelberg (Ref 3) that the sensitivity to impact of aromatic nitro compds increases with increase in the number of substituents for a given member of the nitro groups

Refs: 1) H. van't Hoff, according to H. Brunswig Explosivst, Barth, Braunschweig (1909), 17 2) A. Stettbacher, AngChem **30**, 269 (1917) & CA **12**, 3011 (1918); Ibid, "Die Schiess-und Sprengstoffe", Barth, Leipzig (1919) & CA **14**, 468 (1920) 3) L. Wöhler & O. Wenzelberg, AngChem **46**, 173 (1933); not found in CA 4) W.C. Lothrop & G.R. Handrick, ChemRevs **44** (3), 419–445 (1949) & CA **43**, 6416 (1949) 5) K. Singh, JSciIndResearch(India), **10A**, 406–19 (1951) [A review with 27 refs on the relation between chemical constitution and performance of organic expl compds] 6) A. Schmidt, Chim&Ind **67**, 253 (1952) & CA **46**, 5843 (1952) 7) V. Pletz, ZhObshchKhim-(JGenChem) **5**, 173 (1953); not found in CA 8) D. Smoleńskii & W. Czuba, ZeszytyNauk-PolitWroclawskiej, Chemia **7**, 3 (1955) 9) Urbański **1**, 1–3 (1964)

Performic Acid. (Peroxyformic Acid, Permethanoic Acid, Formylhydroperoxide). ACOOOH, mw 62.03, the 90% soln is a colorl liq, is prone to expld on contact with metals, their oxides, reducing substances, or on distn. A 90% soln is obtained when a mixt of 20g formic acid, 25g 100% hydrogen peroxide and 6.5g sulfuric acid is allowed to interact for 2 hrs and is then distd. Misc with w, alc, eth; sol in benz and chlf (Refs 6 & 8)

Performic acid solns are unstable and undergo a self-accelerating exothermic decompn at ambient temp (Ref 2). An 80% soln expld at 80–85° (Ref 1). A small sample of the pure vacuum distd material cooled to below −10° expld violently when the flask was moved (Ref 5). Although the acid has occasionally been distd, it is an extremely dangerous operation (Ref 7)

With regard to metals or oxides, the violence of reaction depends on concn of the performic acid as well as the scale and proportion of the reactants. The following observations were made (Ref 1) with additions of 2–3 drops of about 90% performic acid. Ni powder becomes violent; Hg, colloidal Ag and Th powder readily cause explns. Zn powder causes a violent expln immediately. Fe powder (and Si) are ineffective alone, but a trace of Mn dioxide promotes deflagration. Ba peroxide, Cu oxide, impure Cr trioxide, Ir dioxide, Pb dioxide, Mn dioxide, and V pentoxide all cause violent decompn, sometimes accelerating to expln. Pb oxide, trilead tetraoxide and Na peroxide all cause an immediate violent expln

Impure C and red P are oxidized violently, and Si, promoted by traces of Mn dioxide, is oxidized with ignition (Ref 1)

Formaldehyde, benzaldehyde and aniline react violently with 90% performic acid (Ref 1). An unspecified organic compd was added to the acid, and soon after the initial vigorous reaction had subsided, the mixt expld violently (Ref 3). Reaction with alkenes is vigorously exothermic, and adequate cooling is necessary. Reactions with performic acid can be more safely accomplished by the slow addition of hydrogen peroxide to a soln of the compd in formic acid (Ref 4)

Sax (Ref 9) states that performic acid is highly toxic by ingestion, inhalation or as an irritant

Refs: 1) J. D'Ans et al, Ber **48**, 1136 (1915) 2) F.P. Greenspan, JACS **68**, 907 (1946) 3) Anon, C&EN **28**, 418 (1950) 4) E.S. Shanley, C&EN **28**, 3067 (1950) 5) A. Weingartshofer et al, C&EN **30**, 3041 (1952) 6) Merck (1968), 798-R 7) D. Swern, Ed, "Organic Peroxides", Vol **1**, 337, Wiley-Interscience, London (1970) 8) CondChemDict (1971), 669-R 9) Sax (1975), 1003

Perminite. See under Permonit in this Vol

Permissible or Permitted Explosives. In many coal mines there is a continual evolution of methane (firedamp) into the air of the workings.

The methane is trapped in the coal or rock, often in pockets within the veins, and is sometimes of relatively high pressure. It is usually of fairly high purity, contg only minor amounts of other hydrocarbons and N_2. Methane, when mixed with air in proportions between 5 and 14%, forms an expl mixt. In gassy mines, therefore, there is always the danger that a mixt may be formed which, if ignited, can cause serious damage and loss of life. In coal mines, also, there is further danger in that the working of the coal produces coal dust. Coal dust, when mixed with air, gives a mixt which when suitably ignited can undergo a dust expln. Indeed, if an expln of firedamp (or coal dust) occurs, the wave produced can stir the dust lying in the mine into the air, producing a mixt which can lead to further propagation and devastating expln. In the history of coal mining there have been many examples of both firedamp and coal dust explns, and the latter in particular have led to serious loss of life (Ref 2)

These frequent coal mine disasters led, early in the HE industry, to the careful regulation of the expls that could be permitted for use in coal mining. Expls allowed for use in gassy and dusty US coal mines are called *permissibles;* those in England and Canada are called *permitted* expls; in France, *explosifs antigrisouteux;* in Belgium, *explosifs S.G.P.* (sécurité, grisou, poussière); and in Ger, *schlagwettersichere Sprengstoffe.* In US permissibles, AN has from the beginning been an important safety ingredient as regards ignition of coal gas and dust. It owes its safety qualities in this regard to the low expln temp in expls contg large percentages of AN (Ref 1)

For an in depth coverage of this topic, the reader is referred to Vol **3**, C368-R to C378, under Coal Mining Explosives, Testing for Permissibility, and Vol **3**, C444-R to C459-R under Coal Mining Explosives, Permissible

Refs: 1) Cook (1958), 10–11 & 15–16 2) S. Fordham, "High Explosives and Propellants", Pergamon, NY (1966), 81–97 3) Urbański **3** (1967), 461–89 4) Blaster's Handb (1969), 43–6 [DuPont permissibles] 5) C.E. Gregory, "Explosives for North American Engineers", Trans Tech Publications, Cleveland (1973), 221–23

Permonite (Permonit, Perminite). Ger blasting expls based on perchlorate, manufd by the Sprengstoff A-G Carbonit before WWI. Typical formulations were: K perchlorate 30 to 37.5, AN 30 to 37.5, K or Na nitrate 7, nitrobody (such as TNT) 10 to 25, woodmeal 3, cereal meal 4, and a mixt of glue, glycerin and gelatin 1% (Refs 2 & 4)

Escales (Ref 1), Marshall (Ref 2) and Barnett (Ref 3) give the compn of Permonite which was on the permitted list in Engl before WWI as K perchlorate 31–34, NG 3–4, collodion cotton 0.5 to 1, AN 39–43, TNT 11–13, starch 5–9, woodmeal 1.5–3.5, and jelly (mixt of 1p glycerin and 3.5g gelatin) 1.5–3.5%. Gap test, 80mm; Trauzl test, 365cc; Sensitivity to Impact, 20cm with a 2kg wt. This expl failed to pass the Rotherdam test

Marshall (Ref 2) gives the compn and properties of the following Permonites:

Permonit I or Gesteins Permonit. K perchlorate 30, AN 40, Na nitrate 7, TNT 15, flour 4, woodmeal 3, and jelly 1%. Gap test, 70mm; Trauzl test, 320cc; Detonation Velocity, 3470m/sec; Sensitivity to Impact, 70cm with a 2kg wt

Permonit S.G.P. (Used in Belg). K perchlorate 24.5, NG 6, AN 29, TNT 25, flour 4, woodmeal 3, and jelly 1%. Gap test, 100mm; Trauzl test, 205cc; Detonation Velocity, 2326m/sec; Sensitivity to Impact, 80cm with a 2kg wt; limit charge, 900g, equiv to 575g of Dynamite No 1

Note: The Gap test (Influence or Propagation test) mentioned above consisted of ascertaining the distance over which the detonation is conveyed from one 30cm cartridge loaded with a test formulation to another lying on the ground

Permonit of Bichel. The following expl was patented in Fr in 1905 by C.E. Bichel, and was called Permonit (Ref 1, p 185): Amm perchlorate + K chloride mixt 70–80, NG 4–10, and TNT 6–10%

Permonit A. Escales (Ref 1, p 185) gives the following compn: K perchlorate + AN, max 54; gelatinized NG, max 4; the balance consisting of nitroaromatic compds (of which TNT, max 20%) and woodmeal

Refs: 1) R. Escales, "Chloratsprengstoffe", Leipzig (1910), 105, 150 & 185 2) Marshall **1** (1917), 384 & **2** (1917), 493 3) Barnett (1919), 111–112 4) Ullmann **4**, 2nd Ed (1926), 788–9 5) A. Pérez Ara (1945), 218

Pernitral. A perchlorate expl authorized in Engl before WWI, but never manufd. It contained Amm perchlorate 40, Na nitrate 30, solid TNT 10, liq TNT 10, and Al powder 10%
Ref: Barnett (1919), 112

Pernitryl Fluoride. See under Nitrogen Trioxyfluoride in this Vol

PEROXIDES

Peroxide compds, both inorganic and organic (see below under each of these sections), are usually described as compds whose structures include the peroxo- group, –O–O–. The electronic structure of this O_2^{2-} ion is depicted in Fig 1. According to Vol'nov (Ref 1) the O_2^{2-} ion has an even number of electrons, 14, and the symbol for the ground state of this ion is Σ, which is in agreement with the diamagnetism and absence of color which characterize compds contg this ion

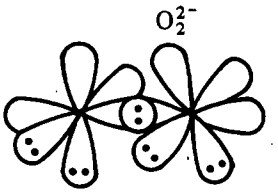


Fig 1. Electron Structure of the O_2^{2-} ion

The molecular orbital notation for the O_2^{2-} ion is $[KK(Z\sigma)^2(Y\sigma)^2(X\sigma)^2(W\pi)^4(V\pi)^4]$. The O_2^{2-} ion represents an ellipsoid of rotation with the major axis 4.19Å long. The radius of the O^- ion in the O_2^{2-} ion is 1.35Å. The O–O bond length is (about) 1.49Å. The major semiaxis of the O_2^{2-} ion is, therefore, equal to 2.09Å. The minor semiaxis (or transverse radius) is 1.23Å. The bond dissociation energy of O–O in hydrogen peroxide is 1.5eV, which is approx (reported from 20 to 50kcal/mole) 35kcal. The heat of reaction of $O_2+2e \rightarrow O_2^{2-}$, is 110kcal (Refs 1 & 4).

Most peroxides can be readily made by air oxidation of the base compd or metal. They are characterized by the formation of hydrogen peroxide upon reaction with dil acid soln, the liberation of oxygen as a result of thermal decompn, and the liberation of oxygen upon reaction with w and other chem agents. The formation of hydrogen peroxide upon the hydrolysis of peroxides clearly indicates the relationship of these compds to hydrogen peroxide. For this reason, peroxides are thought of as being derived from hydrogen peroxide by replacement of one or both H atoms by organic, inorganic or organic/inorganic radicals (Ref 1). The decompn of $H_2O_2 = H_2O+\frac{1}{2}O_2$ is readily accomplished (see Vol **7**, H218-R to H222-L). The release of active (nascent– oxygen by this two-step mechanism in soln or the direct release of oxygen during thermal decompn, makes peroxides strong oxidizing agents, brisant expls, and extreme fire hazards when in contact with combustible materials, especially under high-temp conditions. The primary industrial uses of peroxides are as oxidizing agents and as initiators of polymerization. Mil uses are currently as liq propInt constituents, ingredients in pyrots, and as polymerization initiators and curing agents (see below)

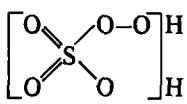
The prefix "peroxo-" is a general term referring to any peroxide linkage

Refs: 1) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 9–13
2) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry . . .", Interscience Pub, NY (1966), 374–77 3) H. Ellern, "Military and Civilian Pyrotechnics", Chem Pub Co, NY (1968) 4) D.Swern, Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970)
5) CondChemDict (1971), 671 6) H.J. Emeléus & A.G. Sharpe, "Modern Aspects of Inorganic Chemistry", John Wiley & Sons, NY (1973), 366–72

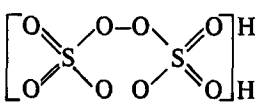
Peroxides, Inorganic. The inorganic derivatives of hydrogen peroxide. These compds are described by a general formula, viz, $E^+{}_2O_2$, $E^{++}O_2$, etc; where "E" is an element. The metallic atoms are bonded to the oxygen bridge with ionic bonding. For convenience, differentiation is made between simple and complex inorganic peroxide compds. According to Vol'nov (Ref 5) simple peroxide compds also

include hydroperoxides. The hydroperoxides are characterized by the presence of the hydroperoxyl ion HO_2^- and are represented by the general formula E–O–OH. In these compds, inclusive of hydrogen peroxide, the peroxo-group is ionically bonded to the element and covalently bonded to the H atom. The ionic peroxides form well-crystd hydrates and hydrogen peroxide adducts. There are some hydroperoxides that can be classified as peroxyhydrates and others as peroxyacids. For example, NaOOH can be shown as a dimer, $Na_2O_2.H_2O_2$, whereas $(OH)_3Ti–O–O–H$ can be considered a peroxyacid. Complex peroxide compds include inorganic peroxides in which the peroxo- group as such (or in the form H_2O_2 and HO_2) is bonded to the element by a covalent bond rather than an ionic bond. Complex peroxide compds also include the addition compds formed with crystd H_2O_2. Again, according to Vol'nov, complex inorganic peroxide compds can be divided into five groups:

1) Peroxyacids and their salts. In these compds the peroxo-group is part of a complex anion. Within this category, one can distinguish between mononuclear and multinuclear peroxyacids and their salts. Generally, in these compds the coordinating atoms are elements of the IV-VI group – nonmetals C, N, P, S, or metals Ti, V, Cr, Mo, W, etc. Peroxymonosulfuric acid



is an example of a mononuclear peroxyacid, and peroxydisulfuric acid is an example of a multinuclear peroxyacid

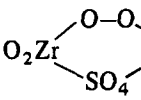


The O–O bond length in a peroxo-group of peroxyacid derivs, for example in the $(NH_4)_2S_2O_8$ compd, is 1.46Å, which is less than the bond length in the O_2^{2-} ion (1.49Å)

2. Peroxide complexes which are neither peroxyacids nor their derivatives. These may also be divided into mononuclear and multinuclear compds

The mononuclear peroxide complexes can further be divided into three subgroups: peroxycomplexes, perhydrocomplexes, and hydroperoxycomplexes. The peroxycomplex subgroup includes compds in which the peroxo-group is in the internal sphere, for example, $[(UO_2)_2(O_2)_2(H_2O)_8]$. The perhydrocomplexes contain hydrogen peroxide molecules in the internal sphere, for example $[Fe(H_2O)_5(H_2O_2)]^{3+}$, while the hydroperoxycomplexes are characterized by the presence of the hydroperoxy radical HO_2, for example, $K_4[(UO_2)_2(O_2)_3(HO_2)(OH)H_2O]$

Among the multinuclear peroxide complexes we may list:



$O_2Zr\langle O–O, SO_4\rangle ZrO_2$; $H_4[Cl_5Re–O–O–ReCl_5].2H_2O$

and

$[(NH_3)_5Co–O–O–Co(NH_3)_5]NO_3)_5$

In the last compd, the O–O bond length is 1.45 ± 0.06Å

3. Peroxide hydrates. For example, $Na_2O_2.8H_2O$

4. Peroxyhydrates – molecular compds. For example, $CaO_2.2H_2O_2$ and $K_2CO_3.3H_2O_2$. Peroxide peroxyhydrates are closely related to the KF.HF type compds. Ammonia and certain organic compds having base properties also form molecular compds contg H_2O_2

5. Peroxyhydrate hydrates – molecular compds contg crystd water and crystd hydrogen peroxide, for example, $BaO_2.H_2O_2.2H_2O$ and $Na_2SO_4.0.5H_2O_2.H_2O$ (Ref 5)

History. The first known peroxide to be produced was BaO_2 as described by A. Humboldt in 1799. Later, G. Gay-Lussac and L. Thenard synthesized Na and K peroxides, and Thenard synthesized H_2O_2 in 1818 (Ref 17)

According to Vol'nov, the historical development of inorganic peroxide chemistry can be divided into four periods. The first period, from 1818 (Thenard's synthesis of H_2O_2) to 1869 (the formulation of the Periodic Table by D.I. Mendele'eff) is characterized by the wide-ranging investigations conducted by Thenard and his co-workers concerning the reaction of "oxidized water" which resulted in the development of a whole series of peroxide derivs as well as a more precise determination of the structure of Na peroxide

"The second period in the development of inorganic peroxide compounds can be considered to extend from the discovery of the Periodic Table to the application of physical chemistry

to the investigation of peroxide compounds at the beginning of this century. This period includes the classical studies of Melikov and Pisarzhevskii, who uncovered a series of regularities in the formation of peroxyacids; the studies of R. de Forcrand in France dealing with the thermochemistry of inorganic peroxides; and the discovery of sodium perborates and carbonate peroxyhydrates of alkaline metals by Tanater. Also, during this period, a new type of peroxide compound was obtained for the first time (peroxyacids and their salts) by the use of electrochemical methods. M. Berthelot synthesized peroxydisulfuric acid, and E. Konstam and A. Henson produced potassium peroxydicarbonate. During this period, methods for industrial production of sodium peroxide and hydrogen peroxide were developed

The third period is characterized by the extensive studies, both in the USSR and abroad, of the structure, properties, and bond characteristics of peroxide compounds. This period includes the work of Kazarnovskii and his coworkers concerning the structure of a series of peroxide compounds, his discovery of sodium superoxide, and the fundamental investigations carried out by the Canadian scientist Otto Maas and his co-workers concerning concentrated hydrogen peroxide . . ."

". . . Significant progress has been made in the Soviet Union in the post-war (or fourth) period in both the theoretical and applied fields. Kazarnovskii made important contributions to this progress as a result of his studies concerning the synthesis, properties, and reactivity of sodium superoxide and of the important new class of peroxide compounds—the inorganic ozonides. It is also appropriate to mention in this context the work of Brodskii, who was the first to establish the mechanism for the formation and disintegration of peroxide compounds via studies involving the use of the heavy oxygen isotopes. Also important was the work of A.M. Gurevich concerning the nature of uranium peroxide compounds, and the work of Kobozev on the synthesis of hydrogen peroxide by electrical discharge. Shpital'skii and his coworkers have made important studies of the catalytic decomposition of hydrogen peroxide. And at the Laboratory of Peroxide Compounds of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, Makarov has directed many important physico-chemical studies of peroxide compounds. . ."

". . . the chemistry of inorganic peroxide compounds is being developed mainly in universities and in private scientific research institutes in the United States, Great Britain, and West Germany. In the United States, for example, systematic studies of the properties of inorganic superoxides, especially the thermodynamic properties of these compounds, have been carried out by Professor Kleinberg at the University of Kansas and Professor Margrave at Wisconsin University. Extensive investigations were conducted at the Massachusetts Institute of Technology, under the direction of Professor C. Satterfield, on the properties of concentrated hydrogen peroxide solutions . . ."

". . . At the Illinois Institute of Technology, Professor I.G. Solomon directed work on the synthesis of inorganic ozonides . . ."

". . . In recent years, systematic X-ray studies of inorganic peroxides have been carried out by G. Föppl in West Germany and by N. Vannerberg and R. Shtomberg in Sweden . . ."

". . . A series of conferences on peroxide compounds took place in the years from 1953 through 1961. A symposium on inorganic peroxides, superoxides, and peroxyhydrates was held in Philadelphia in 1953, and a symposium on peroxide reaction mechanisms was held at Brown University in 1960. In 1961, the British Society of Industrial Chemistry sponsored an international symposium on peroxide compounds. A general meeting dedicated to the chemistry of inorganic and organic peroxide compounds was held in Moscow at the end of 1961. The papers presented at the meeting showed that Soviet scientists have made significant contributions to this field of chemistry. However, the meeting also pointed out the areas of study which require a greater effort. Much more work must be done in the area of thermodynamics and kinetics. Also, a significant lag was noted in the field of analytical chemistry of peroxides and in X-ray structural investigations. To date, no really thorough investigations have been conducted, either by Soviet or foreign scientists, on the reactivity of inorganic peroxide compounds. It was established at that meeting that inorganic chemists working on

peroxides must concentrate their efforts on the synthesis of new superoxides and ozonides especially rich in oxygen. Such research should include the application of superhigh pressures of oxygen and ozone, concentrated solutions of hydrogen peroxide in nonaqueous solvents, and electrochemical methods. Physical chemists have an important role to play be determining the thermodynamic, kinetic, mechanistic, and structural properties of peroxide compounds. . ." (Ref 5)

Besides the ever-broadening scientific investigations which are being conducted world-wide in the field of inorganic peroxide compds, it is also necessary to concentrate in the applied field on the sound development of continuous, safe, efficient and economical prodn methods so as to increase the utilization of inorganic peroxides

Manufacture. In general, inorganic peroxides can be *manufactured* by one of the following methods: (1) by the action of hydrogen peroxide on oxides, hydroxides or salts (such as those of Ca, Sr, Zn, Mg), 2) by combustion of a metal or its lower oxide in air or oxygen (peroxidation), or 3) by electrolysis (anodic oxidation) of some salts. For instance, alkaliperoxides and barium peroxide may be prepd by the 2nd method, while peroxides of Sr, Ca, Zn and Mg are prepd by the action of hydrogen peroxide with the oxide or hydroxide. Another variation of this method is pptn from a soln of a metallic salt with hydrogen peroxide in the presence of alkali

The stability of inorganic peroxides increases as the cation is larger, which allows the spread of the negative charge over the extra oxygen atom. For instance, in the alkaline earth group, Ba, Sr, Ca, and Ba peroxide is the most stable and is the only one that can be prepd by direct peroxidation under atm press. Sr peroxide may also be prepd by peroxidation but, as it would require high pressure, it is preferable to prep it from $Ca(OH_2)$ and hydrogen peroxide

Uses. See below under specific compd. Generally, inorganic peroxides such as BaO_2 and SrO_2 are used in igniter compns for aircraft ejection app, percussion ignition compns, electric detonators, pyrots and gas prodn compns for automotive safety bags. Na_2O_2 is used in analytical chemy, for example, to determine halogens in organic compds. The peroxides of Ca, Mg and Zn are used in medicine. ZnO_2 is employed where a slow evolution of O_2 is desired. Hydrogen peroxide has been used in propint mixts, as, for example, the V-2 rocket of WWII. Inorganic peroxides have also been employed to supply O_2 for breathing purposes in closed spaces such as in submarines or mining operations

Refs: 1) C.F.Girsewald, "Anorgische Peroxide und Persalze", Braunschweig (1914) 2) Mellor **1** (1922), 394 & 956–61 3) R.H. Heiskell, "Pyrotechnic Composition", USP 2726943 (1955) & CA **50**, 5293 (1956) 4) R.H. Heiskell, "Nonluminous Pyrotechnic Mixture, for a Projectile", USP 2714061 (1955) & CA **50**, 8208 (1956) 5) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966) 6) T.A. Doris & T.Q. Ciccone, "Igniter Composition for Aircraft Ejection Apparatus", USP 3317362 (1967) & CA **67**, 55845 (1967) 7) Anon, "Low-Pressure Percussion Ignition Compositions", GerP 1243067 (1967) & CA **67**, 101581 (1967) 8) Anon, "Electric Safety Detonator", FrP 89452 (1967) & CA **68**, 61136 (1968) 9) H. Ellern, "Military and Civilian Pyrotechnics", Chemical Pub Co, NY (1968) 10) M. Hamasaki et al, "Gas Producing Compositions", GerP 2063586 (1971) & CA **75**, 119654 (1971)

Selected inorganic peroxides of military importance are presented below:

Barium Peroxide (Barium Dioxide, Barium Superoxide or Barium Binoxide). BaO_2, mw 169.36, white to grey tetragonal crysts or powd, mp 450° (Refs 15 & 33), bp 790–900° (decompn) (Refs 15, 17 & 33), d 4.96g/cc (Refs 15 & 33) & 5.43g/cc (Ref 17). V sol in cold w, sol in hot w (decompn), sol in dil acids (with decompn forming hydrogen peroxide), insol in acet. *Lab* prepn consists of heating loose BaO in CO_2-free O_2 at 500° (Refs 16 & 28). Other lab prepns are to be found in Refs 1, 3 & 6. A current *industrial* process reacts $Ba(OH)_2$ with 85% hydrogen peroxide vapors, forming the peroxide from a stoichiometric mixt within 20 mins. Most of the w is removed from the product at 55°, with the remaining traces taken off under

vacuum at 110–150°. The yield is 92.1% (Refs 20, 21 & 26)

BaO_2 is a strong oxidizing agent. Mixts with organic mats such as amines, alcohols or oils as well as with readily oxidizable mats such as P, Sb or charcoal are expl, and ignite easily by friction or on contact with a small amt of w (Refs 29, 30 & 31)

Kaye (Ref 11b) has detd the purity of BaO_2 using a non-aqueous titrimetry technique. Norwitz (Ref 16a) has reported techniques for the detn of impurities in BaO_2. In a subsequent report (Ref 32), he evolved a method for the detn of BaO_2 (or SnO_2) in small arms igniter compns. The technique consists of HCl soln of the peroxide, filtn of insol mats, reaction of the

Table 1
Barium Peroxide
Chemical and Physical Requirements

Requirements	Grade A		Grade B
	Class 1	Class 2	
Moisture, max percent [a]	–	–	0.3
Apparent density, gm/ml min [b]	–	–	1.3
Available oxygen, min percent [c]	8.5	8.5	8.8
Total iron, max percent [d]	–	–	0.03
Strontium, max percent [e]	–	–	0.85
Calcium, max percent [f]	–	–	0.15
Magnesium, max percent [g]	–	–	0.02
Sodium, max percent [h]	–	–	0.05
Aluminum, max percent [i]	–	–	0.05
Chlorides (as barium chloride), max percent [j]	–	–	0.1
Nitrate (as barium nitrate), max percent [k]	see footnote 1	see footnote 1	0.1
Insoluble matter, max percent [m]	2.0	2.0	–
Grit, max percent [n]	0.005	–	–
Barium content, max percent [o]	76.0	76.0	–

Footnotes to Table 1

a – by wt loss after heating for 1.5 hrs at 275°
b – by weighing the content of a Scott volumeter cube
c – by K permanganate titration
d – by K permanganate titration after redn using a Jones reductor
e – gravimetrically as Sr sulfate
f – gravimetrically as Ca oxide
g – by bromate-bromide-thiosulfate titration
h – gravimetrically as MgNa uranyl acetate
i – after gravimetrically detg the combined oxides of Al and Fe, Al oxide is calcd by subtracting the percent Fe oxide found
j – by Ag nitrate-ammonium thiosulfate titration
k – by sulfuric acid titration after reaction with Devarda's metal
l – to be specified by the interested agency using the Mil Spec
m– gravimetrically after dil HCl digestion and residue ignition
n – gravimetrically after dil HCl-conc nitric acid treatment and filtn. The grit is then qual identified by the scratching sound it makes on a glass plate when rubbed with a steel spatula
o – gravimetrically as Ba sulfate;
(3) granulation requirements as shown in Table 2 below

Table 2
Particle Size Distribution [a]

	Grade A		Grade B
	Class 1	Class 2	
Thru No 100 US Standard sieve (150 microns)	99.9	–	100
Thru No 140 US Standard sieve, min (106 microns)	–	–	95
Thru No 170 US Standard sieve, min (90 microns)	98.0	–	–
Thru No 200 US Standard sieve, min (75 microns)	–	99.9	–
Thru No 325 US Standard sieve, min (45 microns)	90.0	–	–

Footnote to Table 2
a – gravimetrically, after shaking a sample thru the nest of graduated US Standard
– Sieves shown in the Table

sample soln with Ti soln and detn of the TiO_2 formed spectrophotometrically at 410 nanometers. The procedures for detg BaO_2 and impurities are shown in USAMilSpec, **MIL-B-153A**, and are described briefly below

Toxicity. Highly toxic if swallowed. The LDLO is 100mg/kg; max allowable air concn for an 8 hr day is 0.5mg/m^3 (Refs 15 & 31)

The USA Mil Spec (Ref 25) contains the following requirements for Grade A (anhyd with some BaO and $BaCO_2$), Class 1 (> 45 microns, nominal) and Class 2 (>75 microns, nominal); and Grade B (manufd by wet pptn method and anhyd) BaO_2: (1) the color shall be grayish-white or tan-white; (2) the chemical and physical properties with requirements and criteria are shown in Tables 1 & 2

Uses. BaO_2 is used in a number of igniter/tracer/fuze compns for mil ammo. An example is that of a 40mm tracer compn, $Mg/BaO_2/Ca$ resinate – 17.5/80.5/2.0% (Refs 4, 5, 7, 8, 9, 10, 11, 11a, 12, 13, 14 & 23). It imparts a green color to burning pyrot compns (Refs 4 & 15). Doris and Ciccone have reported the development of an igniter compn for an aircraft ejection app having the compn 100–325 mesh Mg (14.0), BaO_2 (73.9), Zn stearate (0.9), chlorinated rubber (5.3), Toluidine Red (0.9) and Ca resinate binder (5.0%) (Ref 18). A GerP (Ref 7) was obtained on low-pressure percussion ignition compns, one of which has the following compn; Cu (15), B (15), Ca_2Si (15), tetrazine (1.5) and BaO_2 (53.5%). A FrP was reported (Ref 8) for an electric safety detonator using Al powd/BaO_2 – 20/80%. An interesting use for BaO_2 has been found in gas producing compns for automotive safety. As reported by Hamasaki et al (Ref 27) a compn comprised of a mixt of BaO_2 (29.70), Zr (3.33), azodicarbonamide (66.33) and SBR(?) (0.34%); or a similar mixt of a metallic reducing agent, an inorg oxidizer, and a gas former, is used to inflate within 30msec after electrical ignition, a gas bag designed to protect the occupants of an automobile upon impact with an obstacle. Vol'nov (Ref 17) lists other uses for BaO_2, such as in the polymerization of olefins and vinyl chloride; the oxidation of ethylene to ethylene oxide; the prodn of synthetic gas ($CO+H_2$) by partial oxidn of hydrocarbons; the synthesis of hydrazine hydrate from NH_4 and O_2; the decoloring of Pb and Te glasses; as a starting subs for the prodn of metallic barium; and the use in analytical chem when it is added to sulfuric acid to accelerate the combstn of org substances

Refs: 1) Gmelin, Syst No **30** (1932), 92–104; Ibid, Supplement (1960), 177 & 296–8 2) Mellor **3** (1922), 666–9 3) P. Askenasy & R. Rose, ZAnorgChem **189**, 1 (1930) & CA **24**, 2839 (1930) 4) G.J. Schladt, "Stability Tests on Special Pyrotechnic Compositions" PATR **42** (1931) 5) R.W. Scharf, "Investigation of Hercules Non-Gaseous Powder For Use in 21 Second Time Fuze", PATR **648** (1935) 6) J.D. Bernol et al, ZKristallogr **92**, 344 (1935) & CA **30**, 2821 (1936) 7) J.D. Hopper, "Study of Fundamental Properties of High Explosives", PATR **861** (1937) 8) D.R. Beeman, "Improved Functioning of M2 Tracer", PATR **951** (1939) 9) H.J. Eppig, "Sensitivity of Tracer Compositions Containing Barium Nitrate", PATR **1254** (1943) 10) D. Hart, "Compilation of Data On the Compositions of Foreign Igniters and Tracers", PATR **1335**

(1943) 11) D. Hart, "Investigation of Stability of Igniter Composition 'K' and Red Tracer Composition", PATR **1645** (1947) 11a) F.B. Clay & R.A. Sahlin, "Igniter Compositions For Tracer Projectiles", USP 2709129 (1955) & CA **49**, 14326 (1955) 11b) S.M. Kaye, "Determination of The Purity of Inorganic Compounds of Ordnance Interest By Titration In Nonaqueous Medium", PATR **1947** (1953) 12) R.H. Heiskell, "Nonluminous Pyrotechnic Mixture For a Projectile", USP 2714061 (1955) & CA **50**, 8208 (1956) 13) R.H. Heiskell, "Pyrotechnic Composition", USP 2726943 (1955) & CA **50**, 5293 (1956) 14) V.D. Hogan, "Pre-Ignition and Ignition Reactions of The System Barium Peroxide-Magnesium-Calcium Resinate", PAMR **28** (1957) 15) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 53–5 16) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, 2nd Ed, Academic Press, NY (1963), 937 16a)G. Norwitz, "Determination of Barium, Strontium, Calcium, and Iron in Barium Peroxide", **FATR T-65-2-1** (1964) 17) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 66–78 18) T.A. Doris & T.Q. Ciccone, "Igniter Composition for Aircraft Ejection Apparatus", USP 3317362 (1967) & CA **67**, 55845 (1967) 19) Anon, "Low-pressure Percussion Ignition Compositions", GerP 1243067 (1967) & CA **67**, 101581 (1967) 20) N.K. Grigoreva et al, "Production of Peroxides of Alkaline Earth Metals: CaO_2, SrO_2, BaO_2", **NASA No N65-31257** (1965) & CA **66**, 121576 (1967) 21) A.B. Tsent-Kurnakova & R.P. Vasil'eva, "Synthesis of Calcium, Strontium, and Barium Peroxide Compounds in Hydrogen Peroxide Vapours", IzvAkadNaukSSSR,SerKhim (12), 2738–40 (1967) & CA **68**, 110875 (1968) 22) G.T. Okhil'kov et al, "Igniting Composition For Bridgeless Electric Igniting Devices", USSRP 201181 (1967) & CA **68**, 61134 (1968) 23) H. Ellern, "Military and Civilian Pyrotechnics", Chemical Pub Co, NY (1968) 24) Merck (1968), 121 25) Anon, "Barium Peroxide", **MIL-B-153A** (1969) 26) E.M. Mitkevich, "Preparation of Barium Peroxide From Hydrogen Peroxide and Barium Hydroxide", KhimPromUkr (6), 17–19 (1968) & CA **70**, 49058 (1969) 27) M. Hamasaki et al, "Gas-Producing Compositions", GerP 2063586 (1971) & CA **75**, 119654 (1971) 28) CondChemDict (1971), 94 29) Anon, "Fire Protection Guide on Hazardous Materials, 6th Edn", NFPA, Boston (1975) 30) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975) 31) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", Intl Tech Info Inst, Tokyo (1975), 61–2 32) G. Norwitz & M. Galan, "Determination of Barium and Strontium Peroxides (Active Oxygen) in Igniters In Small Arms Tracer Ammunition", **FATR T-75059** (1975) 33) ChemRubHndbk (1975), B-71 & F-147

Calcium Peroxide Octahydrate. $CaO_2.8H_2O$, mw 216.21, white powd or tetr cryst, mp 200° (–$8H_2O$), bp 275° (expl), d 1.672g/cc. Sl sol in cold w, decompd by hot w; sol in acid, NH_4 salts; insol in alc, eth and acet. Can be prepd by reaction of an aq soln of a Ca salt such as $CaCl_2$ with hydrogen peroxide (or sodium peroxide) with subsequent crystn. Readily converted to $CaCO_3$ by CO_2 (Ref 5). It is a strong oxidizing agent and reqs, according to ICC regulations, a yellow label. The octahydrate may be shipped in glass bottles, iron canisters or tins (Ref 8)

Tests. Detd gravimetrically as the oxide after ignition (see under "Calcium . . ." in USA Mil Spec requirements under Barium Peroxide)

Toxicity. V low. However, when large amts of powd mat are being handled, a dust mask and gloves should be worn

Uses. In baking dough, prodn of hydrogen peroxide, vulcanization of rubbers, medicines, pharmacology, dentifrices, farming, chewing gums, etc. (Ref 6)

Refs: 1) Gmelin, Syst No 28 (1956), 49 2) E.H. Riesenfeld & W. Nottebohm, ZAnorgChem **89**, 405 (1914) & CA **9**, 1436 (1914) 3) Mellor **3** (1922), 668 4) C. Nogareda, AnalesSocEspanolaFisicaQuim **28**, 475 (1930) & CA **25**, 2655 (1931) 5) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, 2nd Edn, Academic Press, NY (1963), 937–8 6) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 62 &

64 7) H.J. Emeleus & A.G. Sharpe, "Modern Aspects of Inorganic Chemistry", John Wiley & Sons, NY (1973), 370 8) CondChemDict (1973), 158 9) ChemRubHndbk (1975), B-78

Chromium Triaminotetraoxide. See Vol **3**, C302

Fluorine Peroxide. See Vol **6**, F135-R

Hydrogen Peroxide. See Vol **7**, H218-R to H222-L

Lead Peroxide. See Vol **7**, L9

Manganese Peroxide. See in this Vol under Manganese Dioxide

Potassium Peroxide. K_2O_2, mw 110.20, white (to yel) amorph and delq mass, rhmb cryst; mp 490° (decompn), d 2.40g/cc, decompd by w or alc with evoln of O_2. It can be produced by heating K_2O in a vacuum (10^{-5}mm) at temps above 450°. K peroxide is readily oxidized to KO_2 in air (Refs 1 & 4). It is a powerful oxidizing agent which is shipped under yellow label. The reaction of the peroxide in large amts with w is expl at RT. Spont ign also occurs with metallic powds such Al in the presence of small amts of w, on contact with Ac_2O, by shaking with KOH or NaOH solns and by percn with org mats such as hay, bark, S, cotton, etc (Refs 5, 7 & 8)

Tests. The K content can be quant detd by flame emission spectroscopy (Ref 4a), while the oxygen content can be quant detd by gasometric analysis (see Vol **6**, G15-R thru G16-R) or by $FeSO_4$–$KMnO_4$ titrimetry (Ref 3a)

Toxicity. Poinsonous if ingested. An irritant to skin and eyes (Ref 8)

Uses. Potassium peroxide is used as an oxidizing agent and in oxygen generating units for gas masks (Ref 5). Another use has been found by Hatterer who developed a device which extracts the thermal energy from nuclear reactors in a reaction which generates H_2 and O_2 gases by the disassociation of w; viz, (1) $K_2O_2 + H_2O \rightarrow 2KOH + \frac{1}{2}O_2$; (2) $2KOH + 2K \rightarrow 2K_2O + H_2$; and (3) $2K_2O$ + heat $\rightarrow K_2O_2 + 2K$. This cyclic and self-contained process lowers thermal polution and provides the gases as valuable by-products (Ref 6)

Refs: 1) Gmelin, Syst No 22 (1936), 239–41 2) Mellor **2** (1941), 493 3) Ibid **10** (1947), 897 3a)Scott & Furman **1** (1962), 778 4) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 43–4 4a) W.F. Pickering, "Modern Analytical Chemistry", Dekker, NY (1971), 87–90 5) CondChemDict (1971), 724 6) A.C. Hatterer, "Apparatus and Method for Using Thermal Energy at High Temperatures", FrP 2189108 (1974) & CA **81**, 44569 (1974) 7) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, NFPA, Boston (1975), 248–9 8) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual . . .", Intl Tech Info Instit, Tokyo (1975), 437–8 9) ChemRubHndbk (1975), B-125

Sodium Peroxide (Sodium Dioxide, Superoxide or Solozone). Na_2O_2, mw 77.98, yel-white powd, hex cryst; mp 460° (decompn, Ref 15), 540° (decompn, Ref 10); bp 657° (decompn, Ref 15), 636° (decompn, Ref 10); d 2.805g/cc (Ref 15), 2.47g/cc (Ref 9b) or 2.60–2.62g/cc (Ref 10). Reacts with w to form NaOH and hydrogen peroxide plus a large amt of heat (Q_{soln} +34 ± 0.3kcal/mole). It is decompd by hot w, alc and NH_4; sol in dil acid and insol in alk. Lab prepn of Na_2O_2 involves air oxidn of Na to Na_2O. The Na_2O is then oxidized completely to Na_2O_2 in O_2 at 200–350° (Refs 1, 4, 5 & 11). There are several coml procs for the manuf of Na_2O_2, one of which uses Na which is heated either in Al trays or on a rotating cylindrical drum, and then oxidized by a current of dry air (CO_2-free) (Refs 6a, 13 & 14). In another procedure, hydrazobenzene is oxidized in the presence of Na alcoholate to produce Na_2O_2 and regenerated ethanol plus azobenzene (Ref 10)

Sodium peroxide is a very powerful oxidizing agent. It can be caused to detonate when mixed, in the presence of w, with reducing agents such as $SbCl_3$, As_2O_3, $SbCl_5$, $Al(CNS)_3$,

powd Fe, Al and CaC, as well as finely dispersed S, $AlCl_3$, ethanol, eth, glycerine and sugar (Refs 6 thru 10 & 16). Explns upon intimate mixt at RT have occurred with mats such as acet ac (Refs 3 & 16), Ca acetylide (Ref 6), PCl_3 (Ref 2), MnO_2 (Ref 16), Carbon or P (Refs 3, 6 & 16) and water (Refs 1a, 3a & 7). Also, friction has caused the expln of an NH_4 peroxodisulfate/Na_2O_2 mixt (Ref 8). Spont ign has occurred upon mixt or contact of Na_2O_2 at RT with mats such as moist cloth, paper or wood (Refs 3 & 16); H_2S or various peroxides (Ref 8); CO_2 or metallic Na (Refs 6 & 9); nonmetal halides (Refs 8 & 9); org liqs (benz, eth, aniline, etc) and w (Ref 3); and AgCl and charcoal (Ref 7). Percussion has caused spont ign of mixts of various org mats with NaOH or KOH and Na_2O_2 (Ref 17). Percussion has also caused spont ign to occur when Na_2O_2 is mixed with mats such as hay, bark, cotton or powd S (Ref 17). When Na and Na_2O_2 were heated together to the mp of Na (97.7°) under Ar, expl ign has also occurred (Ref 15)

Tests. The compd can be quant detd by flame emission spectroscopy (Ref 14a) and by $FeSO_4$–$KMnO_4$ titrimetery for "active" O_2 (Ref 9b).

Toxicity. Poisonous if ingested. Highly irritating to skin and mucous membranes (Ref 17)

Uses. Na_2O_2 is prod in tonnage quants by many countries. Currently, the USA produces over 8000 tons/yr (Ref 10). It can be used in oxidizing fusions of metals (Ref 11). However, its primary use is as an oxidizing or bleaching agent (Refs 13 & 14). Another use, of mil interest, is for O_2 generation and purification systs for submarines and space vessels (Ref 14). According to Ellern (Ref 12), Al and Mg, mixed with Na_2O_2, have been recommended as igniters for thermite mixts and other pyrots using the technique of w contact to obt ign. Still other uses are in the synthesis of other peroxides such as peroxide addn compds and various org peroxides; also as the oxidant used in the Parr S bomb proc for estimating the S content of coal, coke, etc (Ref 11a)

Refs: 1) Gmelin, Syst No 21 (1928/1953), 240–7 1a) Daniel (1902), 72 2) E. Comanducci, ChemZtg **15**, 706 (1911) & CA **4**, 2231 (1911) 3) E. von Schwartz, "Fire and Explosion Risks", Griffin, London (1918), 321 3a) J.N. Friend et al, Nature **134**, 778 (1934) & CA **29**, 699 (1935) 3b) G.H. Cheesman et al, Ibid, 971 & CA **29**, 1729 (1935) 4) F. Fehér, AngChem **51**, 497 (1938) & CA **33**, 9139 (1939) 5) P. Pierron, BullFr (5) **6**, 235 (1939) & CA **33**, 9176 (1939) 6) Mellor **2** (1941), 487–90 7) Ibid **3** (1941), 401 8) Ibid **10** (1947), 897 8a) Anon, ChemEngrg **61**, No 7, 282 (1954) & CA **48**, 7859 (1954) 9) Mellor **2**, Suppl 2.1 (1961), 634 9a) G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", Vol **1**, 2nd Ed, Academic Press, NY (1963), 980 9b) Scott & Furman **1** (1962), 778 10) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 28–43 11) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publ, NY (1966), 374 11a) Kirk & Othmer **14** (1967), 748–9 12) H. Ellern, "Military and Civilian Pyrotechnics", Chem Publ Co, NY (1968), 45ff 13) Merck (1968), 963 14) CondChemDict (1971), 807 14a) W.F. Pickering, "Modern Analytical Chemistry", Dekker, NY (1971), 87–90 15) R.N. Newman & C.A. Smith, "Ignition of Sodium Metal, Sodium Peroxide Mixtures", JBritNuclEnergySoc **12** (1), 117–19 (1973) & CA **78**, 115745 (1973) 15a) ChemRubHdbk (1975), B-139 16) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, NFPA, Boston (1975), 391–2 17) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The Intl Tech Info Inst, Tokyo (1975), 486–7

Strontium Peroxide (Strontium Dioxide). SrO_2, mw 119.63; white powd, tetrag cryst; mp 215° (decompn; Ref 14), 357–410° (decompn; Ref 6), 410–450° (decompn; Ref 7); d 4.56g/cc. Sl sol in cold w, decompd by hot w, v sl sol in alc and NH_4Cl soln; insol in acet. Lab prepn from hydroxide and carbonate-free SrO under an O_2 press of 200–50 atm at 350–400° (Refs 1, 3, 7 & 8). Coml prepn consists of reacting a $SrO.H_2O$ soln with a dil soln of hydrogen peroxide (Refs 3, 7 & 8). To produce material dense enough for pyrot usage (2.0–2.1g/cc), the commercial reaction medium is maintd at 50–75°. The final prod is moistened with hot concd $Sr(NO_3)_2$ soln and dried at 120–50° (Ref 4).

Strontium peroxide is considered a dangerous oxidizing material which will readily ignite

explosively when mixed with combustible substances. By itself, heat, shock or catalysts may cause violent decompn of SrO_2. Contact with w produces heat (Refs 6, 9 & 10)

Tests. SrO_2 is detd in the pure state by nonaqueous titrimetry (Ref 5), and in igniter mixts spectrophotometrically at 410 nanometers by reaction with Ti(IV) soln (Ref 13)

Toxicity. Injurious to skin or mucous membranes (Ref 6)

Table 3
Strontium Peroxide
Chemical and Physical Requirements

Requirements	Grade B	Grade C
Available O_2, min, % [a]	12.3	12.3
Moisture, max, % [b]	–	0.1
Hygroscopicity, max, % [c]	–	0.25
Apparent density, min, gm/ml [d]	1.30-2.00	0.85
Barium, max, % [e]	1.0	0.45
Calcium, max, % [f]	0.3	0.15
Magnesium, max, % [g]	0.05	0.02
Sodium, max, % [h]	0.1	0.05
Iron, max, % [i]	0.09	0.03
Aluminum, max, % [j]	0.1	0.05
Nitrate, calcd as $Sr(NO_3)_2$, max, % [k]	0.1	0.05
Chloride, calcd as $SrCl_2$, max, % [l]	0.1	0.10
Total impurities other than SrO, max, %	–	–

Footnotes to Table 3:

a–by K permanganate titration
b–gravimetrically by loss in wt after heating
c–gravimetrically by exposure of a sample to 75% RH
d–by weighing the content of a 50ml graduated cylinder
e–spectrophotometrically by atomic absorption
f–spectrophotometrically by atomic absorption
g–spectrophotometrically by atomic absorption
h–spectrophotometrically by atomic absorption
i–spectrophotometrically at 500 nanometers using ortho-phenanthroline-hydroxylamine acetate solns as colorimetric reagents
j–gravimetrically as the oxide
k–by sulfuric acid titration subsequent to a Devarda redn
l–by Ag nitrate–NH_4 thiocyanate titration

The USA Mil Spec (Ref 12) has the following requirements for Grade B SrO_2 (mfd by a wet pptn method, consisting essentially of anhyd SrO_2), and Grade C SrO_2 (mfd by a wet pptn method, consisting essentially of anhyd SrO_2 with a definite hygroscopicity requirement to control the stability of the mat): (1) The material shall be a free flowing white powd; (2) The chemical and physical properties with requirements and criteria are shown in Table 3

(3) Granulation requirements as shown in Table 4 below:

Table 4
Particle Size Distribution [a]

	Grade B	Grade C
Thru No 80 (180 microns)	–	100
Thru No 100, min (150 microns)	98	98
Thru No 140, min (106 microns)	80	80

Footnote to Table 4:

a–gravimetrically after shaking a sample thru the nest of graduated US Standard Sieves shown in the Table

(4) The SrO_2 shall be free of grit, dirt, foreign matter or other injurious material

Uses. SrO_2 is used as an oxidizer to impart a red color to pyrots, and as a means of reducing projectile base drag (Refs 6 & 11). It is also employed in a variety of igniter compns for pyrot tracers (Ref 5a)

Refs: 1) E.H. Riesenfeld & W. Nottebohm, ZAnorgChem **89**, 408 (1914) & CA **9** (1915), 1436 2) C. Holtermann & P. Lafitte, CR **208**, 517 (1939) & CA **33**, 2833 (1939) 3) Mellor **3** (1941), 667–8 4) L.H. Dawsey & H.A. Rudolph, "Sr Peroxide", USP 2375772 (1945) & CA **39**, 3405 (1945) 5) S.M. Kaye, "Determination of The Purity of Inorganic Compounds of Ordnance Interest By Titration In Nonaqueous Medium", PATR **1947** (1953) 5a) F.B. Clay & R.A. Sahlin, "Igniter Compositions for Tracer Projectiles", USP 2709129 (1955) & CA **49**, 14326 (1955) 6) Anon, EngDesHdbk, "Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963) 7) I.I. Vol'nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline

Earth Metals", Plenum Press, NY (1966), 64–6
8) Kirk & Othmer **14** (1967), 750–1
9) Merck (1968), 988 10) CondChemDict (1971), 830 11) W.J. Richard, "Use of Pyrotechnics to Reduce Base Drag", ProcSymp-ExplosPyrotechnics 8th, No 17, Franklin Inst Res Lab, Phila (1974) & CA **82**, 75112 (1975)
12) Anon, "Strontium Peroxide", **MIL-S-612B** (1975) 13) G. Norwitz & M. Galan, "Determination of Barium and Strontium Peroxides (Active Oxygen) in Igniters in Small Arms Tracer Ammunition", **FA-TT-75059** (1975)
14) ChemRubHdbk (1975), B-143 & F-147

The following Table contains a listing of explosive inorganic peroxides which are not currently used as expl ordn material

Table 5

EXPLOSIVE NATURE OF INORGANIC PEROXIDES

Peroxide	Remarks Concerning Explosiveness	Refs
	Crystalline Hydrogen Peroxidates	
Sodium Borate Hydrogen Peroxidate, $BNaO_2.H_2O$	May react violently in close contact (grinding or heating) with oxidizable materials	Kirk & Othmer **11** (1966), 395
Potassium Fluoride Hydrogen Peroxidate, $FK.H_2O_2$	Ibid	Ibid
Sodium Pyrophosphate Hydrogen Peroxide, $Na_4O_7P_2.2H_2O_2$	Ibid	Ibid
Triethylamine Hydrogen Peroxidate, $C_6H_{15}N.4H_2O_2$	Ibid	Ibid
	Metal Peroxides	
Mercury Peroxide, HgO_2	Explodes on impact or friction when mixed with H_2O_2	Mellor **4** (1940), 781
Zinc Peroxide, ZnO_2	The hydrated peroxide (of indefinite compn), explodes at 212°, and mixts with Al or Zn powders burn brilliantly	Mellor **4** (1940), 530 & Sidgwick, ChemElems **1** (1950), 270
	Metal Peroxomolybdates	
Potassium Tetraperoxo-Molybdate (2^-), K_2MoO_8	An Explosive	K.F. Jahr, FIAT RevGerSci: InorgChem, Part III (1948), 170
Sodium Tetraperoxo-Molybdate (2^-), $MoNa_2O_8$	Explosive decompn under vacuum	H.M. Castrantes et al, "Fire and Explosion Hazards of Peroxy Compounds", ASTM Special Publ **No 394**, Phila (1965), 5
	Peroxides in Solvents	
Peroxomonosulfuric Acid, H_2O_5S: Solvent	Explodes violently on warming above 0° or on contact with w, acet, alcohols or aromatic compds	1) A. Bayer, Ber **33** (1900), 858 2) G. Toennies, JACS **59** (1937), 552 3) Sidgwick, ChemElems **1** (1950), 939 4) J.O. Edwards, C&EN **33** (1955), 3336

(continued)

Table 5 (continuation)
Explosive Nature of Inorganic Peroxides

Peroxide	Remarks Concerning Explosiveness	Refs
	Peroxo Acids	
Peroxodisulfuric Acid, $H_2O_8S_2$	Explodes on uncontrolled contact with aniline, benz, ethanol, eth, nitrobenz or phenol	J. D'Ans et al, Ber **43**, 1910 (1911); Ibid, ZAnorgChem **73**, 1911 (1911)
Peroxomonophosphoric Acid, H_3O_5P	Ignition when an 80% soln contacts org material	H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", ASTM Special Publ **No 394**, Phila (1965), 5
Peroxomonosulfuric Acid, H_2O_5S	Explodes above 0° on w contact and by expl decompn in large amts	J.O. Edwards, C&EN **33**, 3336 (1955); also see Vol **2**, C69-L & R
Peroxonitric Acid, HNO_4	Pure material decomposes explosively at −30°. Solns in w or acet ac over 70% HNO_4 decompose autocatalytically to expln	R. Schwarz, ZAnorgChem **256**, 3 (1948)
	Peroxoacid Salts	
Ammonium Pentaperoxo-Dichromate (2⁻), $CrH_8N_2O_{12}$	Explodes at 50°	G. Brauer, Ed, "Handbook of Preparative Inorganic Chemistry", 2nd Edn, Vol **2**, Academic Press, London (1965), 1392
Ammonium Peroxoborate, BH_4NO_3	Explosive decompn under vacuum	H. Menzel et al, OesterrChemZtg, **28**, 162 (1925)
Ammonium Peroxodisulfate, $H_8N_2O_8S_2$	A mixt with Al and W may explode	H.A.J. Pieters et al, "Safety In The Chemical Laboratory", Academic Press, London (1957)
	Explodes violently on addition of Ag salts	Mellor **10** (1947), 466
Ammonium Tetraperoxo-chromate (3⁻), $CrH_{12}N_2O_8$	Explodes at 50°, on impact, or in contact with sulfuric acid	Mellor **11** (1943), 356
Calcium Peroxochromate (3⁻), $Ca_3Cr_2O_{12}$	Explodes at 100°	J.H. Raynolds et al, JACS **52** (1930), 1851
Calcium Peroxodisulfate, CaO_8S_2	Sensitive to shock; explodes violently	H.M. Castrantas et al, "Laboratory Handling and Storage of Peroxy Compounds", ASTM Spec Pub **No 491**, Phila (1970)

(continued)

Table 5 (continuation)
Explosive Nature of Inorganic Peroxides

Peroxide	Remarks Concerning Explosiveness	Refs
	Peroxoacid Salts (continuation)	
Potassium Diperoxo-orthovanadate (2^-), K_2O_6V	Explodes on heating	Mellor **9** (1939), 795
Potassium Pentaperoxo-dichromate (2^-), $Cr_2K_2O_{12}$	Explodes above 0°	Mellor **11** (1943), 357 & Sidgwick, ChemElems **1** (1950), 1007
Potassium Peroxoferrate (2^-), FeK_2O_5	Explodes on heating, impact, or in contact with charcoal, P, S or sulfuric acid	D.K. Goralevich, JRussPhChem-Soc **58**, 1155 (1926)
Potassium Peroxomonosulfate, HKO_5S	Forms explosive mixtures with as little as 1% of organic matter; *dangerously* unstable	H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", ASTM Publ **No 394**, Phila (1965), 5
Potassium Tetraperoxo-chromate (3^-), CrK_3O_8	Explodes at 178° or in contact with sulfuric acid; the impure salt is explosive	Mellor **11** (1943), 356
Potassium Tetraperoxo-molybdate (2^-), K_2MoO_8	It is an explosive	K.F. Jahr, FIAT Rev of Ger Sci: InorgChem,Part III (1948), 170
Potassium Tetraperoxo-tungstate (2^-), K_2O_8W	Explodes on rapid heating to 80° or by friction	Mellor **11** (1943), 836
Silver Peroxochromate, $AgCrO_5$	Reacts explosively with 50% sulfuric acid upon being warmed from −80° to −30°	E.H. Riesenfeld et al, Ber **47**, 548 (1914)
Sodium Peroxoborate, BH_4NO_3	Detonates upon light friction	Anon, AngChem **65**, 41 (1963)
Sodium Tetraperoxochromate (3^-), $CrNa_3O_5$	Explodes at 115°	Mellor **11** (1943), 356
Sodium Tetraperoxomolybdate (2^-), $MoNa_2O_8$	Explosive decompn under vacuum	H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", ASTM Publ **No 394**, Phila (1965), 5
Sodium Tetraperoxotungstate (2^-), $Na_2O_8W_2$	Explodes feebly on warming	Mellor **11** (1943), 835
Tetraaminezinc Peroxodisulfate, $H_{12}N_4O_8S_2Zn$	Explodes on heating or impact	G.A. Barbieri et al, ZAnorgChem **71**, 347 (1911)
Tetramethylammoniumpenta-peroxodichromate (2^-), $[Cr(O)_8Cr(O_2)_2](NH_3)_2(C_8H_{18})$	Explodes on contact with sulfuric acid or on moderate heating	Mellor **11** (1943), 358

(continued)

Table 5 (continuation)
Explosive Nature of Inorganic Peroxides

Peroxide	Remarks Concerning Explosiveness	Refs
	Peroxoammine Chromium Complexes	
1,2-Diaminoethaneammine-diperoxochromium (IV), $[Cr(C_2H_8N_2)(NH_3)(O_2)_2].H_2O$	The monohydrate explodes or decomps at 115° during slow or moderate heating. It is potentially explosive at 25°	D.A. House et al, InorgChem **6**, 1077 (1967)
1,2-Diaminoethaneaquadi-peroxochromium (IV), $[Cr(C_2H_8N_2)(OH_2)(O_2)_2].H_2O$	Explodes at 96–7° when heated at 2°/min and is light sensitive	D.A. House et al, InorgChem **5**, 840 (1966); R.F. Childers et al, InorgChem **7**, 749 (1968)
1,2-Diamino-2-Methylpropane-aquadiperoxochromium (IV), $[Cr(C_4H_{12}N_2)(OH_2)(O_2)_2].H_2O$	Explodes at 83–4° when heated at 2°/min. It is potentially explosive at 20–5° *Caution* is reqd in prepn	D.A. House et al, InorgChem **6**, 1078 (1967)
1,2-Diamino-2-methylpropane-oxodiperoxochromium (VI), $Cr(C_4H_{12}N_2)(O_2)_2(O)$	A very explosive black ppt formed during the prepn of 1,2-diamino-2-methylpropaneaquadiperoxo-chromium (IV) monohydrate. *Caution* in isolation must be used	D.A. House et al, InorgChem **6**, 1078, footnote 6 (1967)
1,2-Diaminopropaneaqua-diperoxochromium (IV), $[Cr(C_3H_{10}N_2)(OH_2)(O_2)_2].2H_2O$	The dihydrate explodes spontaneously at 20–5° and at 88–90° during slow heating	D.A. House et al, InorgChem **5**, 840 (1966)
Dianilineoxodiperoxo-chromium (VI), $Cr(C_{12}H_{14}N_2)(O_2)_2(O)$	Very explosive when dry. Prepn and sepn of the compd has injured several scientists	D.M. Adams et al, JChemEduc **43**, 94 (1966)
Diethylenetriaminediperoxo-chromium (IV), $[Cr(C_4H_{13}N_3)(O_2)_2].H_2O$	Explodes at 109–10° when heated at 2°/min	D.A. House et al, InorgChem **5**, 840 (1966)
Dimethyletheroxodiperoxo-chromium (VI), $Cr(O_2)_2(O).O(CH_3)_2$	The bl solid explodes with extreme brisance at –30°	R. Schwarz & G. Elstner, Ber **69**, 575–9 (1936)
Hexamethylenetetraammonium Tetraperoxochromate (V)(?), $[(CH)_6(NH_2)_3Cr(O_2)_4]_4$	Dry material explodes in prepn	D.A. House et al, InorgChem **6**, 1078 (1966)
Oxodiperoxodipiperidine-chromium (VI), $Cr(C_{10}H_{22}N_2)(O_2)_2(O)$	Very explosive when dry, a v powerful oxidant, destroy surplus after use with dil alk	D.M. Adams et al, JChemEduc **43**, 94 (1966); S. Caldwell et al, InorgChem **8**, 151–5 (1969); J.C. Collins et al, OrgSynth **52**, 5–8 (1972)
Oxodiperoxodipyridine-chromium (VI), $Cr(C_5H_5N)_2(O_2)_2(O)$	A powerful and selective oxidant which is a v brisant explosive when dry. Destroy surplus after use with alk	Ibid
Triamminediperoxo-chromium (IV), $Cr(NH_3)_3(O_2)_2$	*Caution* in handling reqd! Sudden shock or rapid heating will cause explosion or incandescence. Heating at 20°/min will cause a v brisant explosion at 120°	G.B. Kauffman, InorgSynth **8**, 133 (1966); R.G. Hughes et al, InorgChem **7**, 882 (1968)

Peroxides, Organic. These are compds containing carbon with at least two oxygen atoms linked together in the same manner as the oxygen atoms in molecular oxygen: ie, :Ö:Ö: (see Fig 1 under Inorganic Peroxides above). This type of linkage exists because oxygen is the *primary* source of the –O–O– linkage in organic peroxides. Indeed, this linkage is the result in all types of organic peroxide prepn, whether by direct air oxidation or by reactions of organic compds with peroxidic materials derived from oxygen such as H_2O_2, alkali metal peroxides, or ozone. Organic peroxide compds are more prone to combustion and expln than their inorganic analogues because of the presence of built-in organic fuel. The difference in free energy between a peroxy compd and its decompn prods is often greater in the case of organic compds than inorganic (Refs 4, 12, 14a & 20). Various types of explosive tests have been developed for peroxides which will be presented below under "Safety" and in the treatments of individual peroxide compds when available (Refs 4, 12, 14a, 18, 20, 22 & 26)

Table 6 presents a structural definition of each class of organic peroxide, the chemical reactions of each class and the comparative explosiveness of each class (Refs 4, 12, 14a, 20 & 21). Also, see under Organic Hydroperoxides in Vol **7**, H224-R to H227-R and under Ozonides in this Vol

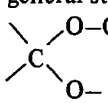
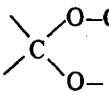
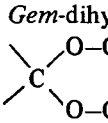
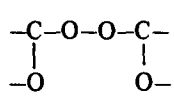
History. According to Kirk and Othmer (Ref 14a), the first synthesis of an organic peroxide was the prepn of benzoyl peroxide reported by B.C. Brodie in 1859. Since then many types of organic peroxides have been synthesized and isolated. Industrial interest in the use of organic peroxides began in the early 1900's when it was found that benzoyl peroxide was an effective bleaching agent for edible oils, and somewhat later, an excellent bleaching agent for flour. With the demand for synthetic rubber and plastics during WWII, the use of organic peroxides as initiators of polymerization began to develop. The continued growth of free radical polymerization after the war stimulated the development of many organic peroxide products to meet a variety of needs. Today, organic peroxides are used as initiators in the manufacture of the major polymers such as polyethylene, poly (vinyl chloride), polystyrene, polyester thermosets, polyacrylates, styrene-butadiene rubber and many others; as crosslinking agents for polyethylene, ethylenepropylene copolymers and silicone rubber; as bleaching agents for flour; and, in the case of peroxyacids, as epoxidizing agents. There are about forty to fifty different organic peroxides commercially available in a total of approximately seventy organic peroxide products

About 8,000 metric tons of peroxides were consumed in 1972. This consumption was strongly stimulated by the rapid growth in reinforced plastics (Ref 23). The largest volume product is benzoyl peroxide which is used in polystyrene and polyester markets for such items as toys, automobiles, furniture, marine, transportation and mil requirements. Also, methyl ethyl ketone peroxide is used in large volumes to cure (as a catalyst) styrene-unsaturated polyester adhesive resins used in mil ammo adhesive applications, as well as in glass fiber reinforced plastic products such as boats, shower stalls, tub components, automobile bodies, sports equipment, etc. The monoperesters are growing slowly because of some substitution of the peroxydicarbonates and azo compds (Refs 8, 9 & 23)

Again, according to Kirk and Othmer (Ref 14a), the systematic study of the chemistry of organic peroxides began in the 1930's. In recent years the amount of research in the field has increased considerably, and not only have many new organic peroxides been isolated but many of the peroxide reaction mechanisms have been elucidated. The development of safer, easily handled and more efficient polymerization initiators is a major goal

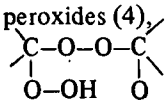
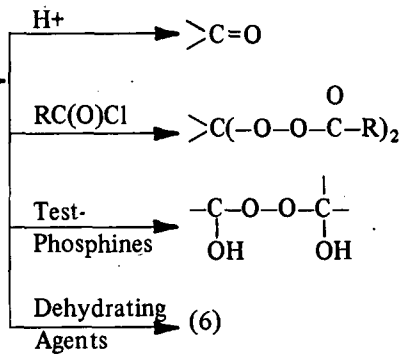
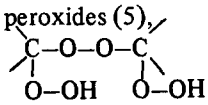
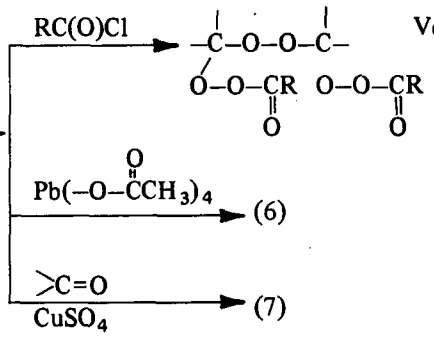
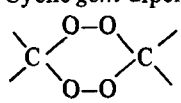
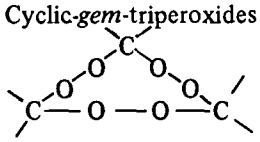
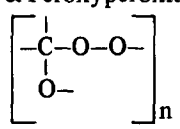
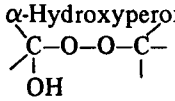
With reference to the mil literature available for unlimited publication, acetone peroxide has been considered for use as a detonating expl (Ref 1a), but was found to be too volatile at RT for such an application (see Vol **1**, A42-R to A45-R)

Table 6
COMPARISON OF THE PROPERTIES OF ORGANIC PEROXIDES

Structure	Chemical Reactions	Explosiveness
Hydroperoxides		
Primary, secondary, or tertiary alkyl hydroperoxides; R–O–O–H	Liqs or crysts; w sol; stronger acids than the corresponding alcs; react readily to form other org peroxides; heterolytic, homolytic and metallic oxidn-redn cleavage of the –O–O– bond can occur; easily reduced, rearranged and decompd; used in org synthesis as oxidizing or hydroxylating reagents	Lower members prone to explosion; brisance decreases with increasing chain length and lower O_2 activity; explode at temps over 80°
Organomineral hydroperoxides; $R_mM(OOH)_n$ (m=metal or metalloid)	Behave as covalent org compds; undergo homolytic thermal decompn or photo-decompn; most compds are v thermally stable; hydrolyzed v readily; form alkyl hydroperoxides with anhyd HCl	Insensitive to friction and impact; explode on rapid heating
α-Oxy- and α-Peroxy-Hydroperoxides and Peroxides		
general structure; viz, 		
α-Oxyhydroperoxides (1), 	Hydrolyze with w to form dihydroxyperoxides or polymers; can be reduced, oxidized or dehydrated to expl polymers $(RCH–O–O–)_n$ with P_2O_5; react with aldehydes to form symmetrical prods	Decomp on heating; lowest member expl; others moderately stable
Gem-dihydroperoxide (2), 	W sol and decomp slowly with evoln of O_2 and formation of expl polymeric peroxides; can be reduced and hydrolyzed; thermal decompn leads to progressive bond cleavage of –O–O–, C–O– and then C–C bonds	Polymeric peroxides formed as a decompn product are extremely expl
α,α′-Dioxyperoxides (3), 	Easily reduced; decompn to dibasic acids by ferrous salts; thermal decompn yields aldehydes, ketones, carboxylic acids and alcohols; dehydrated to ozonides and other cyclic peroxides	Lowest member, $HOCH_2–O–O–CH_2OH$, is a dangerously expl solid; the next higher members are liqs, and the longer chain members are solids of decreasing explosiveness

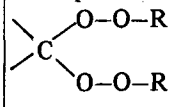
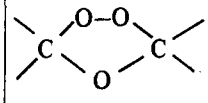
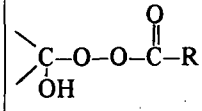
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Table 6 (continuation)
Comparison of the Properties of Organic Peroxides

Structure	Chemical Reactions	Explosiveness
	α-Oxy- and α-Peroxy-Hydroperoxides and Peroxides (continuation)	
α-Oxy-α′-hydroperoxy-peroxides (4), 		Very slight expl qualities
α,α′-Dihydroperoxy-peroxides (5), 		Very slight expl qualities
Cyclic *gem*-diperoxides (6) 	Not readily hydrolyzed; can be reduced by Zn and acet ac or Grignard reagents; thermal decompn yields original ketone, etc	Very expl lower members; aralkylidene members are stable to mp's (180–225°)
Cyclic-*gem*-triperoxides (7) 	Basic hydrolysis yields carboxylic acids as decompn prods	Same as above
Polymeric α-Oxy- and α-Peroxyperoxides (8), 	Viscous liqs or amorph solids; difficult to characterize; low mw members can be sept by chromatography	Dangerously expl!
α-Hydroxyperoxides (9) 	Higher homologs tend to hydrolyze to original aldehyde; redn to carbonyl and hydroxy compds; ferrous salts catalyze decompn to free radicals; thermal decompn involves homolytic and heterolytic processes	Lowest member, hydroxydimethyl peroxide is an unstable expl; other members are less expl than corresponding dialkyl peroxides and are reasonably stable to storage and vacuum distn

(continued)

Table 6 (continuation)
Comparison of the Properties of Organic Peroxides

Structure	Chemical Reactions	Explosiveness
α-Oxy- and α-Peroxy-Hydroperoxides and Peroxides (continuation)		
Gem-peroxides (10), 	Colorl liqs, sol in org solvents, w insol; readily acid hydrolyze to starting reactants; redn to alcohols with H_2 and Raney Ni	Lower numbers are shock-sensitive and explode on spark contact; explosiveness solvent moderated
Ozonides (11), 	Acid and base hydrolysis to yield all possible org compds; redn by LiAlH yields carbonyl and hydroxyl-contg derivs; thermal decompn prods are *all* possible org compds	Highly expl; decompd by ferrous salts, Ag, Pd and Pt; stable in storage; distillable under vacuum
α-Hydroxyalkylperoxy-carboxylates (12), 	No information	No information
Peroxides		
Dialkyl peroxides (1), R–O–O–R′ (R and R′ are = or ≠ primary, secondary, tertiary alkyl, cycloalkyl, aralkyl and heterocyclic radicals	Homolytic decompn when heated or irradiated with prodn of free radicals for org synthesis; difficult to hydrolyze and reduce; rearrangement crosslinking and polymerization; polymeric peroxides are thick liqs or amorph wh powds; used as polymerization catalysts	Primary radicals are unstable, lowest members such as dimet peroxide are shock sens and *dangerous* expls!; sensitivity lessens with increasing mw; polymeric peroxides (copolymers of olefins and O_2) explode on heating
Organomineral peroxides (2), $R_mM(-O-O-R)_n$ and $R_nM-O-O-R_n$	Act as covalent org compds; v thermally stable; homolytic thermal and photo decompd; hydrolyze v readily, hence v useful in org synthesis	Insens to friction and impact; violent decompn on rapid heating
Peroxy Acids (Peracids)		
Peroxycarboxylic Acids (1), $R(CO_3H)_n$ (R=alkyl, cycloalkyl, aryl, or heterocyclic; n=1 or 2)	Acid or base hydrolysis with rate decreasing with mw increase; dil NaOH decomposes acids yielding O_2; dimeric as solids; H-bonded in soln; pure liq and vap state; most *powerful* oxidizing agents of *all* peroxides, decompd by irradiation	Generally not shock sens; deton on heating; peroxy formic and acetic acids *can explode* at −20°; stability increases as mw increases
Peroxysulfonic Acids (2), RSO_2-O-OH	No information	No information

(continued)

Table 6 (continuation)
Comparison of the Properties of Organic Peroxides

Structure	Chemical Reactions	Explosiveness
	Diacyl Peroxides	
Sym or unsym diacyl peroxides (1), $RC(O)–O–O–C(O)R'$ Peroxydicarbonates (2), $ROC(O)–O–O–C(O)OR'$ Peroxysulfonylcarbonates (3), $RSO_2–O–O–C(O)R'$ Peroxydisulfonates (4), $RSO_2–O–O–SO_2R'$ Peroxyaldehydecarbonates (5), $RC(O)–O–O–C(O)OR'$	Low mp solids; rel low decompn temps; autocatalytic and self-accelerating decompn; redn by LiAlH; hydrolyzes to corresponding acids; rearrange via an ionization step; sulfonates form adducts with polymers as styrene	Sens to heat, friction and shock; deton on *slightest* mechanical disturbance; lower members v *dangerous!*; K salts of arylsulfonyl peroxysulfates are expls
	Peroxyesters	
Peroxyesters (1), $R(CO_3R')_n$ Peroxycarbonicesters (2), $ROC(O)–O–O–R'$ Diperoxyesters (3), $C(O)(–O–O–R)_2$ Peroxycarbamates (4), $>NC(O)–O–O–R$ Areneperoxysulfonates (5), $RSO_2–O–O–R$	Difficult to prepare because of ready rearrangement or decompn in polar solvents; peroxy sulfonates decomp heterolytically (no free radicals)	Peroxycarbamates are stable, distillable liqs or cryst solids; rapid decompn at 80–140° and violent decompn at 140–180°. Alkylareneperoxysulfonates have low stability and decomp violently at RT within 10 mins

Safety. Since organic peroxides can be initiated by heat, mechanical shock, friction or contamination, an enormous problem in safety presents itself. Numerous examples of this problem have already been shown in this article. Additional examples include the following: methyl and ethyl hydroperoxides expld violently on heating or jarring, and their Ba salts also are extremely expl; the alkylidene peroxides derived from low mw aldehydes and ketones are very sensitive and expld with considerable force; polymeric peroxides of dimethyl ketene, $\{O–O–C(CH_3)_2C(O)\}_n$, expld in the dry state by rubbing even at −80°; peroxy acids, especially those of low mw, and diacetyl, dimethyl, dipropionyl and methyl ethyl peroxides, when pure, must be handled only in small amts and very carefully. Also, dibenzoyl peroxide dust may expld easily by friction or by contamination. Hydrogen peroxide and compds contg more than 30% by wt of H_2O_2 are potentially expl (Ref 20)

In order that organic peroxides be produced, shipped and used safely, many investigations have been performed and recommended testing procedures evolved (Refs 4, 12, 18, 22 & 26)

Analytical. Since organic peroxides are oxidizing agents the most common chem methods of analysis involve redn of the peroxide group followed by detn of excess reducing agent, or of the oxidized form of the reducing agent. A popular reducing agent is the iodide ion. Its reaction with a diacyl peroxide is illustrated, viz:

$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}R + 2I^- \rightarrow 2R{-}\overset{O}{\overset{\|}{C}}{-}O^- + I_2$$

The liberated iodine may be titrated using std thiosulfate soln, or, in trace analysis, detd by spectrophotometric methods. Other reducing agents commonly used in peroxide analysis are hydriodic acid, ferrous, titanous, stannous, and arsenious ions. Also (recently), triphenylphosphine, which is oxidized to triphenyl phosphine oxide. The excess triphenyl phosphine may be detd gravimetrically, titrimetrically, or spectrophotometrically

Instrumental methods of peroxide analysis feature polarography, which is used to detn hydroperoxides, peroxyesters and diacyl peroxides as well as dicyclohexyl peroxydicarbonate in polystyrene. Other techniques include infrared (800 to 900cm^{-1}) chemiluminescent analysis for kinetic studies, and chromatography for the identification and separation of peroxides in complex mixts (Refs 5, 6, 7, 14, 15, 16, 17, 20 & 21)

Toxicity. The LD_{50} (oral) values of hydroperoxyalkenals and methyl linoleate hydroperoxide are 450 and 39100 micromoles/kg, respectively, in mice according to Yoshioka and Kaneda (Ref 25). Wolf et al (Ref 24) showed that casein, incubated with H_2O_2 and freed of excess H_2O_2 by catalase, is toxic to mice, having negative effects upon growth rate, behavior and motor coordination. According to Swern (Ref 20) intraperitoneal injection of methyl linoleate hydroperoxide into adult rats is lethal at a level of 150 micromgs/100g. However, diluents such as benz used with coml peroxides are far more dangerous to humans than the peroxides. As a group, the organic peroxides have a low order of human toxicity. However, organic peroxides do have an irritating effect on skin, eyes, nose and throat. Indeed, cyclohexanone peroxide can cause dermatitis in allergic personnel. The most damaging effect to humans is produced by peroxides entering the eyes. A study of eye damage effects by the US Public Health Service showed that peroxides extensively affect the cornea, iris and conjunctiva of rabbits (Ref 20, p 92). In addition, prolonged exposure to peroxides can cause lung edema

Recommended precautions for personnel include protective clothing to avoid skin contact, chemical safety goggles, and an inhalation respirator (Ref 27)

Uses. There are about forty to fifty organic peroxides commercially available in more than seventy formulations designed for specific applications which include: (1) initiators for vinyl monomer polymerizations, and copolymerizations of monomers such as vinyl chloride, ethylene, styrene, vinyl acetate, acrylics, fluoroolefins and butadienestyrene; (2) curing agents for thermoset polyesters, styrenated alkyds and oils, silicone rubbers and poly allyl diglycol carbonates; (3) crosslinking agents for polyethylene, ethylene-propylene rubbers and styrenebutadiene rubbers; (4) bleaching agents; (5) epoxidizing agents; (6) attempted usage as detonating expls and expls by the military; (7) nitrating agents for aromatic amines to achieve a 94% yield of p-Dinitrobenzene (DNB); and (8) catalysts and initiators for such reactions as the chain-chlorination of benzene to produce a highly pure yield of hexachlorocyclohexane (Refs 2, 6a, 13, 14a & 20)

Refs: 1) Mellor **1** (1922), 957 2) A.J. Phillips, "Study of the Explosive Characteristics of Acetone Peroxide", PATR **1202** (1942) 3) A.V. Tobolsky & R.B. Mesrobian, "Organic Peeoxides . . .", Interscience Publ, Inc, NY (1954) 4) Anon, "Fire and Explosion Hazards of Organic Peroxides", The National Board of Fire Underwriters, NY (1956) 5) W.S. Brey & R.C. Paule, "Kinetics of Peroxide-Catalyzed Addition Reactions of Halogenated Compounds to Olefins", Florida Univ Contract No nr-1017 (00), ONR (1956) 6) L.P. Kuhn & C. Wellman, "The Reaction of t-Butyl Peroxide With Acetals", **BRL Rept No 1008** (1957) 6a) E.K. Varfolomeeva, "The Effect of Organic Peroxides on the Chlorination of Benzene", UkrainKhimZhur **23**, No 1, 54–58 (1957), ATS Translation RJ-1119, E Orange, NJ (1957) & CA, not found 7) J. Smid & M. Szwarc, "Kinetics of Decomposition of Iso-Butyryl Peroxide and Reactions of Iso-Propyl Radicals", Syracuse Univ, NY, contract DA-30-115-ORD-678 (1958) 8) H.T. Lee et al, "Evaluation of Paramethane Hydroperoxide as a Curing Agent For Polyester Resins", PATR **2663** (1959) 9) J.W. Cywinski, "The Role of Organic Peroxides in Curing Polyester Resins and Their Influence on The Physical Properties of Re-

inforced Plastics", Novadel Ltd, London (1960) 10) E.G.E. Hawkins, "Organic Peroxides . . .", D. Van Nostrand Co, NY (1961) 11) A.G. Davies, "Organic Peroxides", Butterworths, London (1961) 12) H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", **ASTM Publ No 394**, Phila (1965) 13) K.G. Shipp et al, "Synthesis of New High Explosives. IV", **NOL-TR-64-211** (1965) 14) D.D. Des Marteau and G.H. Cady, "The Reaction of Peroxydisulfuryl Difluoride with Anhydrides of Certain Perhalocarboxylic Acids to Form Perhaloacyl Fluorosulfates", Univ Wash, Seattle, **TR No 52**, ONR contract No Nonr 477 (16) (1965) 14a)Kirk & Othmer **14** (1967), 766 to 818 15) B.L. Cauble & G.H. Cady, "Fluorocarbonyl Trifluoromethyl Peroxide", Univ Wash, Seattle, **TR No 63**, ONR contract No N00014-67-A-0103-0002 (1967) 16) A.A. Vichutinsky, "Chemiluminescent Methods for the Determination of the Absolute Magnitude of the Termination Rate Constants of Peroxide Radicals in the Liquid Phase", **PA Tech Translation 66** (1967) 17) R. Czerepinski & G.H. Cady, "A Novel Synthesis of Bis (Fluorocarbonyl) Peroxide", Univ Wash, Seattle, **TR No 64**, ONR Contract No N00014-67-A-1-3-0002 (1967) 17a) Urbański **3** (1967), 225–227 18) V.J. Clancey et al, "Organic Peroxides; Part I. Assessment of the Hazards of Organic Peroxides as offered for Transport", **RARDE MEMO 21/70** (1970) 19) Anon, "Relative Hazard Classification of Organic Peroxides (Tentative)", Organic Peroxide Producers Safety Div (OPPSD) Soc of the Plastics Ind, Inc, NY (1970) 20) D. Swern, Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970) 21) Ibid, Vol **2**, Wiley-Interscience, NY (1970) 22) C. Boyars, "An Evaluation of Organic Peroxide Hazard Classification Systems and Test Methods", **NOLTR 72-63** (1972) 23) L.F. Martin, "Organic Peroxide Technology", Noyes Data Corp, Park Ridge, NJ (1973) 24) A. Wolf et al, "Toxicology of Peroxide Bonds", CeskHyg **19** (2), Prague, 79–84 (1974) & CA **81**, 59074 (1974) 25) M. Yoshioka & T. Kaneda, "Toxicity of The Auto-oxidized Oils. III. Toxicity of Hydroperoxy alkenals", Yukagaku **23** (5), 321–6 (1974) & CA **81**, 115456 (1974) 26) A.H. Lasseigne, "Hazard Classification of Explosives for Transportation. Evaluation of Test Methods", NTIS PB Rept **225422/SGA** (1973) & CA **81**, 79901 (1974) 27) Sax (1975), 1004–5

A selected group of organic peroxides which are considered to be of interest in terms of possible usage as expls is presented below under the appropriate organic structure; viz,

Hydroperoxides; Organomineral Hydroperoxides; α-Oxy and α-Peroxy-Hydroperoxides and Peroxides; Ozonides; Peroxides; Peroxy Acids; Diacyl Peroxides; Peroxy Esters; and **Poly Peroxides**

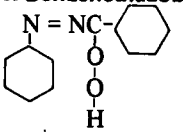
HYDROPEROXIDES

Acetylene Hydroperoxides. See Vol **1**, A66-L to A67-L

Allyl Hydroperoxide (2-Propenyl Hydroperoxide). CH_2:$CHCH_2$.O.OH; mw 74.10; OB to CO_2 −172.74%; mp (deton); RI 1.4200. Sol in eth. Prepn is by reacting (with *caution*) a soln of 10.8g of allyl methanesulfonate in 30ml of methanol and 44g of 30% hydrogen peroxide, with 10.1g of KOH (50% aq) by dropwise addn at 0° in a room illuminated by a photographic red light. Vac distn followed by eth extrn and gas-liq chromatography prod a 58mg yield. The pure compd is fairly stable to UV light, but deton on heating or in contact with solid alks

Ref: S. Dykstra & H.S. Mosher, "Organic Peroxides. VI. Allyl Hydroperoxide", JACS **79**, 3474–5 (1957) & CA, not found

α-Benzenediazobenzyl Hydroperoxide.



mw 228.28; OB to CO_2 −210.27%; canary yel ndls; mp 65–6° (decompn). Sol in petr eth. Prepn is by shaking benzalphenylhydrazone suspended in benz (1 g/6cc) with O_2 for about six hrs. Addn of cold petr eth crystd the prod in a 73% yield. Sens to light, the peroxide may expl on standing. It is insens to friction or

impact, but expl on contact with flame, concd sulfuric or nitric acids
Refs: 1) M. Busch & W. Dietz, "Autooxidation of Hydrazones", Ber **47**, 3277 (1914) & CA **9**, 805–6 (1916) 2) D. Swern, Ed, "Organic Peroxides", Vol **2**, Wiley-Interscience, NY (1971), 19

2,5-Bis(Hydroperoxy-2,5-Dimethyl)-Hexane. See Vol **2**, B144-R

9,9′-Bis(Hydroperoxy)-9,9′-Fluorene+2 Fluorenones (Adduct). See Vol **2**, B145-L

tert-Butyl Hydroperoxide. $(CH_3)_3C.O.OH$; mw 90.15, OB to CO_2 −195.23%; colorl liq, mp 3.8–4.8°; bp 4.5–5.0° at 2mm, 33–4° at 17mm; d 0.896g/cc at 30/4°, RI 1.3983 at 25°. Sol in w. Prepn is by reacting t-butyl hydrogen sulfate with 30% hydrogen peroxide at 0–5°. After standing overnight at RT the mixt is fractionally distd at 4–5° under vacuum (2mm)(with *caution!*) to give a 68% yield. Distn at atm press will cause deton. Expl decompn of the hydroperoxide is obtd at 250°
Refs: 1) N.A. Milas & D.M. Surgenor, "Studies in Organic Peroxides. VIII. t-Butyl Hydroperoxide and Di-t-butyl Peroxide", JACS **68**, 205–8 (1946) & CA **40**, 2106 (1946) 2) H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", **ASTM Special Tech Publ No 394** (1965), 15

Butyrylhydroperoxide. See Vol **2**, B394-L

Cumene Hydroperoxide. See Vol **3**, C574-R to C575-R

Diacetylenic Dihydroperoxides. See Vol **5**, D1120-R to D1121-L

1,6-Dihydroperoxy-(1,6-Endoperoxy)-Cyclodecane. See Vol **5**, D1265-R to D1266-L

Diphenyl Methane Hydroperoxide. See Vol **5**, D1464-R to D1465-L

Diacetylenic Dihydroperoxides. See Vol **5**, D1120-R

1-Ethoxyethyl Hydroperoxide. See Vol **6**, E192-L

1-Ethylcyclohexyl Hydroperoxide-p-Nitrobenzoate. See Vol **6**, E224-L

Ethyl Hydroperoxide. See Vol **6**, E300-R

Hydroperoxides, Organic (Explosiveness). See Vol **7**, H224-R to H227-R

1-Hydroxyethyl Hydroperoxide. See Vol **7**, H241-R

Isopropyl Hydroperoxide. $(CH_3)_2CH_2.O.O.H$, mw 76.12; OB to CO_2 −147.14%; colorl, mobile liq; bp 107–9° (expl decomps just above bp); d 0.8927g/cc at 23/4°; RI 1.8861 at 23°. Miscible with alc, eth and w in all proportions. Prepn is by reacting diisopropyl sulfate with 30% hydrogen peroxide and aq KOH at RT and allowing the mixt to stand for 24hrs. The hydroperoxide is vac distd *(Caution!)* off at 3mm/21–4°
Ref: S. Medvedev & E. Alexejewa, Ber **65**, 133 (1932) & CA **26**, 2411–2 (1932)

Methyl Hydroperoxide (Monomethylhydroperoxide). $CH_3.O.O.H$; mw 48.06; OB to CO_2 −66.58%; colorl liq, mp −72 to −78°; bp 38–40° at 65mm (sl decompn), 90–100° at 760mm (decompn); d 0.9967g/ml at 15/4°; RI 1.3608. Sol in et acet and concd sulfuric acid; sl sol in chlf and benz; v sl sol in petr eth. Miscible with w, eth and alc. Prepn is by reacting dimethyl sulfate with hydrogen peroxide and concd KOH

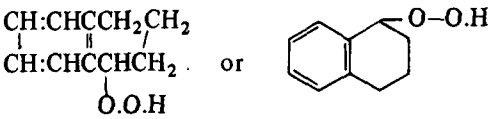
while cooling. A by-product is dimethylperoxide. The monomethylperoxide explds at about 130° or on warming with some catalysts. It also forms Ba and Ca salts that are w sol and expl when dry

Refs: 1) Beil **1**, [270] 2) A. Rieche & F. Hitz, Ber **62**, 2458 (1929) & CA **24**, 1078 (1930) 3) A.C. Egerton et al, Faraday Soc Discussion on Hydrocarbons **10**, 278 (1951) & CA **46**, 3358 (1952) 4) Tobolsky & Mesrobian (1954), 158 5) Encycl, Vol **7** (1975), H225 (table)

Picryl Hydroperoxide (2,4,6-Trinitrophenylhydroperoxide). $(O_2N)_3C_6H_2.O.O.H$; mw 245.16; N 17.14%; OB to CO_2 –35.89%; known and used in the form of its salts, such as the Na salt $(O_2N)_3C_6H_2.O.ONa$; mw 267.14; N 15.73%; OB to CO_2 –32.94%; red-brn cryst; mp 154° (decompn). Sol in w and alc; v sl sol in ether. Prepd by heating equiv mol quants of picrylchloride and sodium peroxide in w until soln is complete. The Na salt is an expl

Refs: 1) Beil **6**, 291–2 2) A. Voswinkel, GerP 96855 (1897); Ibid, ChZtr **1898** (II), 160

1,2,3,4-Tetrahydro-1-Naphthyl Hydroperoxide (Tetralinhydroperoxide).



mw 164.23; OB to CO –233.82%; yel star-shaped ndls; mp 56°; d 1.0988g/cc at 78.8/4°; RI 1.53893 (α), 1.55473 (He). V sol in alks, py and aniline; moderately sol in eth; v sl sol in w. Prepn is by passing air for 50–60 hrs thru coml tetralin at 75°. Vac distn removes the unreacted tetralin at 50–60° and 1–2mm. The 15–17% reacted yield is purified by being recrystd twice from petr eth. Deflgrn occurs above 130°; expln occurs on superheating the hydroperoxide

Refs: 1) H. Hock et al, "Autooxidation of Hydrocarbons. I. A Tetrahydronaphthalene Peroxide Obtained by Autoxidation", Ber **66B**, 61–8 (1933) & CA **27**, 1627 (1933)
2) Tobolsky & Mesrobian (1954), 12–16 & 162

TRIETHYLTIN HYDROPEROXIDE. $(C_2H_5)_3Sn.O.O.H.H_2O_2$; mw 272.95; cryst; mp 35–6°. Prepn is by reacting triethyltin hydroxide with 2 mew of hydrogen peroxide for 20 mins at –60° in the presence of dry magnesium sulfate. The hydroperoxide explds at 150–180°

Ref: Yu.A. Aleksandrov & V.A. Shushunov, ZhOshchKhim **35** (1), 115–7 (1965)(Russ) & CA **62**, 13167 (1965)

Triphenyltin Hydroperoxide. $(C_6H_5)_3Sn.O.O.H$; white crysts; mp, explds at 75°. Sol in dioxane. Prepn is by reacting 1 g of triphenyltin hydroxide in dry eth (100ml) at RT with 1 ml of 98% hydrogen peroxide. Pptn of the hydroperoxide occurs at –10° in a 45% yield from eth. The expln temp of 75° is very reproducible

Ref: R.L. Dannley & W.A. Ave, JOC **30**, 3845 (1965) & CA, not found

α-Oxy and α-Peroxy-Hydroperoxides and Peroxides

Bis(1-Hydroperoxycyclohexyl) Peroxide. See Vol **2**, B145-R

1,1′-Bis(Hydroperoxycyclohexyl) Peroxide. See Vol **2**, B144-L

Bis(Hydroxymethyl) Peroxide. See Di(methylol) Peroxide in Vol **5**, D1357

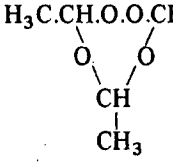
1-Hydroxymethyl Hydroperoxide. See Vol **7**, H248-L

Hydroxymethyl Methyl Peroxide. $CH_3.O.O.CH_2.O.H$; mw 78.10; oil at RT; bp 41–2° at 55mm; d 0.951g/cc at 15/4°; RI 1.3831. Sol in w. Prepn is by reacting 10% hydrogen peroxide and 1 mew of dimethyl sulfate with 1 mew of KOH at RT. The prod is

then extrd with eth using a continuous extractor, followed by vacuum fractional distn to obt a pure yield. The mat is very dangerous to handle, attacking the respiratory organs and producing deep burns on the skin which heal with difficulty. The peroxide is a highly brisant expl which is impact sens when heated

Ref: A. Rieche & F. Hitz, Ber **62B**, 2458 (1929) & CA **24**, 1078–8 (1930)

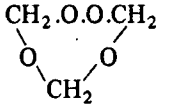
Perparaldehyde or Monoperparaldehyde.



mw 148.20; OB to CO_2 –151.15%; lgt oil; mp 9°; bp 45–6°; d 1.0672g/cc at 19.6°; RI 1.4163 at 19.6°. Sol in eth, alc, benz, petr eth and most organic solvs; v sl sol in w. Prepn is by cracking the dimer of cyclo-di(α,α′-diethyl ether)-peroxide using a vac distn app. *Caution!* The residue is *extremely* sens to mech action and explds on simply touching it. The perparaldehyde explds mildly on heating

Refs: 1) Beil, not found 2) R. Rieche & R Meister, Ber **65**, 1274–9 (1932) & CA **26**, 5906 (1932)

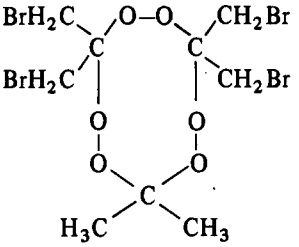
Pertrioxane (Pertrioxymethylene).



mw 106.11; OB to CO_2 –75.39%; colorl oily liq; mp, not avail; bp 35–6° at 12mm; d 1.2765g/cc at 16.7°; RI 1.4216. Sol in alc; insol in w. Prepn is by reacting P_2O_5 with formaldehyde dissolved in eth at RT for more than several days. Evapn of the eth leaves the prod as a non-vol oil. The compd is extremely expl; it detonates readily on being warmed in a test tube

Refs: 1) Beil, not found 2) J.F. Walker, "Formaldehyde", Reinhold, NY (1944), 128 3) A. Rieche & R. Meister, Ber **66**, 720 (1933) & CA **27**, 3447 (1933)

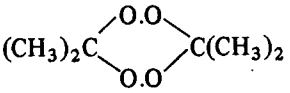
3,3,6,6-Tetrakis(Bromoethyl)-9,9-Dimethyl-1,2,4,5,7,8-Hexaoxaonane.



mw 537.88; OB to CO_2 –56.52%; crysts; mp 159–62°, decompn > 200°. Sol in acet and dioxane. Prepn is by reacting bis[β,β′-dibromo-α-hydroperoxy-isopropyl] -peroxide, obtd by H_2O_2 peroxidation of 1,3-dibromoacetone, dissolved in absol acet with P_2O_5 for 20 mins at RT. After sepn from the P_2O_5 by filtn, the prod is cryst from eth/w. The yield is 42%. The peroxide explds on impact or friction, as do the tetrachloro and 9-ethyl-9-methyl analogues

Ref: M. Schulz et al, Ber **100**, 2242-9 (1967) & CA **67**, 90784 (1967)

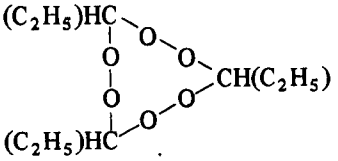
3,3,6,6-Tetramethyl-1,2,4,5-Tetraoxane.



mw 148.20; cryst; mp 132–3° (decompn). Sol in methanol. Prepn is by reacting 50% hydrogen peroxide or permonosulfuric acid with acet at RT. The dimeric acet peroxide explds with extreme brisance on impact, friction or rapid heating

Ref: A. Baeyer & V.Villiger, Ber **33**, 858 (1900) & CA, not found

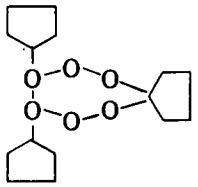
3,6,9-Triethyl-1,2,4,5,7,8-Hexaoxaonane (Propylidene Peroxide)



mw 222.30; OB to CO_2 –151.15%; mobile expl oil; d 1.089g/cc; RI 1.43903. V sol in org solvents; insol in w. Prepn is by allowing equimol amts of hydrogen peroxide and n-propyl aldehyde dissolved in ether to stand at RT for several

days, and then treating the soln with P_2O_5 at 0–5° for a longer time. Evapn of the ether and heating the residue in vacuo gives the peroxide. The oil is extremely expl and friction sens
Ref: A. Rieche & R. Meister, Ber **72B**, 1933–8 (1939) & CA **34**, 712–3 (1940)

Tris(Spirocyclopentane)-1,1,4,4,7,7-Hexaoxaonane.



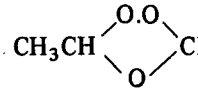
mw 300.42; cryst; mp 166–7°(decompn). Prepn is by reacting 0.52 mole of cyclopentanone with a mixt of 0.43 mole hydrogen peroxide and <0.65 mole of 70% nitric acid at 0°. The prod is a highly brisant expl, v sens to shock, friction and rapid heating
Ref: G.H. Bjorklund & W.H. Hatcher, Trans-RoySocCan **44** (Sect III), 25–30 (1950) & CA **45**, 7951–2 (1951)

OZONIDES

See in this Vol under Ozonides. The following compds are of special interest:

Benzene Triozonide. See Vol **2**, B63

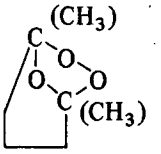
Trans-2-Butene Ozonide.



mw 104.14; colorl gas at RT; bp 15° at 20mm. Sol in CCl_4. Prepn is by ozonolysis of trans-butene-2 at –70° with a 14.5% yield of the ozonide. Sepn of the product was performed using preparative scale gas partition chromatography at RT. Ignition of the ozonide (for analytical purposes) results in a brisant expln. Isom identification is by infrared and nuclear magnetic resonance spectra
Ref: L.D. Loan et al, JACS **87**, 741 (1965) & CA **62**, 12993 (1966)

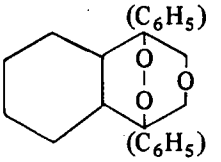
Cyclohexene Ozonide. See Vol **3**, C599-R

1,2-Dimethyl-1-Cyclopentene Ozonide.



mw 144.21; mp –13.2°; bp 58.8° at 15mm; d 1.0718g/cc; RI 1.4370 at 18.5°. Sol in anhyd petr eth and CCl_4. Prepn is by ozonolysis of 18.5g of 1,2-dimethyl-1-cyclopentene dissolved in 120ml of anhyd petr eth with a mixt of O_3/O_2 contg 5.5% O_3 at –70°. After soln, the evapn, distn and refractionation of the residue yields 64.3% prod. The ozonide is stable to vac distn but explds violently at 130° under atm press
Ref: R. Criegee & G. Lohaus, Ber **86**, 1–4 (1953) & CA **48**, 1234 (1954)

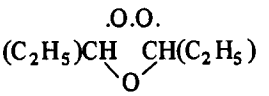
1,3-Diphenyl-1,3-Epidioxy-1,3-Dihydro-isobenzofuran.



mw 302.36; cryst; sol in CS_2. Prepn is by exposing a vigorously stirred soln of diphenylisobenzofuran in CS_2 to sunlight for 70 secs. Vac evapn below 0° yields crysts of the photoperoxide-ozonide. The compd explds at 18°
Ref: C. Dufraisse & S. Ecary, CR **223**, 735–7 (1946) & CA **41**, 2413 (1947)

Ethylene Ozonide. See Vol **6**, E290-R

trans-2-Hexene Ozonide.

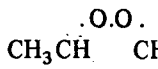


mw 132.20; colorl gas at RT. Sol in CCl_4. Prepn is by ozonolysis of pentene-2 at –70° with an approx 15% yield of the ozonide. Sepn of the prod in 12.3% yield was performed using preparative scale gas partition chromatography at RT. Ignition of the ozonide (for C and H analysis) results in a brisant expln. Isom identifica-

tion is from infrared and nuclear magnetic resonance spectra
Ref: L.D. Loan et al, JACS **87**, 738 (1965) & CA **62**, 12993 (1966)

Isoprene Diozonide. See Vol **7**, I136-R

trans-2-Pentene Ozonide.



mw 118.17; colorl gas at RT. Sol in CCl_4. Prepn is by ozonolysis of 10g of pentene-2 at −70° to 60% completion. Prod sepn in 39.7% yield is obtd with a 20 ft 10% Dow 710 silicone grease column at temps between 70–110° (gas partition chromatography). Ignition of the ozonide (for C and H analysis) results in a brisant expln. Isom identification is from infrared and nuclear magnetic resonance spectra
Ref: L.D. Loan et al, JACS **87**, 740–1 (1965) & CA **62**, 12993 (1966)

PEROXIDES

Acetone Peroxides. See Vol **1**, A41-R to A45-L

Acetylene Peroxides. See Vol **1**, A66-L to A67-L

Ascaridol. See Vol **1**, A494-R

1,1′-Bis(Benzoylperoxycyclohexane). See Vol **2**, B135-L

2,2-Bis(t-Butylperoxy) Propane. See Vol **2**, B137-R to B138-L

Bis(α-Hydroxy-β,β,β-Trichlorethyl) Peroxide. See Vol **2**, B148-R

Bis(Succinyl) Peroxide. See Vol **2**, B156-R & Vol **5**, D1512-R

Butadiene Peroxide. See Vol **2**, B365-R to B366-L

Butadiene Peroxide Polymer. See Vol **2**, B366-R

Butanone Peroxide Dimer, Methyl Ethyl Ketone Peroxide. See Vol **2**, B375

Cyclohexadiene Peroxide, Polymeric. See Vol **3**, C595-L

Cyclohexanone Peroxides. See Vol **3**, C598-L to C599-L

Dianisoyl Peroxide or Anisoyl Peroxide. See Vol **5**, D1152-R to D1153-L

Dibenzal Diperoxide or Dibenzlidene Diperoxide See Vol **5**, D1182-R

Dibenzolsulfonyl Peroxide. See Vol **2**, B62-R

Dibenzophenoneperoxide Dimer. See Vol **5**, D1184-R

Dibenzoyl Peroxide and Derivatives. See Vol **5**, D1186-R to D1188-R

Dibutyl Peroxide or tert-Butyl Peroxide. See Vol **5**, D1197

Di-n-Butyryl Peroxide. See Vol **5**, D1200-R to D1201-L

Di-iso-Butyryl Peroxide. See Vol **5**, D1201-L

Dicamphoryl Peroxide. See Vol **5**, D1201

Dichloroacetyl Peroxide. See Vol **5**, D1204-L

Di(Chlorobenzoyl) Peroxide. See Vol **5**, D1208-R

Dicrotonyl Peroxide. See Vol **5**, D1216-R

Dicuminoyl Peroxide. See Vol **5**, D1216-R

Diethanol-Peroxide. See Vol **5**, D1245-R

Diethyl Peroxide. See Vol **5**, D1246-R to D1247-L

Diethyl Peroxydicarbonate. See Vol **5**, D1247-L

Di-2-Furoyl Peroxide. See Vol **5**, D1260-R

2,2′-Difuroyl Peroxide. See Vol **6**, F246-R to F247-R

Difurylacryloyl Peroxide. See Vol **5**, D1260-R to D1261-L

o,o′-Dimethoxybenzoyl Peroxide. See Vol **5**, D1303

Di(Methoxymethyl)-Peroxide. See Vol **5**, D1303-R

Dimethylborylmethyl Peroxide. See Vol **5**, D1329-R

2,3-Dimethylbutadiene Peroxide, Polymeric. See Vol **5**, D1329-R to D1330-L

Dimethyleneperoxidecarbamide. See Vol **5**, D1337-R

Dimethyleneperoxide-Ethylamine. See Vol **5**, D1337-R

Di(Methylether)-Peroxide. See Vol **5**, D1338-L

Dimethylperoxide or Methylperoxide. See Vol **5**, D1363

Dipropionyl Peroxide or Propionic Peroxide. See Vol **5**, D1492-R

Di(iso-propyl)-Peroxide. See Vol **5**, D1500

Ethylethanol Peroxide. See Vol **6**, E294-L

Ethylhydroxymethyl Peroxide. See Vol **6**, E301-R

Ethylideneperoxide. See Vol **6**, E305-R to E306-L

Ethylideneperoxide, Dimeric and Polymeric. See Vol **6**, E306

Ethylmethyl Peroxide. See Vol **6**, E312-R

Furfuraloxime Peroxide. See Vol **6**, F243-R

Hexamethylenediamine Peroxide. See Vol **7**, H79-L

Hexamethylenetetramine Triperoxide and Hexamethylenetriamine Triperoxide. See Vol **7**, H83-L

7-Hydroxy-1,2-Dioxo-1,2-Dihydro-Naphthalene. See this Vol, N20-R

α-Hydroxyethylmethyl Peroxide. See Vol **7**, H242-L

α-Hydroxypropylethyl Peroxide. See Vol **7**, H248-R

Isoprene(2-Methyl-1,3-Butadiene) Peroxide, Polymeric. See Vol **7**, I136-R

Mesityloxideperoxide. See this Vol, M36-L

Phthalyl Peroxide (or Phthalylsuperoxide). $(C_8H_4O_4)_x$; structure unknown; cryst. Explds ca 136° and on contact with concd sulfuric acid
Refs: 1) Beil **9**, 804 2) H.V. Pechmann & L. Vanino, Ber **27**, 1511–12 (1894) & CA, not found

PEROXY ACIDS

Bis(Phthalic Acid) Peroxide. See Vol **2**, B156

Peroxyacetic or Peracetic Acid (Acetyl hydroperoxide; Peressigsäure, Acetpersäure or Acetylwasserstoffsuperoxyd in Ger). $CH_3C(O).O.O.H$; mw 76.05; OB to CO_2–63.12% w white liq; mp 0.1°; bp 20–30° at 10–20mm, 105° (explds violently when heated quickly ca 110°); d 1.226g/cc at 15/4°; RI 1.3974. V sol in w, eth and sulfuric acid; sol in alc. Prepn is by reacting equimol quants of acet ac with 98% hydrogen peroxide in the presence of a catalyst such as 1% sulfuric acid, or by treating acet ac with either ozone or O_2 under UV, or by oxidn of dry acetaldehyde in the presence of a catalyst such as Co sulfate, or by reaction of aq hydrogen peroxide with gl acet ac and dil sulfuric acid plus propyl acetate with subseq distn of a 25% peroxyacetic acid soln in propyl acetate (Refs 1 to 6 and 9 to 11). Peroxyacetic acid is thermally detonable as a vap, as a soln above 50% in organic media or as a soln above 70 wt % in aq media (Refs 6 & 8). As a liq it is insens to impact (Ref 9), but the solid acid has expld at

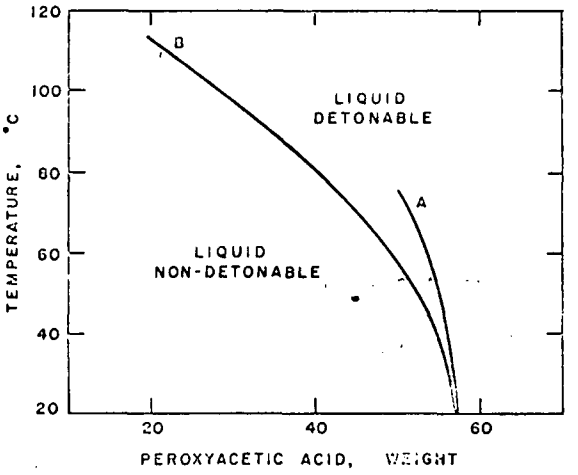


Fig 3 Boundaries between detonable and non-detonable regions from 20–120° for various concentrations of peroxyacetic acid in ethyl acetate (A) and acetic acid (B)

–20° (Ref 7a). According to Swern (Ref 9) experimentation using blasting caps performed on both eth acet and acet ac solns of peroxyacetic acid has resulted in the data presented in Fig 3

Impurities, such as heavy metal ions, accelerate the decompn and may cause an expln to occur at a lower temp. Open Cup flash pt is 105°F (Ref 12). Since the material is an extremely powerful oxid agent it must be handled with extreme caution and kept away from combustible mats (Ref 12)
Tests. Chem analysis consists of reaction with KI soln and titration of the liberated I^- with Na thiosulfate soln. Instrumental analysis consists of measurement of the carbonyl absorption at 1760cm^{-1} using an infrared spectrophotometer. This procedure is valid for any physical state or soln strength of the acid (Ref 10)
Toxicity. The peroxy acid is highly toxic and may cause death or permanent injury after very short exposure to small quants (Ref 12)
Uses. Peroxyacetic acid is the most important epoxidation reagent used today because of its economical availability and ease of use with a wide variety of reactants (Ref 10). It also finds wide usage as an organic oxidizing agent (Ref 11)
Refs: 1) Beil **2**, 169, (78), [174] & {379} 2) J. d'Ans et al, Ber **45**, 1846 (1912) & CA **6**, 2737 (1912) 3) Ibid **48**, 1141 (1915) & CA

9, 2542 (1915) 4) W.H. Hatcher & G.W. Holden, TrRoySoc(Canada) [3] **21**, sec 3, 238 (1927) & CA **22**, 1136 (1928) 5) Tobolsky & Mesrobian (1954), 35–6, 167 & 178 6) Anon, "Fire and Explosion Hazards of Organic Peroxides", Natl Bd of Fire Underwriters, NY (1956) 7) E.G.E. Hawkins, "Organic Peroxides . . .", D. Van Nostrand Co, Inc, NY (1961), 161–85 7a) A.G. Davies, "Organic Peroxides", Butterworths, London (1961), 56 8) H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", **ASTM Special Tech Publ No 394**, Phila (1965), 16 9) D. Swern Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970), 89, 314, 315, 317, 328 & 480–3 10) Ibid, Vol **2** (1971), 375, 436, 437 & 690 11) L.F. Martin, "Organic Peroxide Technology", Noyes Data Corp, Park Ridge, NJ (1973), 216–19 12) Sax (1975), 1001 13) ChemRubHdb (1975), C-90

Peroxybenzoic or Perbenzoic Acid (Benzoylhydrogenperoxide or Perbenzosäure in Ger). $C_6H_5.C(O).O.O.H$; mw 138.12; OB to CO_2 −162.18%; wh monocl lflts; mp 41–3°; bp 97–100° at 13 to 15mm (decomps at 80–100° at 760mm) with gas evoln. Sol in acet, benz and chlf; v sol in alc and eth. Prepn is by reacting benzoic acid in methanesulfonic acid with 50–94% hydrogen peroxide for 1–2 hrs at 20–40°. Yield is 75–95% (Ref 6). Other methods of prepn are given in Refs 1–4. The acid explds weakly on heating (Refs 2, 5 & 8). It is a powerful oxid agent which reacts vigorously with reducing matls

Tests. It absorbs infrared radiation in soln at 3270–3250cm^{-1} and as a solid at 3260–3232cm^{-1} (Ref 7)

Toxicity. Peroxybenzoic acid is moderately toxic but does not cause death or permanent injury (Ref 8)

Uses. It is used to prep oxiranes and has been used for the epoxidation of over 600 unsaturated compds (Ref 7)

Refs: 1) Beil **9**, 128, (93) & [157] 2) A. Baeyer & V. Villiger, Ber **33**, 858, 1569 & 1576–7 (1900) 3) Tobolsky & Mesrobian (1954), 36–7, 168 & 178 4) L.S. Silbert et al, Org-Synth **43** (1963), 95 5) H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", **ASTM Special Tech Publ No 394**, Phila (1965), 16 6) D. Swern Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970) 7) Ibid, Vol **2** (1971) 8) Sax (1975), 1001 9) ChemRubHdb (1975), C-192

N-Peroxycaproic or Percaproic Acid (Caproylhydroperoxide). $C_5H_{11}C(O).O.O.H$; mw 132.195; OB to CO_2 −181.55%; colorl liq; mp 15°; bp 62–3° at 13mm. Sol in alc, eth and petr eth; v sl sol in w. Prepn is by reacting an absol sulfuric acid soln of n-caproic anhydride with concd (98%) hydrogen peroxide for 20 hrs at 0° to RT. The prod is purified by vac distn. The peroxy acid decomps slowly on storage and detonates on rapid heating to 240° with evoln of flame

Refs: 1) Beil **2**, [286] 2) F. Fichter & R. Zumbrunn, Helv **10**, 869 (1927) & CA **22**, 1136 (1928) 3) Tobolsky & Mesrobian (1954), 167 & 178 4) D. Swern, ChemRevs **45**, 10 (1949) & CA **43**, 8352 (1949) 5) Ibid, Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970), 377 & 493

Peroxyformic or Performic Acid (Perameisensäure or Formylhydroperoxyd in Ger). $HC(O).O.O.H$; mw 62.05; OB to CO_2 0%; colorl liq, mp −18.5°. Known *only* in 90% aq solns because of its *explosiveness*, the soln is colorl and is sol in w, alc, eth and sl sol in benz and chlf. Prepn is by reacting 98% formic acid at −10 to −5° with 98% hydrogen peroxide in the presence of 1% concd sulfuric acid, and allowing the mixt to stand for 14 hrs at RT. Very *careful* distn produces a 63% yield of a 90% aq soln of the acid (Ref 6). The solns are extremely unstable and have detond under vacuum distn at −10° (Refs 3, 4 & 6). 80% solns have expld at 80–85° (Ref 2). It is a strong oxidizing agent and reacts with expl violence with metals such as Zn dust, P and some organic compds (Ref 6)

Tests. The acid absorbs strongly in the infrared at 1739cm^{-1} and can be detd by infrared spectroscopy (Ref 7)

Toxicity. It is highly toxic and may cause death or permanent injury after short exposure to a small amount (Ref 8)

Uses. Its solns are used to epoxidize unsatd organic compds (Ref 7)
Refs: 1) Beil **2**, (19–20) & [34] 2) J. D'Ans & A. Kneip, Ber **48**, 1136–7 (1915) & CA **9**, 2542 (1915) 3) F.P. Greenspan, JACS **68**, 907 (1946) & CA **41**, 5445 (1947) 4) A. Weingartshofer-Olmos et al, C&EN **30**, 3041 (1952) & CA **46**, 9845 (1952) 5) Tobolsky & Mesrobian (1954), 34–5, 167 & 178 6) D. Swern, Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970) 7) Ibid, Vol **2** (1971), 400, 402 & 690 8) Sax (1975), 1003

Peroxypropionic Acid (Perpropionic Acid or Propionylwasserstoffsuperoxyd in Ger). $C_2H_5C(O).O.O.H$; mw 90.105; OB to CO_2 −106.54%; colorl liq; mp −13.5°; bp 25° at 20mm; RI 1.4041. Miscible with w, chlf, alkyl acetates, alcohols, ketones, etc. Prepn of 99.5% pure acid is by reacting 1 mole of propionic anhydride with 2 moles of 98% hydrogen peroxide at RT using 1% sulfuric acid as a catalyst until equilibrium is achieved. The mixt is allowed to stand for 12 hrs and then distd under a vac of 20mm at 25°. The pure prod is obtd by fractional freezing and centrifuging (Refs 1 to 4). Peroxy propionic acid puffs off (deflgr) on heating. Although the acid is considered to be more stable than its lower homologues, solns of greater than 60% by wt at 25° in ethyl propionate are unstable to the shock and fire of No 6 blasting caps, decompg vigorously (Ref 4)
Refs: 1) Beil **2**, (108) 2) J. D'Ans & W. Frey, Ber **45**, 1850 (1912) & CA **6**, 2737 (1912) 3) Ibid, ZAnorgChem **84**, 159 (1914) & CA **8**, 923 (1914) 4) D. Swern Ed, "Organic Peroxides", Vol **1**, Wiley-Interscience, NY (1970)

Peroxysuccinic Acid or Monopersuccinicacid (Succininmonopersäure in Ger). $HO_2C.C_2H_4.C(O).O.O.H$; mw 134.125; OB to CO_2 −71.58%; crysts from chlf and eth; mp 107° (decompn). V sol in alc and acetone; sol in w, eth and ethyl acetate; sl sol in chlf. Prepn by treating bis(succinicacid) peroxide with w at 30°. Peroxysuccinic acid explds on contact with flame and is sl shock-sens (Refs 5 & 6). It decomps on long standing
Refs: 1) Beil **2**, 613 2) A.M. Clover & A.C. Houthton, AmChemJ **32**, 61 (1904) 3) Ibid, JCS **1**, 708 (1904) 4) E.G.E. Hawkins, "Organic Peroxides . . .", D. Van Nostrand Co, Inc, NY (1961), 301 5) R. Lombard et al, BullFr **12**, 2800 (1963) & CA **60**, 7927 (1964) 6) H.M. Castrantas et al, "Fire and Explosion Hazards of Peroxy Compounds", **ASTM Special Tech Publ No 394** (1965), 16

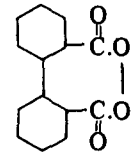
Phthalmonoperacid (or Mono-[2-Carboxybenzoyl]-hydroperoxide). $HO(O)C.C_6H_4.C(O).O.O.H$; mw 182.165; ndles; mp dec ca 110° with gas evoln. V sol in w or eth; sl sol in benz or chlf. Prepn is by reacting phthalic anhyd with an excess of hydrogen peroxide at −10°. Explds with brisance on rapid heating or on impact
Refs: 1) Beil **9**, 804 & [599] 2) A. Baeyer & V. Villiger, Ber **34**, 766 (1901) & CA, not found

Terephthalicdiperoxy Acid. $C_6H_4(C(O).O.O.H)_2$; mw 198.17; ndls; mp explds. Sol in alc. Prepn is by reacting terephthalic acid dichloride dissolved in eth with alk hydrogen peroxide soln at 0°. The diperoxy acid explds on heating or from impact. Its Na salt, $NaC_8H_5O_6$, mw 221.121, is also expl
Refs: 1) Beil **9**, 844 2) A. Baeyer & V. Villiger, Ber **34**, 766 (1901) & CA, not found

Diacyl Peroxides

Acetylbenzoylperoxide and Derivatives. See Vol **1**, A54-R to A55-R

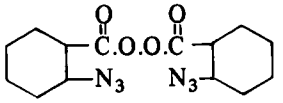
2,2-Biphenyldicarbonyl Peroxide (or Diphenoyl Peroxide).



mw 240.24; pale yel cryst; mp, explds at 70°. Sol in methylene chloride. Prepn is by treating a 0.1M soln of phenanthrenequinone trimethyl phosphite adduct in methylene chloride with 0.0096 mole of ozone at −75° for 400 secs.

The pptd yield (72% of theory) is filtered and then dried in a current of N_2 at 20° for 1 hr; finally at 0.5mm. The peroxide can be detond by impact or on heating to 70°. It is stable at temps below 0°
Ref: F. Ramirez et al, JACS **86**, 4394 (1964) & CA **61**, 14569 (1964)

Bis-o-Azidobenzoyl Peroxide.



mw 324.30; cryst. Sol in aq alc. Prepn is by reacting benzoyl chloride and Na azide in aq et alc at 0°. Recryst from abs et alc. The dry peroxide can be detond by static electricity
Refs: 1) J.E. Leffler, C&EN **41** (48), 45 (1963) 2) J. Hoffman, C&EN **41** (52), 5 (1963)

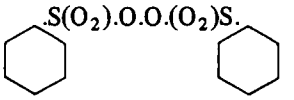
Bis(3-carboxypropionyl) Peroxide. See Bis-(succinyl) Peroxide in Vol **2**, B156-R to B157-L

Bisfluoroformyl Peroxide. FC(O).O.O.(O)CF; mw 126.04; colorl gas at RT. Prepn (with *caution*) consists of using a clean, dry 3ℓ stainless steel cylinder charged to an initial press of 120mm with F, to a total press of 600mm with O_2, and then to a total press of 740mm with CO; and finally keeping the cylinder at RT for 6 hrs. The peroxide is extracted from the mixt by fractional distn at 0.1mm and condensed in a trap at −119° in 57% yield. The peroxide expld s at 200°. It is stable below 30°
Refs: 1) R.L. Talbott, JOC **33**, 2095 (1968) & CA **69**, 2462 (1969) 2) R. Czerepinski et al, InorgChem **7**, 109 (1968) & CA **68**, 38996 (1968)

Bis(hexahydrobenzoyl) Peroxide or Bis(cyclohexanecarbonyl) Peroxide. See Vol **2**, B143-L

Diacetyl Peroxide or Acetyl Peroxide. See Vol **5**, D1121-R to D1122-L

Dibenzenesulphonyl Peroxide.



mw 314.37; colorl prisms; mp, explds at 53–4°. Prepn is by reaction of benzenesulphonyl chloride with sodium peroxide at 0°. Yield is 10%
Ref: A.G. Davies, "Organic Peroxides", Butterworths, London (1961), 65

Dibenzoyl Peroxide and Derivatives. See Vol **5**, D1186-R to D1188-R

Di-tert-Butyl Diperoxycarbonate.

$(CH_3)_3.C.O.O.C.O.O.C.(CH_3)_3$; mw 206.30; colorl crysts; bp > 95° at 4mm; RI 1.4106. Sol in eth. Prepn is by reacting a stirred soln of 18g of 71% t-butyl-hydroperoxide and 16.6g of pyridine in 40ml eth with 0.080 mole of phosgene introduced at a rate of 6mmoles/min, while maintaining the temp at 3–5°. Upon standing in the cold for 45 mins the reaction is stopped by the addn of 100ml of ice-w. Sepn of the eth layer, washing and vac evapn gives the purified 76% yield. The peroxy ester explds with brisance when heated to 135–40°
Ref: F. Strain et al, JACS **72**, 1254–63 (1950) & CA **46**, 1984 (1950)

Di-iso-Butyryl Peroxide. See Vol **5**, D1201-L

Dicamphoryl Peroxide. See Vol **5**, D1201

Di-n-Caproyl Peroxide or Bis(n-caproyl) Peroxide. See Vol **5**, D1201-R

Dicrotonyl Peroxide. See Vol **5**, D1216-R

Diethyl Peroxydicarbonate.

$C_2H_5(O)C.O.O.C(O)C_2H_5$; mw 178.19; colorl oil; bp 28–35° (decompn); RI 1.4017. Sol in eth.

Prepn is by dropwise addn of a cold aq sodium peroxide (1.0 molar) soln to 1.0 mole of vigorously stirred ethyl chloroformate while maintaining the temp at 6–10°. The mixt is stirred for an addnl half hr after all the sodium peroxide has been added. The oily prod is then sepd, washed with distd w and dried using anhyd Na_2SO_4. An 81% yield is obtd. The frozen ester is sens to the shock from a No 6 elect detong cap, producing a more brisant deton than an equal amt (0.25 lb) of benzoyl peroxide
Ref: F. Strain et al, JACS **72**, 1254–63 (1950) & CA **46**, 1984 (1950)

Di-2-Furoyl Peroxide. See Vol **5**, D1260-R

Ethyl Methyl Ketone Peroxide. See Vol **6**, E312-L. *Addnl Refs:* 1) C.S. Marvel & V. Nichols, JOC **6**, 296–304 (1941) & CA **35**, 3997–8 (1941) 2) J.D. Malkemus, ModPlast **41** (4), 119–25 & 167–9–70 (1963) & CA **60**, 6991 (1964)

Furyl-β-Acrylic Acid Peroxide. See Vol **6**, F247-R

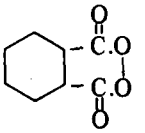
Diisopropyl Peroxydicarbonate.

$(CH_3)_2CHOC(=O).O.O.C(=O)OCH(CH_3)_2$; mw 206.18; OB to CO_2 −131.92%; colorl crysts; mp 8–10°; bp, rapid decompn at 35–8°; d 1.080g/cc at 15.5/4°; RI 1.4034. V sl sol in w; miscible with aliphatic and aromatic hydrocarbons, esters, ethers and chlorinated hydrocarbons. Prepn is by slow addn of 112g of pure sodium peroxide soln to 122.6g of vigorously stirred isopropyl chloroformate while maintaining the mixt at 6–10°. The agitation of the mixt is maintained for an addnl half hr subsequent to the complete addn of the sodium peroxide. Purification of the ester requires w washing, drying with anhyd $NaSO_4$, cooling to 10° and filtn to remove the $NaSO_4$. The yield is 81–89%. The ester is considered dangerous. When warmed sl above 10° it undergoes slow self-accelerating decompn which becomes violent under confinement; at 25–30° decompn occurs within 10–30 mins. Addn of 1% aniline, 1,2-diaminoethane or KI causes instant decompn. N,N-dimethylaniline addn causes an instant expln. Bulk solns of the ester (45%) in benzcyclohexane stored at 5° develop sufficient heat to decomp explosively after a day, and 50–90% solns are impact sens (Ref 1). The solid is normally stored and transported below −18° in loose-top trays

Refs: 1) W.A. Strong, IEC **56** (12), 33 (1964) & CA **62**, 3931 (1964) 2) F. Strain, JACS **72**, 1254 (1950) & CA **46**, 1984 (1950) 3) Anon, "Bulletin T.S. 350", Pittsburgh Plate Glass Co, Pittsburgh (1963) 4) Sax (1968), 677

Diproprionyl Peroxide. See Vol **5**, D1492-R

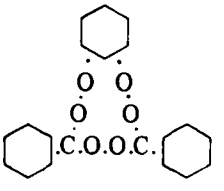
Phthaloyl Peroxide.



mw 164.14; white powd; mp 124.5–5° (decompn). Sol in acet. Prepn is by dissolving 1.6g each of K_2HPO_4 and KH_2PO_4 with 8.3g of Na_2O_2 in 400ml of w at 0°, and then reacting a chlf soln of 20.3g of o-phthaloyl by stirring the mixt for 15 mins while maintaining the temp at 0°. Recryst is from hexane with a yield of 25%. The peroxide deton at its mp and is probably polymeric
Ref: M. Jones & M.R. DeCamp, JOC **36** (11), 1536 (1971) & CA **78**, 15697 (1972)

Peroxy Esters

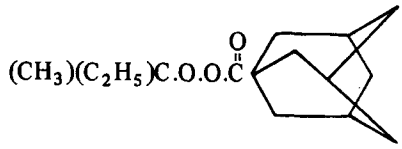
1,1-Bis(Benzoylperoxy) Cyclohexane.



mw 356.43; cryst; mp 117°. Prepn is by reaction of cyclohexanol (with *caution!*) with a mixt of 75% H_2O_2 and 0.01 vol % of concd sulfuric acid at 0°. The mixt is allowed to stand overnight under refrigeration. The 1-hydroxycyclohexyl 1-hydroperoxide formed (see also Vol **3**, C598-L) is then esterified with benzoyl chloride in py at 0°.

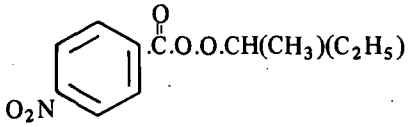
The ester explds sharply into flame when heated
Ref: R. Criegee & H. Dietrich, Ann **560**, 135–41 (1948) & CA **43**, 6189 (1949)

tert-Butyl 1-Adamantaneperoxycarboxylate.



mw 252.41; cryst, mp 26–6.5°. Prepn is by reacting tert-butyl hydroperoxide with acyl chloride in the presence of py at 0°, using hexane as the reaction solvent. The ester yield is 89%. It explds at 90–100°. The ester readily initiates the polymerization of methylmethacrylate at three times the rate induced by benzoyl peroxide at 70°
Refs: 1) Encycl **2**, B385-L (1962) 2) G.A. Razuvaev et al, DoklAkadNaukSSSR **183** (6), 1346–9 (Russ) (1968); Tetrahedron **25**, 4925–31 (1969); CA **70**, 87128 (1969) & CA **72**, 11847 (1970) 3) ChemRubHdb (1975), C-97 & C-548

tert-Butyl p-Nitroperoxybenzoate.



mw 239.275; cryst; mp 78°. Prepn is by reaction of tert-butyl alcohol with *(caution!)* a mixt of 91.5% hydrogen peroxide and 0.01 vol % of concd sulfuric acid at 0°. The mixt is allowed to stand overnight under refrigeration. The tert-butylhydroperoxide formed (see Vol **2**, B385-L) is then esterified with p-nitrobenzoyl chloride. The ester explds in a flame
Ref: R. Criegee & H. Dietrich, Ann **560**, 135–41 (1948) & CA **43**, 6189 (1949)

Butyl Peroxyacetate. See Vol **2**, B387

tert-Butyl Peroxy Benzoate. See Vol **2**, B387-R to B388-L

Ethyl Peroxy Acetate. See Vol **6**, E316-R

Peroxybenzoic Acid, 1,1,4,4-Tetramethyltetramethylene Ester. See 2,5-Bis(Benzoylperoxy)-2,5-dimethyl-hexane in Vol **2**, B135-R

Peroxybenzoic Acid Diester with Bis(1-Hydroxycyclohexyl)-Peroxide. See 1,1′-Bis (benzoylperoxy)-dicyclohexylperoxide in Vol **2**, B135-L

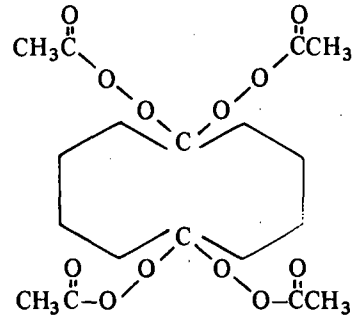
Peroxybenzoic Acid Diester with Bis(9-Hydroxy-9-Fluorenyl) Peroxide. See 9,9′-Bis (Benzoylperoxy fluorenyl)-peroxide in Vol **2**, B136-L

Peroxybenzoic Acid, 9-Fluorenylidene Ester. See 9,9′-Bis(Benzoylperoxy)-Fluorene in Vol **2**, B135-R

Peroxybenzoic Acid, p-Nitrol, 1,4,4-Tetramethyltetramethylene ester. See 2,5-Bis(p-nitrobenzoylperoxy-2,5-Dimethylhexane in Vol **2**, B135-R

Peroxybenzoic Acid, Cyclohexylidene Ester. See 1,1′-Bis(Benzoylperoxy)-cyclohexane in Vol **2**, B135-L

1,1,6,6-Tetrakis (Acetylperoxy) Cyclododecane.



mw 436.52; rhmb platelets; mp 144–5° (decompn, then deton). Prepn is by reaction of trans-decahydro-4a-naphthol with 92% hydrogen peroxide to form the tetrahydroperoxide at 0°. Esterification of the peroxide is performed using acetyl chloride. The prod is crystd from ethanol.

The ester deton with brisance on weak friction
Ref: R. Criegee & H. Dietrich, Ann **560**, 135–41 (1948) & CA **43**, 6189 (1949)

Poly Peroxides

This group consists of polymeric peroxides of indeterminate structure rather than poly-functional molecules of known structure. The compds listed below are considered to be typical of this group:

Butadiene Ozonide Polymer. See Vol **2**, B366-R

Butadiene Peroxide Polymer. See Vol **2**, B366-R

Cyclohexadiene Peroxide Polymer. See Vol **3**, C595-L

Diethylether Peroxide Polymer. See Vol **5**, D1234-L to D1235-L

2,3-Dimethylbutadiene Peroxide, Polymeric. See Vol **5**, D1329-R to D1330-L

Dimethylketene Peroxide, Polymeric. See Vol **5**, D1348-L

1,1-Diphenyl-ethylene Peroxide, Polymeric. See Vol **5**, D1458-R

Ethylidene Peroxide, Polymeric. See Vol **6**, E306-L & R

Peroxysuccinic Acid Polymer or Succinyl Peroxide. (Polymer) (Polymerees Succinylperoxyd in Ger). $\dagger O.C(O).C_2H_4.C(O).O\dagger_n$; mw $(116.10)_n$; OB to CO_2 −82.69%; crysts or amorph; mp (decomps or explds). Prepn is by shaking (while cooling) 1 mole of succinyl-chloride with 1 mole of Na peroxide which is either dissolved in ice w (with a small amt of hydrogen peroxide) or in 10% Na acetate soln. The polymer explds violently at 120° upon slow heating or at 110° when rapidly heated. V sens to friction. It also explds on contact with aniline, concd sulfuric acid or phenylhydrazine. The expln with the latter is so brisant that it will cause a larger quantity of the polymer to detonate at a distance of 2 meters (Refs 3 to 5)
Refs: 1) Beil **2**, 612 & [553] 2) L. Vanino & E. Thiele, Ber **29**, 1724 (1896) 3) A.M. Clover & A.C. Houghton, AmChemJ **32**, 60 (1904) 4) Ibid, JCS **86**, I, 707 (1904) 5) F. Fichter & A. Fritsch, Helv **6**, 330 (1923) & CA **17**, 1954 (1923)

Polycyclopentadiene Ozonide. See Vol **3**, C602-R

Polycyclopentylidene Peroxide Polymer. See Vol **3**, C604-R

Written by **H. L. HERMAN**

Peroxybutyric Acid. See under Butyrylhydroperoxide in Vol **2**, B394-L

Persalites, Gesteins (Gesteins is Ger for Blasting). A group of Ger mining expls manufd from left-over stocks of WWI military expls. Two typical formulations were a) K chlorate 35, AN 43, m-DNT 8, DNN 8, woodmeal 4, and NG 2%; OB to CO_2 −0.3%, Trauzl value 330cc; b) K perchlorate 34, AN 48, m-DNT 10, woodmeal 6 and pulverized coal 2%; OB to CO_2 +1.7%, Trauzl value 325cc
Refs: 1) R. Escales, "Chloratsprengstoffe", Leipzig (1910), 185 2) Naoúm, Expls (1927), 127 & 133

Pertit or Pertite. Italian for Picric Acid

Pertuisset Powder. See under Mundell Powder in this Vol, M161-L

PETA. Acronym for Pentaerythritol Tetraacetate (qv)

Pétard. Fr term for an expl charge designed for demolition purposes. Usually, the pétard consisted of a box (metallic or wooden) contg from 100g up to several kgs of an expl, provided with a primer. In pétards used at the end of the 19th century, the following expls could be found: pressed NC (Ger), Ecrasite (Austria), and Dynamite or Melinite (Fr)

The term pétard was formerly used to designate an ancient device for bursting open gates, barricades, or doors to which it was attached. Basically a case filled with expls, the pétard somewhat resembled a short mortar. A typical pétard might weigh about 60 lbs and have a mouth about 9 inches in diameter
Refs: 1) Daniel (1902), 610–11 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 346

Pétard d'alarme (Fr). A device classed as an artifice de signalisation sonore and used on railroads for signalling purposes. It consisted of a waterproof container with a mixt of 2p Sb sulfide and 1p K chlorate, to which was added a small quantity of powdered glass. After inserting a primer, the ensemble was attached to the upper surface of a rail. When the wheel of a locomotive contacted the primer the charge expld, producing a loud report
Ref: Pepin Lehalleur (1935), 477

Pétard de mineurs (Fr). See under Miner's Squib in this Vol, M134-R

Pétard pour simuler des tirs de batterie (Fr). Pétard simulating the fire of a battery, used in order to deceive the enemy about the location of gun batteries. Most of these pétards consisted of charges of rifle powder enclosed in wood or cardboard boxes, reinforced with cord or wire
Ref: Pepin Lehalleur (1935), 477

Pétards (ou artifices) pour signaux (Fr). Used during WWI to attract the attention of neighboring troop units or fortifications. The devices consisted of boxes filled with about 400kgs of BlkPdr. They produced a report which could be heard for a distance of 3km, and the smoke produced gave the location of the signalling unit
Ref: Pepin Lehalleur (1935), 477

Petavel Pressure Gauge. See under Closed Bomb or Vessel in Vol **3**, C337-R

Peters' and Lindsley's Explosive. AN 75, nitrated wood fiber 20, and oil of mirbane 4% [USP 953798 (1910) & CA **4**, 1678 (1910)]. Three variations of **Peters' Explosives** are: 1) AN 30, NC 30, K chlorate 30, and oil of mirbane 10% [USP 988590 (1911) & CA **5**, 2179 (1911)]; 2) AN 50, K chlorate 30, oil of mirbane 10, and woodmeal 10% [USP 991232 (1911) & CA **5**, 2332 (1911)]; 3) AN 67, nitrated woodfiber 10–20, Na chloride 20, asphalt soln in MNPh 2, and Ca carbonate 1% [USP 994273 (1911) & CA **5**, 2557 (1911)]

PETN. Acronym for Pentaerythritol Tetranitrate. See under Pentaerythritol and its Derivatives in this Vol

Petragite. An expl invented by Doutrelepont and Schreiber in the 19th century. It contained K nitrate 56.4, Nitromolasses 38.6, and nitrated sawdust 5.0%
Ref: Daniel (1902), 612

Petralite. An expl invented in Hungary in the 19th century by Liesch and Prohaska. It contained K nitrate 64, nitrated sawdust 30, and Amm carbonate 6%
Ref: Daniel (1902), 612

Pétralithe or Pétralite (Fr). An expl submitted to the Commission Francaise des Substances Explosives in 1880: NG 60, K or Na or Amm nitrate 16, charcoal (specially prepd) 16, lignite

6, Ca carbonate 1, and spermaceti 1%. Its manuf was authorized by the Commission
Refs: 1) Commission des Substances Explosives, MP **1**, 459 (1882) 2) Daniel (1902), 612 3) Giua, Trattato **VI** (1) (1959), 345

Petrin. See as Pentaerythritol Trinitrate under Pentaerythritol and its Derivatives in this Vol

Petrin Acrylate (Pentaerythritol Trinitroacrylate, Trinitroxypentaerythritol Acrylate). $C_8H_{11}N_3O_{11}$,

$$CH_2{=}CH{-}CO_2CH_2C(CH_2ONO_2)_3$$

mw 325 (monomer), cryst, OB to CO_2 −54%, mp 78–79°, Q_c 2923cal/g, Q_e 791cal/g. Its principal use is as an ingredient of composite rocket proplnts (see below) (Ref 4)
Prepn. The original synthesis for PETRIN acrylate employed trifluoroacetic anhydride and glac acrylic acid as the acrylation agent for PETRIN. These two materials were charged to a reaction vessel and the initial reaction was controlled by the slow addition of PETRIN at a temp of 10–15°. Following a period of one hour, the batch was drowned in w, pptg the PETRIN acrylate. This solid was sepd by filtn, dissolved in chlf, and neutralized in soln with Na bicarbonate. The product was then crystd during a period of 16 hours at 0° and dried under vac to remove traces of solvent. The yield for this process was about 60%

A significant improvement in yield (to about 74%) and purity (approx 98%) was realized by the substitution of methanol for chlf and crystn of the product from the soln without neutralization, residual acid being removed by washing the filter cake with w

Because of the high cost and hygroscopic nature of trifluoroacetic anhydride, a new process, based on dimethylaniline and acrylyl chloride, was considered. Yields averaged 46% and product purities averaged 93.5% (Refs 2, 3 & 4):

$$HOCH_2C(CH_2NO_3)_3 + CH_2{=}CHCOCl +$$

pentaerythritol trinitrate (PETRIN) — acrylyl chloride

$$C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_2HCl +$$

dimethyl aniline — dimethylaniline hydrochloride

$$(O_2NOCH_2)_3CCH_2O\overset{O}{\overset{\|}{C}}CH{=}CH_2$$

pentaerythritol trinitrate monoacrylate (PETRIN acrylate)

Petrin acrylate proplnts. PETRIN acrylate could be used as a monoproplnt because it has a specific impulse of 214 lb-sec/lb and a burning rate of 0.2 inch/sec. The addition of an oxidizer increases both the impulse and burning rate

A typical compn is as follows:

	Composition NM*
PETRIN acrylate (> 97% purity), %	34.3 (binder)
Triethylene glycol trinitrate, %	11.8 (plasticizer)
Glycol diacrylate, %	2.9 (crosslinker)
Ammonium perchlorate, %	51.0 (oxidizer)
Hydroquinone, %	0.014 (polymerization inhibitor)

*Measured specific impulse 238 lb-sec/lb, at d 1.3g/cc

See also under Pentaerythritol Trinitrate in this Vol
Refs: 1) Anon, "Process for the Manufacture of Pentaerythritol Tetranitrate Monoacrylate and Petrin Acrylate Propellants", Rohm & Haas Co, Redstone Ars, Ala (12 March 1956) 2) R.F. Preckel, USP 3116597 (1964) 3) R.F. Gould, Ed, "Advanced Propellant Chemistry", Advances in Chemistry Series 54, American Chemical Society, Washington, DC (1966), 99–100 4) Anon, "Explosives Series, Properties of Explosives of Military Interest", EngrDesHndb, **AMCP 706-177** (1971), 269–71

Petrofacteurs. Chlorate and perchlorate expls used in Austria before and during WWI. Typical formulations include: 1) MNB 10, Sb sulfide 3, K chlorate 67, and K nitrate 20%; 2) DNB 10, Amm perchlorate 35, Na nitrate 45, sawdust 8, and vaseline 2%
Refs: 1) Daniel (1902), 613 2) Colver (1918), 143

Petroklastit or Haloklastit. Ger expl designed for blasting soft materials such as rock salt, etc. It contained Na nitrate 69, K nitrate 5, S 10, coal tar 15, and K dichromate 1%. It was less sensitive to impact than Blk Pdr, and its strength (as detd by the Trauzl test) was about 145% that of BlkPdr. It was less hygroscopic than BlkPdr, and could be ignited at 350°

Ullmann (Ref 3) gives its compn as: Na nitrate 70, K nitrate 5, tar 15, and S 10%

Refs: 1) Daniel (1902), 612 2) Marshall **1**, 89 (1917) 3) Ullmann **4**, 2nd Ed (1926), 780 4) Stettbacher (1933), 111

Petroleum, Nitrated. The nitration of petroleum generally produces either brown, non-cryst solids or liq products that are expl

The first attempts to nitrate petroleum were made in Russia at the end of the last century by Konovaloff, Walden and others. They used dil nitric acid alone under press, and obtained nitrated products in very low yields. None of these expts was on an industrial scale

Edeleanu and Filiti patented in 1902 (Ref 1) a nitration method using mixed nitric-sulfuric acids. The use of petroleum fractions having a d of 0.87g/cc and bp's between 270–380° was recommended. The hydrocarbons were added gradually to a mixt of the concd acids maintained at a low temp. During the reaction the temp was not allowed to exceed 80°. The most suitable proportions were: for 1p of petroleum fraction, 3p of concd nitric acid, previously mixed with 15p of fuming sulfuric acid. When the nitration was completed, the mixt was diluted with a large vol of cold w. This produced a ppt of the nitrated product, while the un-nitrated oil floated to the top of the acid-w soln. After washing, yields ranged from 30 to 90%, depending on the crude oil used. It was found that more stable products of nitration were obtained when the crude oil was purified prior to distn, by treatment with a small quantity (about 1%) of concd sulfuric acid, followed by washing. The nitrated products proved to be expl, sol in most org solvents, and good gelatinizers for NC. No practical application has been made of this patent

In 1913, A.S. Flexer of Vienna patented a process for the manuf of nitrocompds by the action of concd nitric acid on a mixt of illuminating oil and wood tar. The oily compds thus produced were highly expl (Ref 5)

Freund (Ref 2) nitrated a fraction of Galician petroleum (from Borislaw), bp 270–380°, d 0.858–0.870g/cc (previously purified by treatment with 1% concd sulfuric acid), and obtained a red-brown powder with a N content of about 6.8%

Kharichkov (Ref 3) nitrated some machine and spindle oils, obtained from Russian "mazut" (qv) by moderately warming with concd nitric acid (d 1.50g/cc), and obtained thick, very viscous syrups, sol in benz, which can be used for separating them from the excess oil. By dissolving the nitrated products and pptg with w, he was able to obtain several fractions of varying d and N content. For example, one of the fractions contained N=6.66%, its d was 1.103 g/cc and its mp 52–54°

Many other investigators have nitrated petroleum fractions. These are detailed in Ellis' two vols (Ref 4)

Refs: 1) J. Edeleanu & G. Filiti, GerP 154054 (1902); USP 745802 (1903) 2) M. Freund, ZAngChem **25**, 1058–9 (1912) & CA **6**, 2520 (1912) 3) K. Kharichkov, SS **8**, 319 (1913) & CA **7**, 3831–2 (1913) 4) C. Ellis, "Chemistry of Petroleum Derivatives", Vol **1**, 1052–54 (1934), Vol **2**, 1097–99 (1937), Reinhold, NY 5) Colver (1938), 27

Petrolit. An old (1876) Dynamite contg NG 60, K or Na nitrate 16, carbon 16, sawdust 6, cetyl palmitate 1, and Na carbonate 1% (Ref 2)

The same name was applied to a Ger chlorate expl introduced during WWI. It consisted of K chlorate, nitrocompds, kerosene, and neutral salts, and was considered a dangerous mixt (Ref 1)

Refs: 1) Marshall, Dict (1920), 74 2) A. Pérez Ara (1945), 331

Petronel (Poitrinale). See under Bullets in Vol **2**, B324-R

Pettingell. A powder, patented in Engl in 1895, contg crude saltpeter 63, coal dust 20, crude S

15, and wood flour 2%. It was prepd by adding, with agitation, the required amt of coal dust to a hot satd soln of saltpeter. After the w was evapd by heating, S was added and thoroughly blended and then, finally, the wood flour
Ref: Daniel (1902), 613–14

Pettman Cement. Pettman Cement (PC) is described briefly in Vol **2**, C126-R. This water-repellant cement originally consisted of methylated spirit, Stockholm tar, Venetian red, and shellac. It was used as an adhesive in making flares and signals and is mentioned in an early BritP (Ref 1)

In the USA, PC is used in the loading and assembly of ammo as a fastener to secure both threaded and unthreaded parts, such as booster cups and joints. Accdg to Ohart (Ref 5), upon drying, PC "sets up", becoming hard and making a reliable joint. Shellac is used to coat cavities to be loaded with BlkPdr such as delay element cavities and time train ring grooves

Shellac (described in Vol **6**, G187-L under Gum Lac) became a strategic material during WWII, and a mixt of rosin and ethyl cellulose was substituted for it. The modified cement possesses drying time and waterproofing props similar to those of the original PC (Refs 2 & 3)

Two types of PC exist for mil purposes. Type A PC is prepd by mixing pine tar and alc, adding shellac and stirring well. After the mixt has been allowed to stand for about 20 hrs, it is stirred thoroughly and iron oxide is added in small portions until a product of uniform consistency is obtd

Type B, a modified PC, is prepd by mixing alc and ethyl cellulose until a clear soln is obtd, then adding rosin and mixing until it is dispersed. The pine tar is then added with thorough stirring. Finally, iron oxide is added in small portions with continuing stirring until uniform consistency is obtained

The automated inspection for deposition of the solids content of PC is a critical operation in the manufg process of various munition items. Electrical continuity techniques have been used to determine the extent of deposition with standing time (Ref 9). New techniques have also been developed to stabilize PC used for coating proplnt grains in rocket motors. These techniques gave a homogeneous mixt of the cement maintainable over considerable time periods, resulting in increased item reliability and safety (Ref 8). Many adhesive systems, including several commercial paints have been suggested as possible replacements for PC (Ref 8)

US Mil Spec **JAN-C-99** (Ref 4) contains the requirements for each ingredient of PC, including a viscosity test for the finished PC as well as std tests for the ingredient under several Fed Specs. However, some of these Fed Specs are outdated and are currently being replaced. A recent PATR (Ref 8) made recommendations to update **JAN-C-99**

The present US Mil formulations for PC are (Ref 4):

	Type A (PC)	Type B (modified PC)
Iron oxide[(a)], %	50 ± 3	33 ± 2
Alcohol[(b)], %	20 ± 2	19 ± 2
Shellac[(c)], %	18 ± 2	–
Pine tar[(d)], %	12 ± 1.5	17 ± 2
Rosin[(e)], %	–	30 ± 2
Ethyl cellulose[(f)], %	–	1 ± 0.5

(a) Over 96.5% shall be 44 microns in particle size, detd gravimetrically by burning off the combustible material
(b) Grade 2 alc or a mixt of ethyl and methyl alcs; shall cont a mixt of 5% methanol and no benz; detd by wt loss after drying at 75° for 6 hrs for Type A and 2 hrs for Type B
(c) Detd by wt of residue from repeated extrn with carbon tetrachloride
(d) Type A, subtract from 100 the sum of a, b and c
(d), (e) & (f) Type B, subtract from 100 the sum of a and b

Written by **H. T. LEE**[A]

Refs: 1) H. Holt, BritP 131324 (1918) & CA **14**, 125 (1920) 2) A. Phillips, "Substitute for Shellac in Pettman Cement", PATR **1196** (1942) 3) J. Rubin, "Substitute for Shellac In Pettman Cement", PATR **1251** (1943) 4) Anon, "Pettman Cement", **JAN-C-99** (1945) 5) Ohart (1946), 14 6) I. Katz, "Adhesive Materials", Foster, Long Beach, Calif (1973), 130 7) C.V. Cagle, "Handbook of Adhesive Bonding", McGraw-Hill, NY (1973), 33–4

8) S.C. Dollman & S.M. Kaye, "Techniques for the Stabilization of Pettman Cement", (Dist. Limited), PATR **4489** (1973) 9) J. Remier et al, "An Investigation into the Feasibility of Automated Inspection for the Presence of Pettman Cement", PATM **2196** (1975)

PETX. Code name for Tetrakis(nitramino-methyl)-methane or Pentaerythrityltetrakis(nitramine) (qv in this Vol)

Peyton Powder. According to Daniel (Ref 1), this was a smokeless powder patented in Engl in 1895 and later manufd in the USA by the California Powder Co. It contd a jelly consisting of 40p of NC and 38p of NG (acet was used as solvent), blended with 22p of other oxidizer ingredients

According to Colver (Ref 2), the compn of one of the Peyton powders was NC (sol) 40, NG 40, and Amm Picrate 20%

Refs: 1) Daniel (1902), 614 2) Colver (1938), 341

P Gunpowder. One of the varieties of Pebble Powder (Poudre cailloux in Fr) manufd in Engl beginning 1865. It contained 176 grains per kg. Another variety, called **P2 Gunpowder**, containing 15 to 16 grains per kg, was used in larger cal guns. See also under "P" (Pebble Powder) in this Vol

Ref: J.P. Cundill, "A Dictionary of Explosives", Mackay & Co, London (1889)

PGX. Code name for 1,5-Dinitro-3-methyl-3-methylenenitramine-1,5-diazapentane

P.H.E. (Plastic High Explosive). Developed during WWII by the Brit for demolition purposes. It was a putty-like brownish material consisting of RDX 88, oil 11.6 and lecithin 0.6%, and had a d of ca 1.5g/cc. Lecithin was added to prevent the formation of large RDX crystals on prolonged storage. See also Composition C Type Explosives in Vol **3**, C484-L to C488-R

Ref: Anon, "Allied and Enemy Explosives", Aberdeen Proving Ground (1946), 125

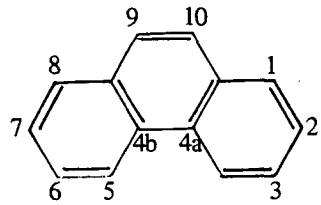
Phenacyl Azide. See w-Azidoacetophenone in Vol **1**, A47-R

Phenacyl-3,5-Dinitrosalicylate. $C_6H_5.CO.CH_2.O_2C.C_6H_2(OH)(NO_2)_2$, mw 346.25, N 8.1%, OB to CO_2 −124.76%. Was prepd in 1931 and found to be a powerful expl

Ref: Ko-Chung Chen, TransSciSocChina **7**, 73–80 (1931) & CA **26**, 49 (1932)

PHENANTHRENE AND DERIVATIVES

Phenanthrene (o-Diphenylenediethylene).



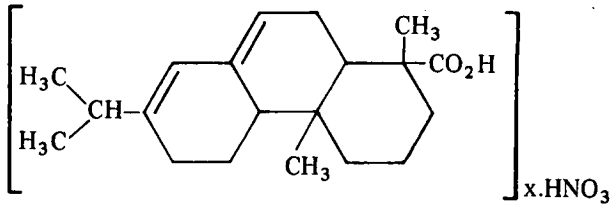
mw 178.22; colorl plates from alcohol; mp 100°; bp 340°. Obtd by fractional distn of high-boiling coal tar oils with subsequent extrn from alc (Ref 1)

Under hyper-pressure conditions combined with shearing stress, Gonickberg et al, in 1968, observed expl behavior by both phenanthrene and perylene at pressures in excess of 50 kilobars (Ref 14), far above any practical value for munitions use. Much earlier, Spica proposed the addition of 2.5% of phenanthrene as a stabilizing and anti-corrosion agent for both NG and NC smokeless powders (Ref 5). Subsequently, Tonegutti found that the stabilizing properties of phenanthrene for NG were intermediate between those of diethylphenylurea (Centralite) and asym-diphenylurea (Acardite) using the test methods of Taliani and Thomas (Ref 8). DeMent has applied for a patent for the use of phenanthrene as a fluorescing agent in smoke used for military signaling (Ref 9)

Phenanthrene Diozonide. $C_{14}H_{10}2O_3$. Harries and Weiss in 1905 reported that the ozonolysis of phenanthrene in chlf soln produced a crystn, expl diozonide (Refs 2 & 4). Subsequently, very detailed studies of the ozonolysis reaction of phenanthrene by three different groups of investigators failed to confirm the existence

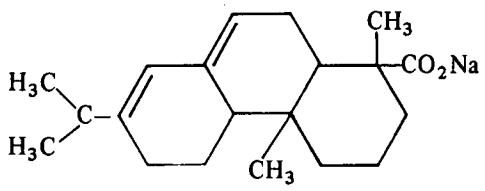
either of a diozonide, or of any products of this reaction that would explode under heating, friction or impact (Refs 10, 11, 12 & 13)

1,2,3,4,4a,4b,5,6,10,10a Decahydro-1, 4a-Dimethyl-7-(1-Methylethyl)-Phenanthrene-1-Carboxylic Acid Polynitrate (Abietic Acid Polynitrate).



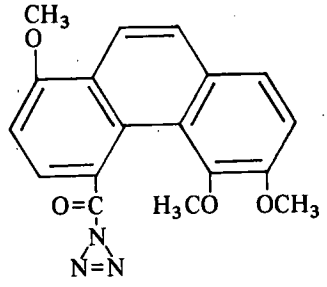
Yellow, amorph solid which explds on heating (Ref 6)

Sodium-1,2,3,4a,4b,5,6,10,10a Decahydro-1,4a-Dimethyl-7-(1-Methylethyl) Phenanthrene-1-Carboxylate (Sodium Abietate).



It has been patented as a 0.1% coatant for aluminum used in expl slurries to improve detonation sensitivity (Refs 3 & 15)

3,4,8-Trimethoxyphenanthrene-5-carboxylic acid azide.



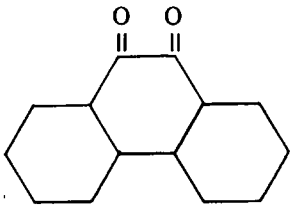
mw 286.17, N 14.68%, OB to CO_2 −159%; decomps at 65° (heated slowly) but explds at 80° when immersed in a bath at that temp (Ref 7)

Numerous molecular compds of phenanthrene and its derivatives have been reported with perchloric acid, PA, styphnic acid, sym-TNT, sym-TNB, and Tetryl. These compds are useful for identification purposes because many have sharp melting points but none have been reported to be expl

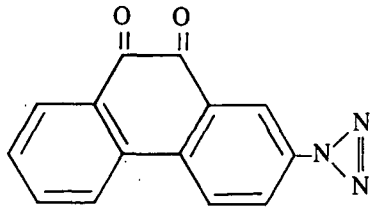
Refs: 1) Beil **5**, 667, (327) & [527] 2) Beil **5**, 670 3) Beil **9**, (428) 4) C. Harries & V. Weiss, Ann **343** (1905) 5) G. Spica, SS **7**, 129 (1913) & CA **7**, 700 (1913) 6) J. Dubourg, BullInstPin **41**, 241 (1927) & CA **22**, 593 (1928) 7) J.M. Gulland & C.J. Vieden, JCS **1928**, 921 & CA **22**, 2567 (1928) 8) M. Tonegutti, AttiVCongrNazlChimPuraApplicata, Rome **1935** Pt II, 899 (1936) & CA **31**, 8198 (1937) 9) J. DeMent, USPAppl 175883, OfficialGazette **668**, 540 (1953) & CA **47**, 11604 (1953) 10) W.J. Schmitt, E.J. Moriconi & W.F. O'Connor, JACS **77**, 5640 (1955) & CA **50**, 6413 (1956) 11) P.S. Bailey, JACS **78**, 3811 (1956) & CA **51**, 339 (1957) 12) P.S. Bailey & S.B. Maintha, JOrgChem **21**, 1335 (1956) & CA **51**, 17865 (1957) 13) J.P. Wibant & Th.J. DeBoer, Rec **78**, 183 (1959) & CA **53**, 19994 (1959) 14) M.G. Gonickberg et al, IsvAkadNaukSSSRSerKhim **1968** (3), 486 & CA **69**, 8034 (1968) 15) R. Fox & D.H. Gilbert, GerP 2335317 (1974) & CA **81**, 144 (1974)

9,10 Phenanthrenequinone and Derivatives

9,10-Phenanthrenequinone (9,10-Dioxophenanthrenedihydride-9,10). Mw 208.2; orange needles; mp 209°, sublimes above 360° to give orange-red plates. Obtd from phenanthrene by chromic acid oxidn in acetic acid (Ref 1)

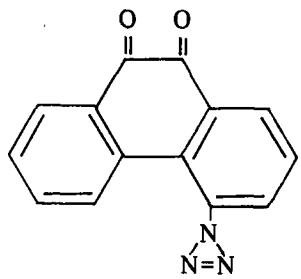


2-Azidophenanthrenequinone.



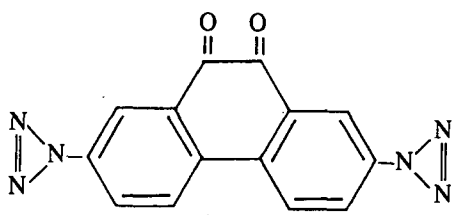
mw 249.14, N 16.86%, OB to CO_2 −189%; cinnabar-red, or sometimes, copper-bronze colored leaflets. When heated dry in a test tube it at first darkens at 175°, melts at 186°, then on further heating, during emission of a thick brown smoke, in addition to exploding it deposits a brown sublimate in the cold parts of the tube (Refs 3 & 7)

4-Azidophenanthrenequinone.



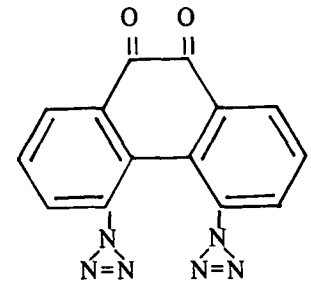
mw 249.14, N 16.86%, OB to CO_2 −189%, garnet-red, irregularly star-shaped crysts that on heating expld before melting (Refs 4 & 8)

Phenanthrenequinone-2,7-diazide.



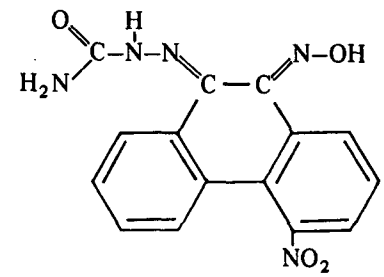
mw 290.22, N 28.96%, OB to CO_2 −149%, brown crysts, mp 248° with expln. When mixed with concd sulfuric acid it explds, deflagrating with incandescence and emission of a thick brown smoke. It is stable to impact (Refs 5 & 9)

Phenanthrenequinone-4,5-diazide.



mw 290.22, N 28.96%, OB to CO_2 −149%, mp 160°, on further heating it explds. It dissolves in concd sulfuric acid with the emission of nitrogen, but without violent decompn (Refs 5 & 9)

4-Nitrophenanthrenequinonemonoxime mono semi carbazone.



mw 325.27, N 21.53%, OB to CO_2 −155%, yellowish-green cryst powd, mp 240° (dec). Schmidt et al observed that, "When one heats somewhat larger amounts of this preparation a lively detonation occurs. This was, for example, the case when the carbon and hydrogen determination by combustion of the substance in a little boat was carried out in the usual way. The detonation was so forceful that the cupric oxide was shot out of the combustion tube. Because of the all-too-great danger accompanying a repetition of the intended combustion, we had to be satisfied to determine the nitrogen content of the compound. To this end a suitably small amount of the substance was mixed with a suitably larger charge of copper oxide and then the Dumas nitrogen determination was carried out in a long combustion tube. Handled in this way the substance was completely decomposed, slowly, without any danger." (Refs 2 & 6).

The foregoing quotation points out that the publication of routine elemental analytical combustion results can serve to separate stable compds from those that expld before pyrolyzing

Written by **D. J. VEAL**

Refs: 1) Beil **7**, 796, (416) & [724] 2) Beil **7**, 419 3) Beil **7**, (730) 4) Beil **7**, (731) 5) Beil **7**, (731) 6) J. Schmidt, O. Schairer & E. Glatz, Ber **44**, 276 (1911) & CA **5**, 1445 (1911) 7) K. Brass, E. Ferber & J. Stadler, Ber **57**, 121 (1924) & CA **18**, 2156 (1924) 8) K. Brass & J. Stadler, Ber **57**, 128 (1924) & CA **18**, 2156 (1924) 9) K. Brass & G. Nickel, Ber **58**, 204 (1925) & CA **19**, 1569 (1925)

Phenetedines. See under Aminophenetoles and Derivatives in Vol **1**, A240-R

Phenetole And Its Derivatives

Phenetole (Ethylphenylether, Phenylethylether). $C_6H_5OC_2H_5$, mw 122.16, oily liq, mp −30°, bp 171–73°, d(20/4°) 0.967g/cc, RI 1.507. Practically insol in w, freely sol in alc, ether. Can be prepd from phenol or its salts by the use of the following ethylating agents: ethyl chloride, ethyl bromide, ethyl p-toluenesulfate, dimethyl sulfate or triethyl phosphate. Combustible. On nitration it yields products which are suitable for use in expl compns

Refs: 1) Beil **6**, 140, (80) & [142] 2) Merck (1968), 807 3) CondChemDict (1971), 676

Mononitrophenetoles. $C_2H_5OC_6H_4NO_2$, mw 167.17, N 8.4%, OB to CO_2 −167.5%

o-Mononitrophenetole. Yellowish oily liq, mp 2.1°; bp 267–8° at 757mm, 275° at 760mm; d 1.1903g/cc at 15°; RI 1.5425 at 20°. Nearly insol in w, sol in alc and eth. Q_C^V 1021kcal/mole

Refs: 1) Beil **6**, 218, (114) & [210] 2) F. Swarts, Rec **33**, 288 (1914) 3) H.E. Fierz-David, H. Edward & L. Blangey, "Grundlegende Operationen der Farbenchemie", Springer, Vienna (1943)

m-Mononitrophenetole. Light yel crysts, mp 36°, bp 284° decomp, Q_C^V 1009.4kcal/mole

Refs: 1) Beil **6**, 224, (117) & [214] 2) F. Swarts, Rec **33**, 288 (1914) 3) J. Whiston, JSCI **43**, 369T (1924)

p-Mononitrophenetole. Colorl prisms; mp 58–60°; bp 283°; d 1.18g/cc at 15°, 1.1416 at 75°; can be prepd by ethylation of p-nitrophenol with ethyl chloride. Nearly insol in w; easily sol in eth, hot alc or hot petr eth; difficultly sol in cold alc or cold petr eth. Q_C^V 1006.1 kcal/mole

Refs: 1) Beil **6**, 231, (119) & [221] 2) F. Swarts, Rec **33**, 289 (1914) 3) H.E. Fierz-David, H. Edward & L. Blangey, "Grundlegende Operationen der Farbenchemie", Springer, Vienna (1943) 4) CondChemDict (1971), 624

Dinitrophenetoles. $C_2H_5OC_6H_3(NO_2)_2$, mw 212.16, N 13.2%, OB to CO_2 −113.1%

2,3-Dinitrophenetole. Light yel leaflets from alc, mp 101°. Was prepd by Blanksma (Ref 2) by the deammination of 2,3-dinitro-4-aminophenetole

Refs: 1) Beil **6**, 251 2) J.J. Blanksma, Rec **27**, 50 (1908)

2,4-Dinitrophenetole. Colorl leaflets from dil alc; needles from w or alc; mp 86–7° subl, decomps at higher temps. Can be prepd by the nitration of phenetole with fuming nitric acid or by other methods given in Ref 1. Desvergnes (Ref 3) gives a detailed description of its lab scale prepn. The Japanese (Ref 4) prepd it on a large scale by the reaction of dinitrochlorobenzene with alc NaOH:

$(O_2N)_2C_6H_3Cl + NaOH + C_2H_5OH \rightarrow (O_2N)_2C_6H_3OC_2H_5 + NaCl + H_2O$

The resulting dinitrocompd was used for the prepn of the trinitrocompd (see below), used to some extent as a military expl

Refs: 1) Beil **6**, 254, (126) & [242] 2) A. Cahours, AnnChim(Paris) [3], **27**, 465 (1849) 3) L. Desvergnes, MP **19**, 285–90 (1922); MonitScientQuesneville [5], **14**, 254 (1924) 4) Anon, PB Rept No 50394 (1946), 28–30

2,5-Dinitrophenetole. Crysts, mp 96–98°; was prepd by deammination of 2,5-dinitro-4-aminophenetole

Refs: 1) Beil **6**, [245] 2) F. Reverdin & H. Roethlisberger, Helv **5**, 303 (1922)

2,6-Dinitrophenetole. Colorl needles, mp 57–8°; was prepd by treating Ag 2,6-dinitrophenetole with ethyl iodide, or by other methods detailed in the ref

Ref: Beil **6**, 257 & (127)

3,5-Dinitrophenetole. Colorl crysts from alc; mp 96–7°; was prepd in small yield from Na ethylate and 1,3,5-TNB

Ref: Beil **6**, 258

Trinitrophenetoles. $C_2H_5OC_6H_2(NO_2)_3$, mw 257.0, N 16.3%, OB to CO_2 –77.8%

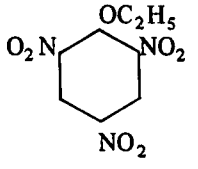
2,3,4-Trinitrophenetole. Colorl crysts from alc; mp 117°; can be prepd by nitrating 2,3-dinitrophenetole with mixed nitric-sulfuric acid

Refs: 1) Beil **6**, 264 2) J.J. Blanksma, Rec **27**, 49–51 (1908)

2,3,5-Trinitrophenetole. Light yel crysts; mp 80°; can be prepd by nitrating 3,5-dinitrophenetole with mixed nitric (d 1.44g/cc) and concd sulfuric acids

Refs: 1) Beil **6**, 264 2) J.J. Blanksma, Rec **24**, 41 (1905)

2,4,6-Trinitrophenetole (TnPht; Ethyl Picrate; Aethyl-[2,4,6-trinitrophenyl]-ather, Pikrinsaureaethylather or Aethylpikrat in Ger; Keineyaku or Keyneyaku in Japanese).



$C_8H_7N_3O_7$, $(O_2N)_3C_6H_2OC_2H_5$, mw 257.16, N 16.3%, OB to CO_2 –77.8%, yellowish crysts, mp 78–80°, Q_C^v 936kcal/mole

TnPht can be prepd by nitration of 2,4-dinitrophenetole or by other methods given in Refs 1 & 10. Desvergnes (Ref 4) gives a detailed procedure for its lab prepn:

Dissolve 53g of 2,4-dinitrophenetole in 175g of concd sulfuric acid with agitation. Add 62% nitric acid so that the temp rises rapidly to 30°. Continue the addition, while maintaining the temp between 30–40° (by cooling), until a total of 40.75g of nitric acid has been added. Pour the resulting yellow slurry into about 1500ℓ of cold w, filter and wash the crysts with cold w and dry. This method yielded 61.8g of product, 96% of theoretical, mp 78.5°

Nitration on an industrial scale at "la Poudrerie de Bouchet" gave a product with mp 76–77° in 78% yield. The Japanese manufd it as a mil expl by nitrating 2,4-dinitrophenetole (Ref 9)

The solubility of TNPht in grams per 100g of various solvents was detd by Desvergnes (Ref 4, pp 255–6), and are given below in rounded figures:

Water. 0.013 at 15°, 0.044 at 50° and 0.354 at 100°. TNPht is slowly saponified by hot w with the formation of iso-Picric Acid, in a manner similar to the saponification of 2,4,6-Trinitroanisole

	Temp 15°	50°
Ethyl Acetate	36.53	185.2
Acetone	120.3	410.5
Ethanol (96%)	1.20	7.82
Ethanol (abs)	1.67	9.32
Methanol	3.99	24.0
Benzene	49.2	297.3
Chloroform	20.79	174.7
Ether	3.79	7.66 at 33.5°
Pyridine	185.3	327.9
Carbon Disulfide	0.43	1.69
Carbon Tetrachloride	0.667	6.43
Toluene	30.8	163

Explosive Properties. 2,4,6-TNPht is an expl, almost as powerful as TNT and slightly less powerful as PA (as detd by the Trauzl test). Its rate of detonation, as detd by the Dautriche method, was about the same as that of TNT (6880m/sec). Its sensitivity to impact, as detd in Fr, was considerably lower than for PA, but according to tests conducted in Engl, TNPht was more sensitive than PA (Ref 8). When pellets of TNPht (d 0.25g/cc) were fired in a manometric bomb, the pressure developed was 2490kg/sq cm, as against 3230 for PA

When used as a booster in a 75mm shell loaded with "Schneiderite", the TNPht gave the same performance as cryst TNT

Uses. The possibility of using TNPht as a bursting charge in projectiles was studied in Fr as early as 1917. Several mixts contg TNPht were prepd and tested, eg: 1) TNPht 30, PA 70%; 2) TNPht 70, Na nitrate 30%; and 3) TNPht 60, AN 40%. The third compn was loaded into shells at d 1.5 to 1.6g/cc, and gave very good fragmentation results. It was about as sensitive to impact as PA, and the pressure developed in a manometric bomb at a loading d of 0.25g/cc was 2741kg/sq cm vs 3230 for PA

The Japanese used TNPht during WWII for cast loading some of their projectiles, and considered it a suitable substitute for TNT, which was then on the critical list because of a shortage of toluene (Ref 9)

Note: According to Brady and Horton (Ref 6), TNPht forms an unstable addition compd with 2,4,6-Trinitroanisole (TNAns) consisting of 2 moles of TNPht and 3 moles of TNAns. The mp of this compd is about 40°

When a satd soln of TNPht in pyridine is cooled, orange crysts corresponding to the compd $C_6H_2(OH)(NO_2)_3.2C_5H_5N$ are deposited, mp 84.5 to 85.5°. When heated to a higher temp, the crysts deflagrate (Ref 4, p 257)

Refs: 1) Beil **6**, 264, 290, (140) & [281] 2) P. Austen, Ber **8**, 666 (1875) 3) M. Marqueyrol et al, BullFr [4], **27**, 106 (1920) 4) L. Desvergnes, MP **19**, 269 & 291–99 (1922) & CA **17**, 469 (1923) 5) Ibid, MonitScient-Quesneville [5], **14**, 254–7 (1924) 6) O.L. Brady & H.V. Horton, JCS **127**, 2230–33 (1925) 7) Davis (1943), 172 8) Blatt, OSRD **2014** (1944) 9) PB Rept No 50394 (1946), 28–30 10) J. Vaganay & L. Molard, MP **40**, 19–45 (1958)

2,3,5,6-Tetranitrophenetole. $(O_2N)_4C_6HOC_2H_5$, mw 302.18, N 18.5%, OB to CO_2 −52.9%, light yel crysts from alc, mp 115°. Can be prepd by heating a mixt of 3,5-dinitrophenetole, concd nitric and concd sulfuric acids on a w bath. It can also be prepd by the nitration of 2,3,5-Trinitrophenetole. It is an expl, and was patented in Ger during WWI (Ref 3) for use in initiating compns

Refs: 1) Beil **6**, 293 & (142) 2) J.J. Blanksma, Rec **24**, 42 (1905) 3) C. Claessen, GerP 288655 (1915); ChemZtr **1916**, I, 240

Phenixsprengstoffe. Mining expls patented in 1899 by the Sprengstoffwerke Dr Nahnsen & Co in Hamburg, Ger. Five typical compns are shown in Table 1:

Table 1

	Composition %				
Ingredients	1	2	3	4	5
NG	25	25	30	30	30
K nitrate	34	–	–	–	–
Na nitrate	1	35	32	30	32
Sawdust	40	–	38	–	–
Rye flour	–	40	–	40	38

Composition No 5 had a Q_e of 780cal/g and an expln temp of 2125°

Refs: 1) Daniel (1902), 449 2) Gody (1907), 715 3) PATR **2510** (1958), Ger 130-R

PHENOL AND ITS DERIVATIVES

Phenol (Carbolic, phenic or phenylic acid; Hydroxybenzene; Oxybenzene). C_6H_5OH, mw 94.11; white, cryst mass or colorl, acicular crysts which turn pink or red if not perfectly pure or if under the influence of light; absorbs w from the air and liquifies; distinctive odor; sharp burning taste; mp 42–43°; bp 182°; flash pt 79°; d 1.071g/cc; combustible, autoignition temp 1319°F. Sol in alc, w, eth, chlf, glycerol, CS_2, petrolatum, fixed or volatile oils and alkalies. Obtained from coal tar, or made by fusing Na benzene sulfonate with NaOH, or by heating monochlorobenzene with aq NaOH under high press. The cryst article of commerce contains at least 98% phenol. Modern manuf processes are described in detail in Ref 2. Highly toxic by ingestion, inhalation and skin absorption. Strong irritant to tissue. Tolerance 5ppm in air (Refs 3 & 4)

Phenol has been used as a starting material for the prepn of such expls as Dinitrophenol, Trinitrophenol and Picric Acid (PA). Although the prepn of PA from phenol is no longer practiced in the USA, it was used as late as WWII in Engl, Fr, Ger, Italy, Japan and the USSR

Analyses and tests for phenol are given in Ref 1, 134–36, (77) & [135–137]

Refs: 1) Beil **6**, 110–137, (70–79) & [116–139] 2) A. Dierichs & R. Kübicka, "Phenole und Basen, Verkommen und Gewinning", AkademieVerlag, Berlin (1958) 3) Merck (1968), 810-L 4) CondChemDict (1971), 676-R

2-Azidophenol (Phenol azide, o-Hydroxyphenylazoimide, o-Oxydiazobenzolimid). $N_3.C_6H_4.OH$, mw 135.12, N 31.10%, OB to CO_2 −159.9%; colorl crysts with 1/3 H_2O from w; mp, darkens and decomps at 120–130°; bp, detonates violently at 140–150°. Sol in alc, AcOH, acet and ethyl acet; difficulty sol in w, chlf and petr eth. Can be prepd by acidifying its Na salt (see below) as described by Forster and Fierz (Refs 1 & 2). It is an expl compd and forms many salts, some of which are expl. For example:

Sodium Azidophenolate. $N_3.C_6H_4.ONa$, mw 157.11, N 26.75%, OB to CO_2 −132.4%, colorl crysts. Can be prepd by diazotizing o-aminophenol with Na nitrite, adding hydroxylamine hydrochloride, followed by pouring the mixt into ice-cooled Na carbonate;

$$C_6H_4(OH).NH_2 \xrightarrow[HCl]{NaNO_2} C_6H_4(OH).N_2OH \xrightarrow{NH_2OH.HCl} C_6H_4(OH).N_3$$

$$2C_6H_4(OH).N_3+Na_2CO_3 \rightarrow 2C_6H_4(ONa).N_3+CO_2+H_2O$$

Na azidophenolate explds with considerable violence when heated. The corresponding K salt only chars when treated under similar conditions. The K, Pb and Ag salts were also prepd by Forster and Fierz (Ref 2, 1356–7), but were not investigated from the point of view of their explosibility

Refs: 1) Beil **6**, 293–4 2) M.O. Forster & H.E. Fierz, JCS **91**, 1352–7 (1907)

2-Azido-4,6-Dinitrophenol (4,6-Dinitrophenol azide, 1-Hydroxy-4,6-dinitrophenylazide). $(HO).N_3.C_6H_2(NO_2)_2$, mw 225.12, N 31.11%, OB to CO_2 −60.4%. Certain metallic expl salts of this compd have been proposed by J.D. McNutt for use in the manuf of primer mixts:

Lead Dinitroazidophenolate. $Pb[O.N_3.C_6H_2.(NO_2)_2]_2$. This was prepd by the reaction between diazodinitrophenol, Na azide and Pb nitrate (Refs 1 & 3). By employing this material, McNutt claimed that MF can be eliminated, thus providing non-mercuric priming mixts. Although its impact and friction sensitivity is approx that of MF, smaller percentages of Lead Dinitroazidophenolate than that of MF can be employed because of its lower d and greater ability to propagate flame. Its brisance is between that of MF and Pb Azide, and it is very stable and compatible with most common ingredients of priming mixts suitable for small arms ammo, commercial detonators, artillery ammo, etc. The following examples of priming mixts are given by McNutt (Ref 1): 1) Pb Dinitroazidophenolate (PbDNAzP) 15, Ba nitrate 30, Pb dioxide 25, Sb silicide 18, Ca silicide 6, & Trinitroresorcinol 6%; 2) PbDNAzP 15, Ba nitrate 25, Pb dioxide 12, Diazodinitrophenol 17, Trinitroresorcinol 8, ground glass 22, & gum arabic 1%

The same investigator (Ref 3) proposed the following primer mixts for small arms ammo: 1) PbDNAzP 13, Basic Pb Styphnate 27, double salt of K and Ba nitrate 30, Sb silicide 7, & ground glass 23%; 2) PbDNAzP 8, Basic Pb Styphnate 22, double salt of K and Ba nitrate 40, Sb silicide 23, & Ca silicide 7%

In other primer mixts, McNutt proposed (Ref 2): 1) PbDNAzP 15–20, Ag salt of Tetrazene 7–12, Ba nitrate 17–35, Pb dioxide 10–25, Sb silicide 15–25, & Ca silicide 0–10%; 2) PbDNAzP 15–25, Ag salt of Tetrazene 15–25, Pb dinitroxybenzoic acid 8–15, Ba nitrate 15–25, Pb dioxide 5–10, & ground glass 20–25%

Refs: 1) J.D. McNutt, USP 1906394 (1933) & CA **27**, 3612 (1933) 2) Ibid, USP 1930653 (1933) & CA **28**, 328 (1934) 3) Ibid, USP 2002960 (1935) 4) Blatt, OSRD **2014** (1944)

Potassium Dinitroazidophenolate (called Potassium Dinitrophenylazide by McNutt). $KO.N_3.C_6H_2(NO_2)_2$. It was proposed as an ingredient of primer mixts suitable for small srms and artillery ammo, commercial blasting caps, etc. Typical mixts suggested were: 1) K Dinitroazidophenolate 16, Basic Pb Styphnate 15, Ba nitrate 40, & Sb silicide 29%; 2) K Dinitroazidophenolate 17, Basic Pb Styphnate 18, Ba nitrate 35, Pb thiocyanide 5, & ground glass 25%

Ref: J.D. McNutt, USP 2005197 (1935) & CA **29**, 5274 (1935)

Sodium Dinitroazidophenolate (called Sodium Dinitrophenylazide by McNutt). $NaO.N_3.C_6H_2(NO_2)_2$. Prepd from diazodinitrophenol and Na azide as an intermediate in the prepn of Pb Dinitroazidophenolate, which is obtained on addition of Pb nitrate to the Na salt (see above). No mention is made in the ref about using this salt in expl mixts

Ref: J.D. McNutt, USP 1930653 (1933) & CA **28**, 328 (1934)

Mononitrophenols. $O_2N.C_6H_4.OH$, mw 139.11, N 10.07%, OB to CO_2 −133.17%. Three isomers are possible but only two (o- and p-) are obtained by direct nitration. The nitration of phenol is much easier than that of aromatic hydrocarbons such as benz or toluene

Ortho-(or 2-) Mononitrophenol. Yel needles or prisms, mp 44–45°, bp 214–16°, d 1.495g/cc. Prepd by the action of dil nitric acid on phenol at low temp; some p-compd is formed at the same time; the o-form is sepd by steam distn. Sl sol in cold w; freely sol in hot w, alc, benz, eth, CS_2 and alkali hydroxides. Highly toxic by ingestion and inhalation. Forms salts, of which the Pb salt explds mildly when heated rapidly (Ref 1, [209])
Refs: 1) Beil **6**, 213–17, (113–114), [205–09] & {794} 2) Colver (1938), 282–4
3) Merck (1968), 741-L 4) CondChemDict (1971), 624-R

Meta-(or 3-) Mononitrophenol. Monoclinic prisms from eth or dil HCl; mp 97°; bp 194° at 70mm, decomps when distd at ordinary pressure; d 1.485g/cc at 20°, 1.2797 at 100°. Does not volatilize with steam; cannot be prepd by the nitration of phenol. Can be obtained by boiling diazotized m-nitroaniline with w and sulfuric acid (Ref 3). Sl sol in w, sol in alc. Highly toxic by ingestion and inhalation
Refs: 1) Beil **6**, 222–24, (116), [212–14] & {805} 2) Colver (1938), 282–4
3) Merck (1968), 741-L 4) CondChemDict (1971), 624-R

Para-(or 4-) Mononitrophenol. Yellowish monocl prismatic crysts; mp 113–14°; bp 279° decompn; d 1.479–1.495 at 20°. Can be prepd from p-chloronitrobenzene. Sol in hot w, alc & eth. Most toxic of the three isomers by ingestion and inhalation
Refs: 1) Beil **6**, 226–30, (117–19), [215–20] & {811} 2) Colver (1938), 232 3) Merck (1968), 741-L 4) CondChemDict (1971), 624-R

Commercial Mononitrophenol. Yel cryst mass; mp about 45°; mostly ortho- with some para-nitrophenol. Can be prepd by the nitration of phenol with dil nitric acid (1:3) at a temp below 35° (see Ref, p 283). Although it does not possess expl properties and does not gelatinize NC, it has been used as the fuel component of some commercial expls. It forms salts, some of which are weak expls which were used in expl compns, for example, **Voight Explosives** (qv)
Ref: Colver (1938), 283–4 & 286

Dinitrophenols. $(O_2N)_2.C_6H_3.OH$, mw 184.11, N 15.22%, OB to CO_2 −78.30%. Six isomers are possible, and all are expl. The most important one is 2,4-Dinitrophenol, which has been used as a component of various expl mixts. The expl properties of 2,5- and 2,6-Dinitrophenol have also been examined

2,3-Dinitrophenol. Yel needles from w or thick crysts from alc; mp 144–5°; d 1.681 at 20°. Can be prepd by the nitration of m-nitrophenol, with 2,5- and 3,4-Dinitrophenols being formed simultaneously. Very easily sol in eth and hot alc
Ref: Beil **6**, 251, (125), [239] & {854}

2,4-(or alpha-) Dinitrophenol. Yel orthorhombic crysts from w, leaflets from alc; mp 112–14°; bp (decomp); d 1.683g/cc at 24°, 1.4829 at 72.5/4°. Sublimes when carefully heated; volatile with steam. Can be prepd by the nitration of phenol, but this method is not considered commercially practicable because of partial decompn of the phenolic ring. A better method is by hydrolysis under pressure of 2,4-dinitrochlorobenzene, which in turn can be obtained by nitrating chlorobenzene. Other methods are given in Ref 1

Its solubility in various solvents was detd by Desvergnes, RevChimInd **36**, 196 (1927), and are given in Ref 1, p [240] in g/100g of solvent at the temps listed:

Solvent	15°	34°	34.5°	50°
Ethyl acetate	15.5	–	–	39.5
Acetone	35.9	–	–	98.3
Methanol	5.0	–	–	16.9
96% alcohol	3.0	–	–	11.7
Abs alcohol	3.8	–	–	13.3
Benzene	6.4	–	–	25.7
Chloroform	5.6	–	–	19.8
Ether	–	3.1	–	–
Pyridine	21.0	–	–	71.0
Carbon Disulfide	–	–	0.4	–
Carbon Tetrachloride	0.4	–	–	1.8
Toluene	6.4	–	–	20.0

Solubility in w: 12.5°, 0.02; 54.5°, 0.137; 75.8°, 0.301; 87.4°, 0.587; 96.2°, 1.22; 100°, 1.32

2,4-Dinitrotoluene is a highly toxic material, and is readily absorbed thru intact skin. Vapors are absorbed thru the respiratory tract. It produces a marked increase in metabolism and temp, profuse sweating, collapse and death. It can also cause dermatitis, cataracts, wt loss, granulocytopenia, polyneuropathy, and exfoliative dermatitis (Ref 10)

Commercial Dinitrophenol consists almost entirely of 2,4-Dinitrophenol, and its properties are identical with those given above

2,4-Dinitrophenol is an expl less powerful and brisant, and less sensitive to mechanical action than TNT, but more sensitive than DNB or DNT. Some of its expl props were detd in Ger by Will (Ref 2) and Wöhler (Ref 4), in Fr by Burlot (Ref 6), and in the USA by the Ordnance Dept (Ref 9):

Brisance (by Sand Test). A 0.4g sample, using an MF detonator, crushed 23g of sand vs 43g for TNT

Impact Sensitivity. PicArsn app with 2kg wt, 17" vs 14" for TNT

Explosion temp. About 315°

Q_C^v 647.6cal/mole

Power (by BalMort). 70% of TNT

Rifle bullet test. No detonations from impact of .30 cal bullets fired from a distance of 90 ft

Reaction with metals. Forms salts except with Al and Sn

Thermal stability. Satisfactory

Velocity of detonation. About 5000m/sec vs 6900 for TNT

Uses. 2,4-Dinitrophenol has not been used alone as a shell filler because of its high mp (it would require press loading), and because it is comparatively expensive to manuf. When added in quantities of up to 40% to PA, it lowers its mp sufficiently to permit cast loading. Such mixts were known as **Tridites** in the USA, as **Shellite** (PA 70/2,4-DNPh 30) in Engl, as **DD Explosifs** (see Vol **3**, D19-L) in Fr, and as **MBT** (PA 60/2,4-DNPh 40) in Italy. These mixts were used for loading bombs and shells

Salts of 2,4-Dinitrophenol. 2,4-DNPh forms numerous metallic salts, most of which are expl, eg:

Ammonium salt. $NH_4C_6H_3O_5N_2.H_2O$, yel needles, mp about 220° with partial sublimation; sl sol in w and alc; expl (Ref 5, 290)

Barium salt. $Ba(C_6H_3O_5N_2)_2.4H_2O$, golden-yel crysts, sol in hot w or 90% alc (Ref 1, 253)

Cobalt salt. $Co(C_6H_3O_5N_2)_2 + HO.Co(C_6H_3O_5N_2) + 3C_2H_5OH$; orange-red prisms from alc; loses $3C_2H_5OH$ at 95°; explds on heating on a Pt foil (Ref 1, [241])

Lead salt (basic). $(O_2N)_2C_6H_3.O.PbOH.2H_2O$, yel spears; mp, explds violently when heated; d 2.817g/cc at 20/20°, sl sol in hot w (Ref 1)

Lead salt (neutral). $[(O_2N)_2C_6H_3O]_2Pb.6H_2O$; orange-yel powder, which is, according to Colver, one of the most violently detonating expls (Ref 5, 290)

Potassium salt. $KC_6H_3O_5N_2.H_2O$, yel prisms, d 1.778g/cc at 20°, expl (Ref 1, 253)

Silver salt. $AgC_6H_3O_5N_2.H_2O$, needles, d 2.755g/cc at 20°, explds violently when heated (Ref 1, 253)

Sodium salt. $NaC_6H_3O_5N_2.H_2O$, pale yel needles, sol in w, expl (Ref 1, 253; Ref 5, 290)

Additive Compounds of 2,4-Dinitrophenol. 2,4-DNPh forms low mp additive compds with ammonia or amines (aniline, toluidine, naphthylamine, etc), which on intimate mixing with oxidants (AN, K nitrate, Na nitrate, K chlorate, K perchlorate, etc) form easily detonatable expls. Colver (Ref 5, 291) describes preparative methods and gives mp's of some of the additive compds. For example, 2,4-DNPh (mp 112–14°) combines with aniline to form an additive compd of mp 82° [See also GerP 72945 (1893) & 73205 (1893), described in Ber **27** (Referate), 356–7 (1894)]

Refs: 1) Beil **6**, 251–54, (125–26), [239–42], & {854} 2) W. Will, SS **1**, 212 (1906)

3) M. Marqueyrol & P. Loriette, BullFr [4] **25**, 375 (1919) 3a) W.M. Rinkenbach, JACS **52**, 115 (1930) 4) L. Wöhler & O. Wenzelberg, AngChem **46**, 175 (1933) 5) Colver (1938), 287–91 6) E. Burlot & M. Thomas, MP **29**, 262 (1939) 7) Anon, Bull No 271, US Public Health Service (1941), 131 8) Davis (1943), 162 9) Anon, "Allied and Enemy Explosives", Aberdeen Proving Ground, Md (1946), 9 & 157 10) Merck (1968), 381-R 11) CondChemDict (1971), 318-R

2,5-Dinitrophenol (γ-Dinitrophenol). Yel monocl, prisms or needles (recryst from dil alc, w, ligr); mp 108°, also given as 104°; can be prepd by nitrating 2-nitrophenol or by other methods. Volatile with steam; sl sol in w or cold alc; sol in hot alc, eth, and fixed alkali hydroxides

It is an expl, slightly less sensitive to impact than TNT, and slightly more sensitive than 2,4-Dinitrophenol (Ref 4). Forms metallic salts, some of which are expl

Refs: 1) Beil **6**, 257, (127), [244] & {866} 2) A.F. Holleman & G. Wilhelmy, Rec **21**, 432 (1902) 3) N.V. Sidgwick & W. McAldons, JCS **119**, 1002 (1921) 4) L. Wöhler & O. Wenzelberg, AngChem **46**, 175 (1933) 5) Merck (1968), 382-L

2,6-Dinitrophenol (β-Dinitrophenol). Pale yel rhomb needles or leaflets from dil alc; mp 63–4°; heat of fusion 4.41kcal/mole; can be prepd by nitrating 2-nitrophenol or by other methods. Volatile with steam, although less so than 2,4-Dinitrophenol

Solubility in g/100g of solvent at 14°, as detd by Desvergnes (Ref 1, 245): ethyl acetate 68.8, acet 162.2, methanol 14.7, alc (96%) 6.5, alc (abs) 5.5, benz 33.7, chlf 31.8, eth 8.8, py 68.0, C disulfide 0.7, C tetrachloride 0.7, toluene 28.3; w at 15°, 0.03 and 1.2 at 100°

It is an expl, slightly less sensitive to impact than TNT, and slightly more sensitive than 2,4-Dinitrophenol

It forms metallic salts, some of which are expl

Refs: 1) Beil **6**, 257, (127), [245] & {867} 2) A.F. Holleman & G. Wilhelmy, Rec **21**, 433 (1902)

3,4-Dinitrophenol (δ-Dinitrophenol). Colorl, shiny crysts; mp 134–35° (when in w, it melts at 50–60° and remains liq for a long time); d 1.672g/cc; heat of fusion 6.05kcal/mole. It is formed, together with 2,3- and 2,5-Dinitrophenol, on nitration of 3-nitrophenol. It does not volatilize with steam, is sl sol in hot w, v sol in alc and ether. Its expl props have not been examined

Refs: 1) Beil **6**, 257, (127), [246] & {868} 2) A.F. Holleman & G. Wilhelmy, Rec **21**, 434 (1902)

3,5-Dinitrophenol (ε-Dinitrophenol). Colorl leaflets from w; mp 126.1°; d 1.702g/cc. Can be prepd by heating 3,5-dinitroanisole in a sealed tube with concd HCl at 170–80° for 5–6 hrs, or by other methods. Very sol in alc or eth, sol in chlf or benz, sl sol in w or petr eth. Its expl props have not been examined

Refs: 1) Beil **6**, 258, (128), [246] & {869} 2) A.F. Holleman & G. Wilhelmy, Rec **21**, 438 (1902)

Trinitrophenols. $(O_2N)_3.C_6H_2.OH$, mw 229.11, N 18.3%, OB to CO_2 –45.3%. Several isomers are known, all of them expl:

2,3,6-Trinitrophenol (γ-Trinitrophenol). Yel needles from w, mp 118°. Can be prepd by the nitration of 2,3-Dinitrophenol or by other methods. Very sol in alc, eth and benz; sol in hot w, diff sol in cold w. It is an expl; forms metallic salts such as those of K, Ba, Ag and Pb

Refs: 1) Beil **6**, 265, (129) & [253] 2) R. Henriques, Ann **215**, 326 & 332 (1882) 3) J.J. Blanksma, Rec **21**, 258 (1902) 4) Urbański **1**, 524 (1964)

2,4,5-Trinitrophenol (β-Trinitrophenol). White needles from dil alc, mp 96°. Can be prepd by the nitration of 3,4-Dinitrophenol or by other methods. Very sol in alc, eth and benz, sol in hot w, diff sol in cold w. It is an expl; forms metallic salts such as those of K and Ba

Refs: 1) Beil **6**, 265 & [253] 2) R. Henriques, Ann **215**, 325 & 331 (1882)

2,4,6-Trinitrophenol (α-Trinitrophenol). See under Picric Acid

2,4,6-Trinitrophenol, Ammonium Salt. See under Ammonium Picrate (Explosive D) in this Vol

Trinitrophenols, Halogen Derivatives of.

Several more or less expl halogen compds of Trinitrophenols are listed in Beilstein, ie:

3-Chloro-2,4,5-Trinitrophenol. $(O_2N)_3C_6H(OH)Cl$, crysts, mp 112.5–113.5° (Beil **6**, [283])

3-Chloro-2,4,6-Trinitrophenol. Yel crysts, mp 112–116° (Beil **6**, 292 & [283])

3,5-Dichloro-2,4,6-Trinitrophenol. $(O_2N)_3C_6(OH)Cl_2$, colorl crysts, mp 135–40° [Beil **6**, 292 & (141)]

3-Bromo-2,4,6-Trinitrophenol. $(O_2N)_3C_6H(OH)Br$, yel crysts, mp 144–49° (Beil **6**, 292 & [283])

3,5-Dibromo-2,4,5-Trinitrophenol. $(O_2N)_3C_6(OH)Br_2$, crysts, mp 146° (Beil **6**, [283])

3,5-Dibromo-2,4,6-Trinitrophenol. $(O_2N)_3C_6(OH)Br_2$, colorl crysts, mp 173° (Beil **6**, 292 & [283])

5-Chloro-3-bromo-2,4,6-Trinitrophenol. $Br(O_2N)_3C_6(OH)Cl$, pale yel prisms, mp 165.5° (Beil **6**, [283])

3-Iodo-2,4,6-Trinitrophenol. $(O_2N)_3C_6H(OH)I$, crysts, mp 197° (Beil **6**, [283])

2,3,4,6-Tetranitrophenol. $(O_2N)_4C_6HOH$, mw 274.10, N 20.44%, OB to CO_2 –23.3%, light yel needles from chlf, mp 140° (decomps at higher temps). Sol in alc, chlf and ethyl acetate; diff sol in benz or ligr

It was first prepd by Nietzki and Burckhardt (Ref 2) by the action of 50% nitric acid followed by 63% nitric acid on diquinoyltrioxime, $C_6H_2(:O)(:NOH)_3$ (Beil **7**, 886), at a temp lower than room temp. By neutralizing the soln, a sparingly sol K salt was pptd, which in turn was converted by double decompn into a still less sol Ba salt. From the latter, by the action of a calcd quantity of sulfuric acid, free Tetranitrophenol was obtained

A product of higher purity than that obtained by Nietzki was prepd by Blanksma (Ref 3) by the nitration of m-nitrophenol with a mixt of nitric acid (d 1.52g/cc) and concd sulfuric acid. As shown later (Ref 4), the product, if of high purity, exhibits fairly high heat stability. It explds at 245–251°, whereas if it is contaminated it decomps after being brought to its mp (140°)

Its expl props were incompletely examined by van Duin and van Lennep (Ref 4). They reported an expln temp of 251° when heated at 20° per minute; 245° when heated at 5° per minute. Its impact sensitivity was less than PETN and more sensitive than Tetryl, and it evolved nitrous gases after being heated at 70° for 4 hours

Refs: 1) Beil **6**, 292, (141), [284] & {973} 2) R. Nietzki & E. Burckhardt, Ber **30**, 175 (1897) 3) J.J. Blanksma, Rec **21**, 256 & 336 (1902); Ibid Ber **47**, 687 (1914) 4) C.F. van Duin & B.C.R. van Lennep, Rec **39**, 145, 162, 166, 170 & 174 (1920) 5) Urbański **1** (1964), 530–1

Tetranitrophenol, Halogen Compounds of.

5-Chloro-2,3,4,6-Tetranitrophenol. $(O_2N)_4C_6(OH)Cl$, colorl crysts from chlf or C tetrachloride, mp 174°. Can be prepd by the nitration of 5-chloro-3-nitrophenol with mixed nitric-sulfuric acids. It is an expl

5-Bromo-2,3,4,6-Tetranitrophenol. $(O_2N)_4C_6(OH)Br$, colorl crysts from chlf or C tetrachloride, mp 157°. Can be prepd by the nitration of 5-bromo-3-nitrophenol with mixed nitric-sulfuric acids. It is an expl

Ref: Beil **6**, 293

Pentanitrophenol. $(O_2N)_5C_6OH$, mw 319.12, N 21.95%, OB to CO_2 –7.52%, yel crysts from chlf, mp 190° (decompn). Was prepd by Blanksma (Ref 2), who nitrated 3,5-dinitrophenol with an anhydr mixt of nitric-sulfuric acids. The product was pptd and recrystd from chlf. It is a powerful expl

Refs: 1) Beil **6**, 293 & [284] 2) J.J. Blanksma, Rec **21**, 256 & 336 (1902)

Nitrosophenols. $HO.C_6H_4.NO$, mw 123.11, N 11.38%, OB to CO_2 –162.5%

o-Nitrosophenol (1,2-Benzoquinone Monoxime). Oil. Can be prepd in 20% yield by treating a hot aq soln of o-nitrosoanisole with a boiling K disulfate soln, or by other methods. It explds on heating or in contact with concd acids (Ref 2). It forms expl Ag, Cu and Na salts

Refs: 1) Beil **7**, 600, (337) & [566] 2) A. Baeyer & E. Knorr, Ber **35**, 3037 (1902) 3) O. Baudisch & N. Karzew, Ber **45**, 1164–71 (1912)

p-Nitrosophenol (1,4-Benzoquinone Monoxime). Pale yel orthorhombic needles; mp, browns at 126°, decomps at 144°. Can be prepd from phenol by the action of nitrous acid in the cold. Moderately sol in w; sol in dil alkalies giving green to brownish green solns; sol in alc, ether & acet. Q_C^v 713.9kcal/mole

p-Nitrosophenol explds on contact with concd acid, alkali or fire. A technical grade expld on storage (Ref 4). According to Kuznetzov (Ref 6), its exothermic decompn, often resulting in spontaneous ignition, is caused chiefly by contaminating alkalies. A more stable product can be obtained by washing with dil HCl followed by w. By converting p-Nitrosophenol into its Na salt and drying it at 70°, Kuznetzov obtained a product which could be stored indefinitely at room temp. It changed very little when heated at 130°

Refs: 1) Beil **7**, 622, (344) & [574] 2) A. Baeyer & H. Caro, Ber **7**, 963 (1874) 3) C.H. Sluiter, Rec **25**, 8 (1906) 4) W.D. Milne, IEC **11**, 489 (1919) 5) H.H. Hodgson & F.H. Moore, JCS **127**, 2260 (1925) 6) B.I. Kuznetzov, OrgChemInd(Russia) **3**, 407–9 (1937); CA **31**, 7252 (1937) 7) Merck (1968), 742-L 8) CondChemDict (1971), 625-R

Phenolsulfonic Acids and Derivatives

$HO.C_6H_4.SO_3H$, mw 174.17. Three of these acids are known, o-, m-, and p-, but only two of them, o- and p- acids form during the sulfonation of phenol in the manuf of PA by the phenolic process. The formation of small quantities of the m-acid was reported, but not definitely proven

o-Phenolsulfonic Acid. Crysts with $\frac{3}{4}H_2O$; mp, begins to melt at 50° and then decomps; can be prepd by the sulfonation of phenol

Ref: Beil **11**, 234, (53) & [131]

m-Phenolsulfonic Acid. Crysts with $2H_2O$; mp, loses $1.5H_2O$ at 100° and the remainder at 140°; can be prepd by diazotizing metanilic acid, $H_2N.C_6H_4.SO_3H$, or by other methods

Ref: Beil **11**, 239, (54) & [133]

p-Phenolsulfonic Acid. Deliq needles; can be prepd by the sulfonation of phenol or by other methods

Refs: 1) Beil **11**, 241, (55) & [134] 2) Merck (1968), 811-L

Mononitrophenolsulfonic Acids.

$O_2N.C_6H_3(OH).SO_3H$, mw 273.22. Several acids are described in Beilstein, of which only the o- and p- are formed as intermediate products in the manuf of PA from phenol

o- (or 1,4,2-)Nitrophenolsulfonic Acid. Crysts with $3H_2O$; mp, loses H_2O at 100°and then decomps at about 110°; can be prepd by treating 4-nitrophenol with concd sulfuric acid

Refs: 1) Beil **11**, 237, (53) & [132] 2) F. Olsen & J.C. Goldstein, IEC **16**, 67–69 (1924)

p- (or 1,2,4-) Nitrophenolsulfonic Acid. Plates from ethyl acet/benz; mp 141–2°, its trihydrate melts at 49°; can be prepd by treating 2-nitrophenol with fuming sulfuric acid; v sol in w, ethyl acet, alc and hot chlf

Refs: 1) Beil **11**, 245–6, (57) & [137] 2) F. Olsen & J.C. Goldstein, IEC **16**, 67–9 (1924)

Sodium Salt of Nitrophenolsulfonic Acid. $O_2N.C_6H_3(OH).SO_3Na$, mw 241.16, N 5.8%, orange-red crysts. Can be prepd by treating the product obtained on sulfonation of phenol with Na nitrate and an excess of sulfuric acid. This salt, which is a mixt of Na o- and p-nitrophenolsulfonates, was patented in 1911 by A. Voight for use in expl mixts such as: Na nitrophenolsulfonate 22.5 to 25, K or Na nitrate 45 to 65, K perchlorate 10 to 22.5, and AN 10%

The Vereinigten Köln-Rottweiler Fabriken patented in 1910 its use in the manuf of detonating expls, eg, Na nitrophenolsulfonate (or Na nitrocresolsulfonate) 25, Na nitrate 25, and K perchlorate 50%

Ref: Colver (1938), 284–6 & 351

Dinitrophenolsulfonic Acids. $(O_2N)_2C_6H_2(OH)SO_3H$, mw 264.18, N 10.60%

4,6-Dinitrophenolsulfonic Acid [(4,6-Dinitrophenolsulfonsäure-(2) in Ger]. Yellowish crysts. It is obtained during the prepn of PA by the sulfonation and nitration of phenol. Forms various metallic salts, such as those of Ba and K (Ref 3)

Refs: 1) Beil **11**, 238 & (53) 2) M. Marqueyrol & P. Loriette, BullFr [4], **25**, 371 (1919) 3) F. Olsen & J.C. Goldstein, IEC **16**, 71 (1924)

2,6-Dinitrophenolsulfonic Acid (2,6-Dinitrophenolsulfonsäure-(4) in Ger). Yellowish crysts; mp, with $3H_2O$, about 111°; can be prepd by the nitration of p-phenolsulfonic acid. Forms numerous metallic salts

Refs: 1) Beil **11**, 247, (57) & [138] 2) M. Marqueyrol & P. Loriette, BullFr [4], **25**, 371 (1919)

2,4,6-Trinitrophenolsulfonic Acid [2,4,6-Trinitrophenolsulfonsäure-(3) in Ger] $(O_2N)_3C_6H(OH)SO_3H$, mw 309.18, N 13.59%, crysts; can be prepd by heating m-phenolsulfonic acid with concd nitric acid; sol in w. Forms expl metallic salts, such as:

Potassium salt. $KC_6H_2N_3O_{10}S.H_2O$, orange-red crysts, sol in w

Barium salt. $Ba(C_6H_2N_3O_{10}S)_2.3H_2O$, yel prisms, sol in w

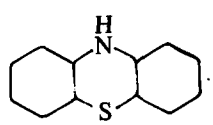
Both salts expld violently when heated on a Pt foil

Refs: 1) Beil **11**, 240 2) A. Berndsen, Ann **177**, 97 (1875)

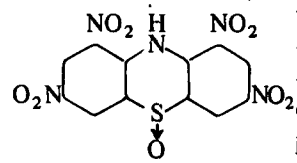
5-Bromo-3,4,6-Trinitrophenolsulfonic Acid. $(O_2N)_3C_6Br(OH)SO_3H$, can be prepd by nitrating 3-bromophenol with mixed nitric-sulfuric acid. Its **Potassium salt**, $K_2C_6O_{10}N_3BrS$, yel crysts from alc, explds on heating

Refs: 1) Beil **11**, [132] 2) H.H. Hodgson & F.H. Moore, JCS **1926**, 161

Phenothiazine (Thiodiphenylamine, Dibenzotiazine, Phenoxur, Contraverm). $C_{12}H_9NS$, mw 199.26; yel rhomb leaflets or diamond-shaped plates from toluene or butanol; mp 185.1°; bp 371° (760mm), 290° (40 mm), subl at 1mm Hg at 130°. Can be prepd by reaction of diphenylamine and S in the presence of an oxidizing catalyst. Sol in benz & eth, insol in petr eth, chlf & w. Moderately toxic by ingestion; a skin irritant. Can be nitrated to form a tetranitroderivative which is expl (Refs 1, 3, 6, 7 & 8)



1,3,5,7-Tetranitrophenothiazine (Phenothiazine Tetranitrosulfoxide). Yel solid, mp 368°. Can be prepd in 70% yield by the nitration of phenothiazine with a mixt of 98% nitric acid and anhydr sulfuric acid at 60°. In addition to nitration, oxidation of the S atom also takes place, resulting in the formation of the sulphoxide (Ref 5). It was used in Ger during WWII as a component of a non-fusible expl compn known under the name of "Pressling" (qv) (Refs 2 & 4)



Refs: 1) Beil **27**, 63–5 2) C. Monard et al, MP **34**, 179 (1952) 3) L. Médard & M. Thomas, MP **39**, 347–8 & 355 (1957) 4) B.T. Fedoroff et al, PATR **2510** (1958), Ger 135-R 5) Urbański **1** (1964), 572 6) Merck (1968), 812-L 7) CondChemDict (1971), 677-R 8) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 407

β-Phenoxyethanol and Derivatives

β-Phenoxyethylalcohol (Phenylethyleneglycol-ether, Glycol monophenylether). $C_6H_5O.CH_2CH_2OH$, mw 138.16; colorl liq with faint aromatic odor, fr p 14°; bp 240–48°; d 1.094 at 20/20°; RI 1.534 at 20°; vap press 0.03mm at 20°; sl sol in w, sol in alc & eth. Can be prepd by heating phenol and ethylene oxide in a closed tube at 150°. It can be nitrated to obtain the expls β-(2,4-Dinitrophenoxy) ethanol Nitrate and β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (see below)

Refs: 1) Beil **6**, 146, (84) & [150] 2) W.H. Bentley et al, JCS **69**, 164 (1896) 3) W.R. Kirner, JACS **48**, 2748 (1926) 4) Curme & Johnston (1952), 116 & 306 5) CondChemDict (1961), 469-L

β-(2,4-Dinitrophenoxy) ethanol (Glycoldinitrophenylether). $(O_2N)_2C_6H_3.O.CH_2CH_2OH$, mw 228.18, N 12.27%, wh needles, mp 111.3–111.4°, d (apparent) 0.5g/cc. It was first prepd by Fairburne and Toms (Ref 2) by heating a glycolic soln of Na hydroxide with a glycolic soln of dinitrochlorbenzene at 100°. Practically the same method was used by other investigators. Its industrial prepn was patented by duPont and others. Wasmer (Ref 4, p 176) gives its properties, including solubility in various solvents at 20°. By nitrating it, the expl β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (see below) is obtained

Refs: 1) Beil–not found 2) A. Fairburne & H. Toms, JCS **119**, 207 (1921) 3) C. Dosios & Tsatsas, CR **180**, 1275 (1925) 4) A. Wasmer, MP **28**, 171 (1938) & CA **33**, 8405 (1939) 5) H. Ficheroulle, MP **30**, 123 (1948) & CA **45**, 10586 (1951)

β-(2,4-Dinitrophenoxy) ethanol Nitrate (Glycoldinitrophenylether Nitrate, Dinitrophenylglycolether Nitrate). $(O_2N)_2.C_6H_3.O.CH_2.CH_2(ONO_2)$, mw 273.16, N 15.38%, OB to CO_2 –67.4%, crysts, mp 64–67°, Q_C^V 3455cal/g, Q_f 181cal/g (Ref 5)

It can be prepd from dichlorbenzene and ethylene glycol, followed by nitration of the resulting glycol monophenyl ether. It is an expl, slightly less powerful than TNT (Trauzl block expansion gave 270–277cc vs 290–294cc for TNT), and very insensitive to impact (using the Kast app with a 2kg wt, it detonated at > 120cm vs > 40cm for TNT). It was proposed for use in proplnts, primers or detonators (Ref 6)

Refs: 1) Beil–not found 2) Westfälisch-Anhaltische Sprengstoff AG, Chem Fabrik, GerP 548427 & CA **26**, 3670 (1932) 3) Ibid, GerP 551306 & CA **26**, 4474 (1932) 4) M.S. Fishbein, VoyennayaKhimia(Russia) **1933**, No 6, 3–8 & CA **29**, 7077 (1935) 5) A. Schmidt, SS **29**, 263 (1934) 6) L. Médard & M. Thomas, MP **39**, 345 & 354 (1957)

β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (2,4,6-Trinitrophenoxyethyl Nitrate, Glycoltrinitrophenylether Nitrate, TNPEN). $(O_2N)_3.C_6H_2.O.CH_2.CH_2(ONO_2)$, mw 318.16, N 17.61%, OB to CO_2 –45.3%, light yel crysts, mp 104.5–107°, Q_C^V 291.8kcal/mole, Q_f 66.7 kcal/mole. Schmidt [SS **29**, 263 (1934)] gives Q_C^V as 897.7kcal/mole

TNPEN was first prepd by Lewis (Ref 2), and subsequently by several other investigators (see Refs 3, 4, 5 & 7). Ficheroulle (Ref 7) prepd it in 1937 at the Laboratoire Central des Poudres, by the nitration of β-(2,4-Dinitrophenoxy) ethanol, but the results were not published until 1948 (Ref 3). The substance was purified by pptn of the nitrated mixt with w, and crystn from acet

Wasmer (Ref 4) investigated several methods proposed prior to 1938, and developed his own method, which he describes in detail

Elderfield (Ref 5) gives the following method of prepn: "A solution of 10g of β-(2,4-Dinitrophenoxy) ethanol in 100g of 94% sulfuric was added slowly and with stirring to 75g of mixed acid (52.5% sulfuric, 26.5% nitric and 21% water) at 0–10°. Since the reaction is distinctly exothermic, an ice-salt bath was necessary for cooling. When the addition was complete, the temp was raised in 1/2 hour intervals to 20°, 30°, 40°, 60°, and then in 1/4 hour intervals to 70°. After chilling, the cream-colored crysts were filtered on sintered glass, washed free of acid and recrystd by dissolving in acet and adding alc"

TNPEN ignites when heated in an open dish and explds when struck with a hammer upon an iron surface. It is a good gelatinizer for NC

Properties. According to Wasmer (Ref 4):

Solubility. At 20° in g/100ml of solvent; acet 27.7; benz 2.1; chlf 0.6; eth 0.3; CS_2 0.06; CCl_4 0.03; w <0.01; concd sulfuric acid, sl sol; concd nitric acid, sol

C.U.P. (Trauzl block value), 109 (PA 100)

Impact sensitivity. Between that of PA and Tetryl

Stability

Stability. Bergmann-Junk test at 132°; one g of the pure product, mp 104.5°, evolved between 0.3 and 1.7cc of NO; the impure (crude) material, mp 102–102.5°, deflagrated

It was found to be a good gelatinizer for NC, and for this reason was recommended as an ingredient of smokeless powders

According to WASAG (Ref 3):

Impact sensitivity. 2kg wt, positive at > 45cm vs > 40cm for TNT, ie, comparable to TNT

Power. (Trauzl test). 122% of TNT

According to Ficheroulle (Ref 7):
C.U.P. (Trauzl block value), 115 (PA 100, Tetryl 120)
Gap test. 23cm vs 22cm for Tetryl
Impact sensitivity. 5kg wt; 50% explns obtained with a fall of 80cm; comparable to Tetryl
Sensitivity to initiation. Comparable to that of Tetryl
Detonation velocity at various densities and pressures.

	β-(2,4,6-Trinitrophenoxy) ethanol Nitrate		Tetryl	
Density, g/cc	P*	VD**	P	VD
1.15	75	5500	40	5638
1.25	100	6100	100	6100
1.35	175	6606	175	6602
1.40	200	6856	225	6777
1.45	300	6700	–	–
1.50	400	6600	360	7137
1.60	–	–	450	7240

*P = Press in kg/sq cm necessary to obtain desired d
**VD = Detonation velocity (mean) in m/sec

Uses. Lewis (Ref 2) recommended the use of TNPEN in boosters and detonators, while WASAG (Ref 3) advocated its utilization as an addition to proplnts as well as in the manuf of primers and detonators

WASAG also prepd and tested the following formulation: TNPEN 64, Pentaerythritol dimethylether dinitrate 18, and Al powder 18%. It had a mp 94°; impact test value with a 5kg wt, max height (29cm) with no expln vs 20cm for PA; Trauzl block value 440cm^3 vs 310cm^3 for PA (10g sample)

Both Wasmer (Ref 4) and Ficheroulle (Ref 7) employed TNPEN as an ingredient in solventless smokeless powders (poudres SD)

Lang (Ref 8) investigated mixts of TNPEN with AN, and noted that they were more hygroscopic than AN alone. These mixts were fairly stable at room temp, but when heated to 115° they combined in equimolecular proportions, forming a complex more volatile than either of the constituents

Refs: 1) Beil–not found 2) H.A. Lewis, USP 1560426 (1925) & CA **20**, 112 (1926) 3) Westfälisch-Anhaltische Sprengstoff AG (WASAG), GerP 551306 (1931) & CA **26**, 4474 (1932); GerP 572937 (1933) & CA **27**, 4402 (1933) 3a) M.S. Fishbein, VoyennayaKhimia-(Russia), No 6, 5–8 (1933) & CA **29**, 7077 (1935) 3b) WASAG, GerP 638432 (1936); SS **32**, 44 (1937) 4) A. Wasmer, MP **28**, 177 (1938) & CA **33**, 8405 (1939) 5) R.C. Elderfield, "Explosives from Hydroxy and Amino Compounds", OSRD **907** or **PB 31085** (1942) 6) Davis (1943), 227 7) H. Ficheroulle, MP **30**, 123–126 (1948) & CA **45**, 10586 (1951) 8) F.M. Lang, MP **34**, 189–94 (1952) 9) L. Médard & M. Thomas, MP **35**, 159 & 172 (1953)

Phenylaminobutane. See N-Butylaniline and Derivatives in Vol **2**, B378-L ff

Phenylaminobutanol (Phenylaminobutyl alcohol). See Anilinobutanol and Derivatives in Vol **1**, A422-R

Phenylaminoethane. See N-Ethylaniline and Derivatives in Vol **6**, E206-L

Phenylaminoethanol (Phenylaminoethyl alcohol). See Anilinoethanol and Derivatives in Vol **1**, A424-L ff

Phenylaminomethane. See N-Methylaniline and Derivatives in this Vol, M97-R ff

Phenylaminopropanediol. See Anilinopropanediol and Derivatives in Vol **1**, A434-R

Phenylaminopropanol. See Anilinopropanol and Derivatives in Vol **1**, A436-L

Phenylaniline. See Aminobiphenyls and Derivatives in Vol **1**, A191-L

Phenylarsonic Acid (Phenylarsinic Acid). $C_6H_5AsO(OH)_2$, mw 202.03, crysts, mp 157–8° (loses H_2O > 158°), d 1.760g/cc. Prepn and properties are given in Ref 1

Lead-2,4,6-trinitrophenylarsonate. $(O_2N)_3.C_6H_2.AsO(O_2Pb)$, mw 542.23, N 7.75%, ochre-colored solid, mp 215–237°. Can be prepd by treating K trinitrophenylarsonate, $(O_2N)_3.C_6H_2.AsO(OK)_2$ (obtained by the reaction between 2,4,6-trinitrobenzoylchloride and K arsenite) with Pb acetate

It is an expl, comparable in sensitivity to Tetryl and about 51% as powerful as TNT (by BalMort test); explds when heated to 270°. It is rather volatile and hygroscopic, but fairly stable even at temps as high as 135°

Refs: 1) Beil **16**, 868, (448) & [457] 2) R. McGill, OSRD **830** (1942), 36

Phenylazide and its Nitrated Derivatives. See under Azido and Azidonitro Derivatives of Benzene in Vol **2**, B42-L ff

Phenylazoanilines. See under Aminoazobenzenes and Derivatives in Vol **1**, A184-R to A185-L

Phenylbenzoic Acid. See Biphenylcarboxylic Acid and Derivatives in Vol **2**, B125-L

Phenyl Cyanide. See Benzonitrile and Derivatives in Vol **2**, B76-R

Phenyldiazosulfide [Di(Benzenediazo) Sulfide]. $C_6H_5.N{:}N.S.N{:}N.C_6H_5$, mw 242.27, N 23.13%, red solid. It was prepd at PicArsn in quantities of 0.5 to 1.0g by diazotizing aniline, and either passing hydrogen sulfide thru the diazochloride soln or adding Na sulfide to it at 0°. It pptd in the form of a yel colloid which slowly agglomerated to produce a red solid which floated on the surface. The red solid turned to an oil in a short time when the soln was allowed to warm to room temp, and during the change nitrogen was evolved and the odor of thiophenol was apparent. The wet material expld easily under the action of friction, impact, or heat from a match flame. When removed from soln, pressed dry on filter paper, and air dried at room temp, the compd detonated spontaneously

p-Nitrophenyldiazosulfide. $(O_2N).C_6H_4.N{:}N.S.N{:}N.C_6H_4(NO_2)$, mw 332.27, N 25.30%, fine yel crysts. It was prepd at PicArsn by diazotizing p-nitroaniline, neutralizing the mixt, and either passing hydrogen sulfide thru the soln or adding Na sulfide to it at 0°. It is more stable than Phenyldiazosulfide, and is difficult to expld when wet. It can be dried without change at room temp, but the resulting dry compd is extremely sensitive to friction; it can be detonated by rubbing on smooth linoleum with a soft object

p-Nitrophenyldiazosulfide is readily decompd by org solvents at room temp with the evolution of nitrogen. It expld at 82° in 5 seconds (vs 335° for LA, 260° for Tetryl and 208° for MF); impact sensitivity with a 500g wt on the BuMines app, 5cm fall for expln vs 65cm for commercial LA

Refs: 1) E. Bamberger & J. Kraus, Ber **29** (1), 272–86 (1896) 2) W.R. Tomlinson, PATR **1208** (1942) 3) Ibid, C&EN **29**, 5473 (1951) & CA **46**, 3279 (1952)

Phenyldichloramine (N,N-Dichloraniline). $C_6H_5.NCl_2$, mw 162.02, yel-red oil. It was prepd by Goldschmidt (Ref 2) by action of hypochlorous acid on aniline in ethereal soln at −15° to 20°. Sol in eth; the soln is fairly stable when kept at 0° and in the dark. The oil alone is stable at −40°, but explds at higher temps. It also explds on contact with concd sulfuric acid

Refs: 1) Beil **12**, (287) 2) S. Goldschmidt, Ber **46**, 273 (1913) 3) Sidgwick, ChemElems **1** (1950), 708

PHENYLENEDIAMINES OR DIAMINOBENZENES

$H_2N.C_6H_4.NH_2$, mw 108.14, N 25.91%. There are three isomers; ortho-, meta- and para-. Phenylenediamines were first prepd in the 1860's by P. Griess and then by A.W. Hofmann. Inasmuch as some confusion existed in regard to the structure of these compds, it is difficult to say which isomers they were

o- or 2-Phenylenediamine(1,2-Diaminobenzene). Colorl monocl crysts, darkens in air; mp 102–104°; bp 252–58°; sol in alc, eth, w and chlf; somewhat toxic. Can be prepd by reducing o-nitroaniline with Zn and NaOH; many other methods are known (Ref 1)

Forms numerous salts as well as additive compds, some of which are expl

Salts and Additive Compounds:

Perchlorate. $C_6H_8N_2+2HClO_4$; mw 309.16; N 9.1%; OB to CO_2, Cl_2 & H_2O –46.6%; crysts; explds at 250° (Ref 1, p 6 & Ref 3)

With Zn Perchlorate. $4C_6H_8N_2+ZnClO_4$; prisms; difficultly sol in w; puffs off on heating (Ref 1, p 11 & Ref 4)

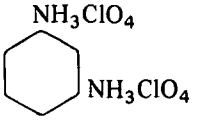
Refs: 1) Beil **13**, 6, (5) & [8] 2) P. Friess, Ber **5**, 202 (1872) 3) R.L. Datta & N.R. Chatterjee, JCS **115**, 1010 (1919) 4) W. Hieber, C. Schliessman & K. Ries, ZAnorgChem **180**, 101 (1929) 5) Merck (1968), 816-R 6) CondChemDict (1971), 680-R

m- or 3-Phenylenediamine(1,3-Diaminobenzene). Colorl needles, unstable in air; usually in the form of the stable hydrochloride; mp 63°, bp 282–87°, d 1.1389g/cc. Sol in alc, eth & w. Can be prepd by the reduction of m-dinitrobenzene or nitroaniline with Fe and hydrochloric acid. It is a strong skin irritant. Forms salts and additive compds, some of which are expl

Salts and Additive Compounds.

Monoperchlorate. $C_6H_8N_2+HClO_4$; colorl crysts; can be prepd by treating m-phenylenediamine with perchloric acid. Explds when heated to about 250°, or on impact. It is less sensitive to mechanical action than the diperchlorate

Diperchlorate. mw 309.16, N 9.1%, OB to CO_2, Cl_2 & H_2O –46.5%; yel crysts; mp, explds at about 263°. Can be prepd by treating m-phenylenediamine with perchloric acid. It is fairly sol in w, v sol in alc, sol in acet & eth with decompn, difficultly sol in acet ac, insol in chlf. Stable toward light



The expl properties of the diperchlorate were examined in 1917 by Spallino [Ref 1, p (11)], and then by Datta & Chatterjee (Ref 2). It explds on heating, impact or friction. Its power and brisance are slightly below those of PA, while sensitivity to mechanical action is much higher (for example, the impact test with a 2kg wt is only 15cm vs 85cm for PA). When ignited, it burns rapidly with sooty smoke [Ref 1, p (11)]

With 1,3,5-Trinitrobenzene.

$C_6H_8N_2+C_6H_3O_6N_3$; mp 168°; was prepd by Kremann et al (Ref 3). There are also eutectics; at 45° with m-phenylenediamine 82, TNB 8%; and at 105° with m-phenylenediamine 7, TNB 93% (Ref 1, p [24])

With 2,4,6-Trinitrotoluene.

$C_6H_8N_2+C_7H_5O_6N_3$; mp 105°; was prepd by Kremann et al (Ref 3). There are also eutectics; at 57.5° with m-phenylenediamine 90.5, TNT 9.5%; and at 70° with m-phenylenediamine 6, TNT 94% (Ref 1, p [24])

Refs: 1) Beil **13**, 33, (10–11) & [23] 2) R.L. Datta & N.R. Chatterjee, JCS **115**, 1010 (1919) 3) R. Kremann & O. Mauermann, Monatsh **43**, 318–20 (1922) & CA **17**, 1462–3 (1923) 4) Merck (1968), 816-R 5) CondChemDict (1971), 680-R

p- or 4-Phenylenediamine (1,4-Diaminobenzene). White to light purple crysts, oxidizes on standing in air to purple and black; mp 145–147°; bp 267°; sl sol in w & chlf; easily sol in alc & eth; affected by light; flash pt 155.5°; combustible

Can be prepd by reduction of p-nitroaniline with Fe and hydrochloric acid; other methods given in Ref 1. It is highly toxic by ingestion and inhalation; strong irritant to the skin. Tolerance, 0.1mg per cubic meter of air

It forms salts and additive compds, some of which are expl

Salts and Additive Compounds

Perchlorate. $C_6H_8N_2+2HClO_4$; mw 309.16, N 9.1%, OB to CO_2, Cl_2 and H_2O –46.6%, yel to brownish leaflets; mp, explds at about 260°; very easily sol in w, difficultly sol in acet ac, insol in eth. Explds on heating or on impact

Was prepd and examined by Spallino [Ref 1, p (20)] and Datta et al (Ref 2). Its sensitivity to impact (60cm with a 2kg wt) is much lower than the corresponding orthocompd (15cm with a 2kg wt). When ignited in air, it burns rapidly with the production of a sooty flame

p-Phenylenediamine-picrate.

$H_2N.C_6H_4.NH_2.C_6H_2(OH)(NO_2)_3$, mw 337.25, N 20.8%. Can be prepd by mixing equimolar quantities of PA and p-phenylenediamine dis-

solved in alc or other solvent. Kaiser (Ref 4) proposed that it be used in combination with diazodinitrophenol in percussion caps

p-Phenylenediamine-dipicrate. $H_2N.C_6H_4.NH_2.[C_6H_2(OH)(NO_2)_3]_2$, mw 566.36. Can be prepd by the interaction of 1 mole of p-phenylenediamine with 2 moles of PA in alc or other solvent. It was patented by J. Piccard (Ref 5) for use in delay electric caps for igniting time fuses, etc

Compound with 1,3,5-Trinitrobenzene. $C_6H_8N_2+C_6H_3O_6N_3$, mp 145.5°. Was prepd by Kremann & Mauermann (Ref 3). There are also eutectics; at 101–5° with p-phenylenediamine 9, TNB 91%; and at 116° with p-phenylenediamine 64, TNB 36% (Ref 1, p 70 & [37])

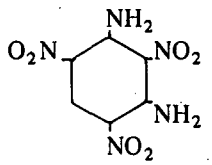
Compound with 2,4,6-Trinitrotoluene. $C_6H_8N_2+C_7H_5O_6N_3$, mp 93°. There are also eutectics at 64° with p-phenylenediamine 8, TNB 92%, as well as at 88° with p-phenylenediamine 64, TNT 36%

Refs: 1) Beil **13**, 61, (18) & [34] 2) D.L. Datta & N.R. Chatterjee, JCS **115**, 1010 (1919) 3) R. Kremann & O. Mauermann, Monatsh **43**, 319 (1922) & CA **17**, 1462 (1923) 4) H.E. Kaiser, USP 1852054 (1932) & CA **26**, 3114 (1932) 5) J. Piccard, USP 1939365 (1933) & CA **28**, 1538 (1934) 6) Merck (1968), 816-R 7) CondChemDict (1971), 680-R

Nitrophenylenediamines or Nitrodiaminobenzenes

Mono-, di-, and tri-nitrophenylenediamines are described in the literature (Ref 1), but no tetracompd. The 2,4,6-Trinitro-m-phenylenediamine is an expl

2,4,6-Trinitro-m-phenylenediamine (2,4,6-Trinitro-1,3-diaminobenzene, 2,4,6-Trinitrophenylendiamin-(1,3) in Ger, 2,4,6-Trinitrometaphenylenediamin in Fr). $C_6H_5N_5O_6$, mw 243.14, N 28.81%, OB to CO_2 –55.9%, yel needles or plates from alc, mp 280–288° (decomps 301°).



It was prepd in 1884 by Nölting and Collin (Ref 2) from ethyl- or methyl-esters of Styphnic Acid and alc ammonia. Blanksma (Ref 3) prepd it from 3-chlor-2,4,6-trinitroanisole (or 3-chlor-2,4,6-trinitrophenetole) and alc ammonia, Körner and Contardi (Ref 4) from 2,4-dibrom- (or dichlor)-1,3,5-trinitrobenzene and alc ammonia, and Flürscheim (Ref 5) from tetranitroaniline and ammonia

C.F. van Duin et al (Ref 6) reviewed all of the methods previously used, and described the following method of prepn: "Mix 10g of finely pulverized trinitro-m-anisidine (or phenetidine) with 80ml of concd ammonia (d 0.90g/cc) and leave for 24 hours at room temp. Shake frequently. Filter, wash the ppt with w to remove the ammonia, and boil with alc to remove traces of non-reacted TNAnis or TNPhenet. The mp of the product should be around 285°, but it rises slightly to 287–288° if the product is recrystd from gl acet ac" (See also Ref 1, pp 60, (17) & [33])

Except for being somewhat sol in acet ac and alc, it is nearly insol in all solvents

Its expl properties were examined by van Duin et al (Ref 6) and are as follows:

Explosion Temperature (Ref 6, pp 169–171). Using the method prescribed by the Ger Railway Commission (see Vol **7**, I26-L);

Method A. Temp 335° (by heating the bath at a rate of 20° per minute). TNT=321°, PA 316° & Tetryl 196°

Method B. Temp 320° (by heating the bath at a rate of 5° per minute). TNT=304°, PA 309° & Tetryl 187°

Impact Sensitivity. (Ref 6, pp 171–175). Using the Lenze-Kast app (see Marshall **2** (1917), 423) at a temp of 19–23° with 33mg samples:

Explosive	Maximum Fall for 0/6 Shots		Minimum Fall for 6/6 Shots	
	2kg wt	10kg wt	2kg wt	10kg wt
2,4,6-Trinitro-m-phenylenediamine	> 60cm	> 24cm	> 60cm	> 24cm
Tetryl	51cm	14cm	> 60cm	> 24cm
TNT	> 60cm	> 24cm	> 60cm	> 24cm
Picric Acid	> 60cm	> 24cm	> 60cm	> 24cm

Thermal Stability. When heated at 95° for 30 eight-hr days, no change in compn took place

From the above results, it was concluded that 2,4,6-Trinitro-m-phenylenediamine is comparable to TNT in expl properties

Refs: 1) Beil **13**, 29, 32, 57–60, (10, 16–17, 38), [21, 30–33, 59–60] 2) E. Nölting & A. Collin, Ber **17**, 260 (1884) 3) J.J. Blanksma, Rec **21**, 324 (1902) 4) W. Körner & A. Contardi, AttiAccadLinceiMem (5), **17**, I, 465 (1908); Ibid (5), 18, I, 93 (1909) 5) B. Flürscheim, ChemZtr **1912**, I, 620 6) C.F. van Duin & B.C.R. van Lennep, Rec **39**, 145, 151, 165, 170 (1920) 7) H.F.J. Lorange, Ibid **46**, 649–50 (1927)

α-Phenylethanol (α-Phenylethyl alcohol, Methylphenyl carbinol). $C_6H_5.CHOH.CH_3$, mw 122.16, liq, bp 203.6° at 475mm, d 1.019g/cc at 13/4°. Prepn and other properties are given in Beil **6**, 475, (236) & [445]

β-Nitro-α[2-nitrophenyl]-ethanol nitrate (α-[2-Nitrophenyl]-β-nitroethyl nitrate, 1-[o-Nitrophenyl]-2-nitroethyl nitrate). $(O_2N).C_6H_4.CH(ONO_2).CH_2.NO_2$, mw 257, N 16.4%, OB to CO_2 −77.8%, pale yel crysts, mp 132–133°. Sol in acet-alc and is decompd by warm w. Can be prepd by nitrating the condensation product of o-nitrobenzaldehyde and nitromethane in the presence of trimethylamine

It is an expl with a ballistic strength about 99% that of TNT, and its sensitivity is comparable to that of Tetryl. Its thermal stability is satisfactory, and its hygroscopicity is slight

Refs: 1) Beil–not found 2) L.F. Fieser et al, OSRD **176** or **PBL 31091** (1941), 9–12

β-Phenylethanol (Benzylcarbinol). $C_6H_5.CH_2.CH_2OH$, mw 122.16, colorl oil, bp 219–221° at 750mm, d 1.023g/cc at 13/4°, sol in alc and eth. Methods of prepn are given in Beil. Nitration of this product resulted in an oily product which expld from a hammer blow. It was probably impure trinitrophenylethanol (see below)

Ref: Beil **6**, 478, (237) & [448]

β-[2,4,6-Trinitrophenyl] ethanol (2,4,6-Trinitrobenzylcarbinol). $(O_2N)_3.C_6H_2.CH_2.CH_2OH$, light yel crysts, mp 112°; sl sol in w, sol in benz & toluene. It was prepd by heating α-TNT with formaldehyde in weak alkaline soln. Its expl properties have not been examined. On nitration it gives the expl:

β-[2,4,6-Trinitrophenyl] ethanol Nitrate (β-[2,4,6-Trinitrophenyl] ethyl nitrate). $(O_2N)_3.C_6H_2.CH_2.CH_2(ONO_2)$, mw 302, N 18.5%, OB to CO_2 −53.0%, crysts, mp 83°. It was prepd by Vender (Ref 2) by nitrating the above trinitrophenyl alcohol. It is an expl which can be detonated by heat or impact

Refs: 1) Beil **6**, (239) 2) V. Vender, Gazz **45**, II, 97 (1915); Ibid, JCS **108**, I, 956 (1915) 3) Blatt, OSRD **2014** (1944)

Phenylether or Phenyloxide. See under Diphenylether and Derivatives in Vol **5**, D1352-R ff

Phenylethylamine. See under Ethylaniline and Derivatives in Vol **6**, E206-L ff

Phenylethyleneglycol (Phenylglycol). $C_6H_5.CH(OH)CH_2OH$, needles from ligr or benz, mp 67–68°, bp 272–274° at 755mm. Sol in w, alc, benz, eth, chlf & acet ac; sl sol in ligr. Can be prepd by heating styrene dibromide, $C_6H_5CHBr.CH_2Br$, at 125° with Pb acetate and acet ac, and then heating the resulting acetate with K carbonate soln (Refs 1 & 2). Other methods of prepn are given in Ref 3

On nitration, it gives the expls detailed below

Refs: 1) Beil **6**, 907, (444) & [887] 2) W.L. Evans & L.H. Morgan, JACS **35**, 58 (1913) 3) H.H. Lewis, M. Nierenstein & E.M. Rich, Ibid **47**, 1731 (1925)

Phenylethyleneglycol Nitrated Products. Nitration of phenylethyleneglycol with mixed nitric-sulfuric acid gave an expl product, mp ca 85°, which was claimed to be 110% as powerful as TNT, as detd by the Trauzl test, and whose performance was intermediate between that of Tetryl and TNT (Ref 1)

Fishbein's subsequent investigations (Ref 2) showed that this expl consisted of about 80% mononitrophenylglycol dinitrate,

$(O_2N)C_6H_4.CH(ONO_2)CH_2(ONO_2)$, and about 20% dinitrophenylglycol dinitrate, $(O_2N)_2C_6H_3.CH(ONO_2).CH_2(ONO_2)$

This mixt, as well as other nitro-nitrates of aryl-substituted polyhydric alcohols, was recommended for use in expls, either alone or with appropriate additives, eg, in proplnts, primer compns, detonators, etc

It was suggested that trinitrophenylglycol dinitrate, $(O_2N)_3C_6H_2.CH(ONO_2).CH(ONO_2)$, might be prepd by further nitration

Refs: 1) Westfälisch-Anhaltische Sprengstoff AG, GerP 558126 (1932); ChemZtr **1932**, II, 3185 2) M.S. Fishbein, VoyennayaKhimia-(Russia), No 6, 3–8 (1933); ChemZtr **1934**, II, 1074–5 & CA **29**, 7077 (1935)

Phenylethyleneglycolether Derivatives. See under β-Phenoxyethanol and Derivatives in this Vol

bis (Phenylethyleneglycol)-ether Derivatives. See under Ethyleneglycol Diphenylether in Vol **6**, E255-R

Phenylglycolether Derivatives. See under β-Phenoxyethanol and Derivatives in this Vol

Phenylguanidine. $C_6H_5.NH.C(:NH).NH_2$, mw 135.19, monoclinic crysts, mp 65–67°. Prepn and other properties are given in Beil **12**, 369, (235) & [216]

Dinitrophenylnitroguanidine. $(O_2N)_2C_6H_3.NH.C(:NH).NH(NO_2)$, mw 258.19, N 27.90%, OB to CO_2 –68.2%, crysts from alc, mp 175–178°. It was prepd by Elderfield et al (Ref 2) by gradually adding 2g of nitrophenylguanidine sulfate (dissolved in 5ml concd sulfuric acid) to 10ml of fuming nitric acid (d 1.5g/cc) at such a rate that the temp remains at 10°. The mixt was then stirred for 30 minutes at 25–30°, then for 45 minutes at 45–50°, and finally drowned in ice w. It is an expl

2,4,6-Trinitrophenylguanidine (Picrylguanidine). $(O_2N)_3C_6H_2.NH.C(:NH).NH_2$, mw 270, N 35.5%, OB to CO_2 –65.3%. Prepd by the action of cyanamide on trinitroaniline. Reported impact sensitivity, FI 110% of PA. It was too reactive for use as a HE (Ref 4)

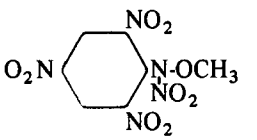
N-2,4,6-Trinitrophenyl-N′-nitroguanidine. $(O_2N)_3C_6H_2.NH.C(:NH).NH(NO_2)$, mw 315.19, N 31.11%, OB to CO_2 –43.1%, colorl crysts, mp 225–226° (decompn). Can be prepd by heating a soln of 5g of dinitrophenylnitroguanidine in mixed acid (5ml sulfuric, 20ml nitric, d 1.5g/cc) for 1 hr at 80°, and then pouring onto ice. Another method is the one step nitration of nitrophenylguanidine sulfate, as described in Ref 3

Trinitrophenylnitroguanidine expld with a bright flash and little smoke when heated in an open dish, or when struck by a hammer on an Fe plate

Refs: 1) Beil **12**–not found 2) R.C. Elderfield et al, OSRD **158** or **PBL 31085** (1941), 18–21 3) Ibid, OSRD **907** or **PBL 31094** (1942), 12–13 4) Blatt, OSRD **2014** (1944)

Phenylhydrazine and Derivatives. See under Hydrazinobenzene and Derivatives in Vol **7**, H207-L ff

2,4,6-Trinitrophenylmethoxynitramine (Tetroxyl).



$C_7H_5N_5O_9$, mw 303, N 23.1%, OB to CO_2 –39.6%. Sensitivity to impact, FI 36% of PA. Pb block expansion, 131% of PA

Refs: 1) Beil–not found 2) Blatt, OSRD **2014** (1944)

Phenylmethyl Ether, Nitrated Compounds. See under Anisole and Derivatives in Vol **1**, A448-L ff

Phenylnitramine (Nitranilide, Diazobenzolic Acid). $C_6H_5.NH.NO_2$, mw 138.13, N 20.28%, OB to CO_2 –150.6%, wh leaflets, mp 46–46.5°, explds on rapid heating. Sol in w, sl sol in cold ligr, v sol in alc and other org solvents. Can be prepd by the action of N_2O_5 on an ethereal soln of aniline at –20°, or by other methods. Its Ag

and Pb salts are expl
Refs: 1) Beil **16**, 661–3, (395) & [343] 2) E. Bamberger et al, Ber **26**, 486–90 (1893); **27**, 584–7 (1894) 3) Hackh's (1972), 47-R

2-Nitrophenylnitramine. $O_2N.C_6H_4.NH.NO_2$, mw 183.12, N 22.95%, OB to CO_2 –91.2%, pale yel needles or brownish yel plates, mp 65.5°, explds on rapid heating. Can be obtained by nitrating 2-nitroaniline with nitric acid and Ac_2O. Forms salts, some of which are expl

3-Nitrophenylnitramine. Pale yel needles, mp 92°, explds on rapid heating. Can be prepd by nitrating 3-nitroaniline as above. Forms salts, some of which are expl

4-Nitrophenylnitramine. Pale yel needles, mp 110–111°, explds on rapid heating. Can be prepd by nitrating 4-nitroaniline as above. Forms salts, some of which are expl

Refs: 1) Beil **16**, 666 2) E. Bamberger & E. Hoff, Ber **28**, 401 (1895) 3) E. Bamberger, Ber **30**, 1253 & 1256 (1897) 4) E. Hoff, Ann **311**, 107–110 (1900)

2,4,6-Trinitrophenylnitramine (2,4,6-Trinitro-N-nitroaniline, Picrylnitramine). $(O_2N)_3.C_6H_2.NH.NO_2$, mw 273.12, N 25.64%, OB to CO_2 –32.2%. Golden yel crysts, mp explds <90°, easily sol in eth and most other org solvents. Can be prepd by the action of K nitrite on 2- or 4-nitroaniline, dissolved in sulfuric acid monohydrate, cooled to 5°

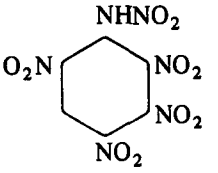
It is a very powerful and sensitive expl. Forms salts, some of which are expl

Refs: 1) Beil **16**, 688 2) O. Witt & E. Witte, Ber **41**, 3090–94 (1908)

2,4,6-Trinitrophenylbutylnitramine. See under "Butyl Tetryl" in Vol **2**, B379-R

2,4,6-Trinitrophenylethylnitramine. See under "Ethyl Tetryl" in Vol **6**, E207-L & E319-R

2,3,4,6-Tetranitrophenylnitramine. $C_6H_2N_6O_{10}$,



mw 318, N 26.4%, OB to CO_2 –15.1%, mp 98° decompn. It was prepd prior to WWII in Engl and was considered too reactive and sensitive for consideration as a mil HE. Pb block expansion 170% PA

Refs: 1) Beil–not found 2) Blatt, OSRD **2014** (1944)

Phenylnitromethane. $C_6H_5.CH_2.NO_2$, mw 137.13, N 10.21%, yel liq; bp 135° at 25mm and 141–2° at 35mm (with slight decompn); d 1.160g/cc at 20/0°. Can be prepd by heating toluene with dil nitric acid (d 1.12g/cc) in a sealed tube (Ref 2) or by other methods (Refs 3 & 4)

Refs: 1) Beil **5**, 325, (161) & [249] 2) M. Konovalov, Ber **28**, 1861 (1895) 3) M.L. Sherrill, JACS **46**, 2756 (1924) 4) J.R. Johnson, Ed, "Organic Syntheses", **19**, 73, J. Wiley, NY (1939)

3,5-Dinitrophenylnitromethane. $(O_2N)_2.C_6H_3.CH_2(NO_2)$, mw 227.14, N 18.50%, OB to CO_2 –74.0%; nearly colorl, large flat plates; mp 130–132°. Was first prepd by Holleman (Ref 2). Later, Urbański (Ref 3) prepd it by nitrating 3-mononitrophenylnitromethane with fuming nitric-sulfuric acid, which in turn was obtained by treating phenylnitromethane with fuming nitric acid at 15°. Fieser et al (Ref 4) verified Urbański's method, obtaining yields of 71–73.5%

Dinitrophenylnitromethane is an expl with about the same power as TNT, but is more sensitive to impact. It is very stable to heat. It ignites at about 343° when heated unconfined at the rate of 10° per minute. Some of its salts are expl

Refs: 1) Beil–not found 2) A.F. Hollemann, Rec **14**, 121 (1895) 3) T. Urbański, CR **206**, 1124 (1938) & CA **32**, 4959 (1938) 4) L. Fieser et al, OSRD **176** (1941), 2, 15 & 19 5) Urbański **1**, 598 (1964)

(m-Nitrophenyl)-dinitromethane. $(O_2N)C_6H_4.CH(NO_2)_2$, mw 227.14, N 18.50%,

OB to CO_2 –74.0%, yellowish to colorl prisms, mp 121–130° (various investigators), d 1.29 g/cc, insol in w, sol in methanol and acet

It was first prepd by Milone & Massa (Ref 2) by nitrating phenyldinitromethane with strong nitric acid (d 1.52g/cc). Fieser et al (Ref 3) prepd it using two methods: a) nitration of phenyldinitromethane; and b) by direct synthesis using the "Ponzio" reaction in which an ethereal soln of m-nitrobenzaldoxime is added dropwise and under reflux to an ethereal soln of nitrogen peroxide;

$2(O_2N).C_6H_4.CH:NOH + 5NO_2 \rightarrow 2(O_2N).C_6H_4.CH(NO_2)_2 + 3NO + H_2O$

The yield in the latter method was low, about 27.5%

Its expl properties are given below:

Ballistic Strength. 100% TNT (BuMines)

Explosion Temperature. Does not expld or ignite at 360° or below

Heat of Combustion. 818.1kcal/mole

Hygroscopicity. Practically none

Impact Sensitivity. Comparable to TNT

Power. By Trauzl test, 103% TNT

Rifle Bullet Test. No detonations from impact of .30 cal bullet at 90 ft

Thermal Stability. Unsatisfactory, loses 49% of wt in 48 hrs at 75° (International Test)

Velocity of Detonation. No information

Salts of (m-Nitrophenyl)-dinitromethane. Milone and Massa (Ref 2) prepd several metallic salts and found that their expl power decreased with increasing atomic wt of the metal. Following are some of the expl salts: K salt–yel crysts; Ag salt–golden yel crysts; Ba salt–yel needles; Pb salt–orange yel ppt; Amm salt–yel flakes. In general, the salts are more sensitive and less powerful than the parent compd

Refs. 1) Beil–not found 2) M. Milone & A. Massa, Gazz **70**, 196 (1940) & CA **34**, 457 (1940) 3) L.F. Fieser et al, OSRD **176** (1941), 32 4) R. McGill, OSRD **830** (1942), 49 5) L.F. Fieser & W. vonDoering, JACS **68**, 2252 (1946) 6) Urbański **1** (1964), 598

1-[5-Phenyloxazolyl-(2)]-benzenediazonium hydroxide-(2). $C_6H_5.C(O).C(C_6H_5).N(:N).OH$ (derivative of oxazole). Its chloride, $C_{15}H_{11}ON_3Cl$, orange colored crysts with mp 128° (decompn), can be prepd by treating 5-phenyl-2-[2-aminophenyl]-oxazole with isoamyl nitrate and eth. This diazonium chloride forms a stable **aurichloride** salt, $C_{15}H_{11}ON_3+AuCl_3$, which melts and then explds at about 163°

Refs: 1) Beil **26**, (441) 2) J. Lister & R. Robinson, JCS **101**, 1311 (1912)

2-Nitro-2-(3′-nitrophenyl)-propanediol-1,3-dinitrate (2-Nitro-2-(m-nitrophenyl)-propane-1,3-diol-dinitrate). $(O_2N)C_6H_4.C(NO_2):(CH_2ONO_2)_2$, mw 332, N 16.9%, OB to CO_2 –57.8%, pale yel acicular prisms, mp 71–73.6°. Can be prepd by nitrating 2-nitro-2-(3′-nitrophenyl)-propanediol-1,3 with mixed nitric-sulfuric acid, as described in Ref 2, p 23. Sol in most common organic solvents

It is an expl, having a ballistic strength of 114% (TNT=100); impact sensitivity–less sensitive than TNT; friction sensitivity–no detonations; ignition temp–270°; practically non-hygroscopic and of satisfactory thermal stability

Refs: 1) Beil–not found 2) L.F. Fieser et al, "Aromatic, Aliphatic Nitrocompounds and Nitrate Esters", OSRD **176** (1941) 3) R. McGill, OSRD **830** (1942), 48

2-Nitro-(3′,5′-dinitrophenyl)-propanediol-1,3-dinitrate. $(O_2N)_2.C_6H_3.C(NO_2):(CH_2.ONO_2)_2$, mw 377.19, N 18.57%, OB to CO_2 –40.3%; yellowish, flat, rectangular plates (sometimes prisms); mp 114–115.8°, d 1.70g/cc. Sol in acet, sl sol in cold alc. Q_c 1022.9kcal/mole

Can be prepd by gradually adding, over a 6 minute period, 20g of 2-nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 to 130ml of fuming nitric acid (d 1.5g/cc), cooled to 5° (this raises the temp to about 10°). This mixt is drowned in 1.5ℓ of ice w, and after about 15 minutes, the gummy solid is washed with cold w. The gummy material is dissolved in acet, and the soln filtered and dild with alc until the first appearance of turbidity. Crystn occurs when the suspension is allowed to stand

It is an expl comparable to Tetryl in strength, and to PETN in sensitivity to mechanical action

Bal Mort Test. 126% TNT

Explosion Temp. Ignites but does not expld at about 360°

Friction Sensitivity. Comparable to Cyclonite
Hygroscopicity. Practically non-hygroscopic
Impact Sensitivity. Slightly less sensitive than PETN
Thermal Stability. Satisfactory
Refs: 1) Beil–not found 2) L.F. Fieser, "Aromatic, Aliphatic Nitrocompounds and Nitrate Esters", OSRD **176** (1941) 3) R. McGill, OSRD **830** (1942)

4-Nitrophenylpropiolic Acid. $(O_2N)C_6H_4.C{:}C.COOH$, mw 191.14, N 7.33%, needles from alc or eth, mp 181° (decomps explosively on further heating). Easily sol in hot alc, acet ac or eth, very sl sol in carbon disulfide, difficulty sol in w, benz and chlf, insol in petr eth

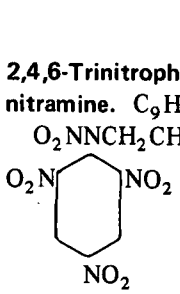
Can be prepd by treating phenylpropiolic acid, $C_6H_5.C{:}C.COOH$ (Beil **9**, 633, (265) & [436]) with nitric acid (d 1.5g/cc) at −20° (Ref 3), or by other methods (Refs 1 & 2)

It is a weak expl and forms salts which are more or less expl:

Ba salt. Needles, insol in w; puffs off on heating
Ca salt. Needles, puffs off on heating
Ag salt. Yel amorph powder; puffs off violently on heating; ignites on contact with concd sulfuric acid

Refs: 1) Beil **9**, 637, (267) & [438] 2) V.B. Drewsen, Ann **212**, 154 (1882) 3) S. Reich, CR **162**, 129 (1916); Ibid, JCS **110**, I, 210 (1916)

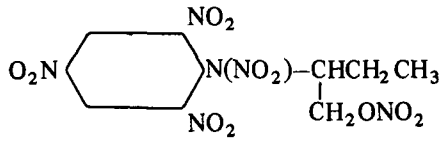
2,4,6-Trinitrophenyl (β,γ-Dinitroxy) Propylnitramine. $C_9H_7N_7O_{14}$, mw 437, N 22.4%,



OB to CO_2 −27.4%. Can be prepd by condensing aniline with glycerol, and the product nitrated. Ref 2 states that this material has adequate stability and sensitivity, together with "the greatest power of any known nitro compound"

Refs: 1) Beil–not found 2) Westfälisch-Anhaltische Sprengstoff AG, GerP 576152 (1933) & CA **27**, 3823 (1933) 3) Blatt, OSRD **2014** (1944)

2,4,6-Trinitrophenyl-(1-Methylol) Propylnitramine Nitrate. $C_{10}H_{10}N_6O_{11}$, mw 390,



N 21.5%, OB to CO_2 −57.4%, mp 140° (decompn). Can be prepd by condensing dinitrochlorobenzene and 2-amino-1-butanol, and nitrating the product

Its impact sensitivity is comparable to Tetryl; BalMort 117% TNT. It ignites at 210°, but does not expld to 360°. It explds in 30 minutes at 135°, but no expln results after 300 minutes at 100°. At 25°, it gains 0.19% by wt at 100% relative humidity

Refs: 1) Beil–not found 2) Blatt, OSRD **2014** (1944)

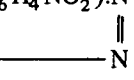
(1-Phenyl,3-ethyl)-tetrazene(1) [(3-Ethyl, 1-phenyl)-tetrazene(1), Benzoldiazo-[α-athylhydroazid] or 3-Aethyl-1-phenyltetrazen(1) in Ger]. $C_6H_5.N{:}N.N(C_2H_5).NH_2$, mw 164.24, N 34.12%, oily liq, bp explds. Was prepd by Fischer and Troschke in 1879 (Ref 2) by introducing a benzenediazonium salt into a cold aq soln of ethylhydrazine. It is sol in eth and is decompd by alkalies. A very unstable compd, which deflagrates on rapid heating. It forms salts which are also unstable

Refs: 1) Beil **16**, 746 2) E. Fischer & H. Troschke, Ann **199**, 306–7 (1879) 3) E. Fischer, Ber **43**, 3500 (1910)

Phenylaminotetrazoles. See under Aminophenyltetrazoles and Derivatives in Vol **1**, A246-R to A249-L

1-Phenyl-tetrazole. mw 146.17, N 38.34%, crysts from aq alc or benz with ligr, mp 65–66°. Can be prepd by the oxidation of 1-phenyl-5-mercaptotetrazole with Cr trioxide in boiling acet acid, or by treating sym diformylhydrazine, OHC.NH.HN.CHO, and benzenediazonium chloride, $C_6H_5.N_2Cl$, with dil Na hydroxide soln. Insol in w, diff sol in ligr, sol in methanol, ethanol, chlf, acet and benz

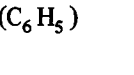
[1-(p-Nitrophenyl)]-tetrazole (Called 1-[4-Nitrophenyl]-tetrazol by Beil). Mw 191.17, N 36.64%, OB to CO_2 −121.4%, white crysts, mp 205° (with violent decompn).



Can be prepd by the nitration of 1-phenyltetrazole with fuming nitric acid, or by heating sym diformylhydrazine, OHC.HN.NH.CHO, and p-nitrobenzenediazonium chloride, $O_2N.C_6H_4.N_2Cl$, with dil Na hydroxide soln. Insol in w and ligr, diff sol in benz and eth, sol in ethanol and methanol, v sol in acet. Puffs off when heated above its mp

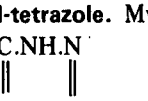
Refs: 1) Beil **26**, 347 & (109) 2) M. Freund & T. Paradies, Ber **34**, 3120–21 (1901) 3) O. Dimroth & G. deMontmollin, Ber **43**, 2907–8 (1910) 4) F.R. Benson, ChemRevs **41**, 5 (1947)

2-Phenyl-tetrazole. Mw 146.17, N 38.34%, liq, bp (puffs off on heating above 170°). Can be prepd by heating 2-phenyl, 5-carboxytetrazole (Beil **26**, 560) to 150–170°. Nearly insol in w; sol in concd acids, alc & eth



Refs: 1) Beil **26**, 347 2) J.A. Bladin, Ber **18**, 2911 (1885) 3) E. Wedekind, Ber **31**, 948 (1898) 4) F.R. Benson, ChemRevs **41**, 5 (1947)

5-Phenyl-tetrazole. Mw 146.17, N 38.34%; white rhomb-pyramidal crysts; mp 213–15° (decompn). Can be prepd by treating benzhydrazideimide, $C_6H_5.C(:NH).NH.NH_2$ (Beil **9**, 328), with Na nitrite plus HCl or HNO_3, or by treating N,N′-bis [α-imino-benzyl]-hydrazine, $C_6H_5.C(:NH).NH.NH.C(:NH).C_6H_5$ (Beil **9**, 329), with Na nitrite plus acet acid. Nearly insol in cold w, benz and petr eth; sl sol in hot w and in eth; sol in alc. Decomps explosively on rapid heating above about 250°



Forms salts, some of which are expl:

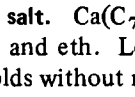
Calcium salt. $Ca(C_7H_5N_4)_2.4H_2O$. Needles from alc and eth. Loses w at 140–150° and then explds without melting (Ref 1)

Copper salt. $Cu(C_7H_5N_4)_2$. Crysts, mp decomps at 130° and deflagrates when heated rapidly on a Pt foil

Other salts are also known, such as the NH_4, Ba, K and Ag, but they have not been reported as being expl

5-Phenyltetrazole also forms nitrocompds, such as:

[5-(m-Nitrophenyl)]-tetrazole (Called 5-[3-Nitrophenyl]-tetrazol by Beil). Mw 191.17, N 36.64%, OB to CO_2 −121.4%, mp 145° (when heated under w). Was prepd by Lossen & Statius (Ref 4, p 104) by treating 5-phenyltetrazole with nitric acid (d 1.5g/cc). V sol in alc, sol in eth and hot w, insol in benz. Explds on heating above its mp. It forms salts, some of which are expl:



Silver salt. $AgC_7H_4(NO_2)N_4$. Pale yel solid which puffs off on heating on a Pt foil (Ref 1, p 364)

Refs: 1) Beil **26**, 362 & 364 2) W. Lossen, C. Lossen et al, Ann **263**, 101–108 (1890) 3) A. Pinner, Ber **27**, 990–99 (1894); Ann **297**, 229, 235, 248 & 249 (1897) 4) W. Lossen & F. Statius, Ann **298**, 91–105 (1897) 5) A. Pinner, Ann **298**, 104 (1897)

[1-Phenyl, 5-azido]-tetrazole. Mw 187.19, N 52.39%, leaflets, mp 99°. Can be prepd by adding dropwise, a soln of Na nitrite to a well-cooled HCl soln of phenyl-1-hydrazine-5-tetrazole. Insol in w, sl sol in eth, sol in hot alc, sl sol in cold alc. Puffs off with a loud report when heated rapidly in a sealed tube

Refs: 1) Beil—not found 2) R. Stolle, JPrakt-Chem **134**, 284 & 297 (1932)

[2-Phenyl, 5-carboxy]-tetrazole. Mw 182.18, N 30.76%; mp, for the anhydr salt, 137–38° (decomps at about 150°). Crystallizes from w as needles with one H_2O, but loses it on desiccator drying. Was prepd by Bladin in 1885 (Ref 2) by heating 2-phenyl, 5-cyanotetrazole with alc KOH. Wedekind prepd it by the oxidation of 2-phenyl-5-[4-aminophenyl]-tetrazole with K permanganate in warm dil nitric acid (Ref 3)

Sol in w, v sol in methanol and alc, diff sol in eth

It forms salts, some of which are expl:

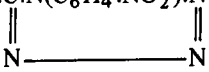
Copper salt. $Cu(C_8H_5O_2N_4)_2.2H_2O$. Greenish-

blue plates, losing w at 125° and exploding at higher temps

Silver salt. $AgC_8H_5O_2N_4$. Colorl powder, puffs off on heating

Phenylcarboxytetrazole forms nitrocompds, such as:

[2-(p-Nitrophenyl), 5-carboxy]-tetrazole (Called 2-[4-Nitrophenyl]-carbonsäure-(5) by Beil).



$(HOOC).C.N(C_6H_4.NO_2).N$
$N———N$

Mw 235.18, N 29.78%, mp 175° (decompn). Can be prepd by treating 2-phenyl, 5-carboxy-tetrazole with fuming nitric acid

Rathsburg (Ref 5) patented some expl salts and derivatives of phenylcarboxytetrazole, which he called phenyltetrazole-carboxylic acid, for use in detonators and percussion caps

Refs: 1) Beil **26**, 560 2) J.A. Bladin, Ber **18**, 2908 (1885); **25**, 1411 (1892) 3) H. Wedekind, Ber **31**, 943 (1898) 4) O. Dimroth et al, Ber **41**, 4057–58, 4066–68 (1909) 5) H. Rathsburg, BritP 185555 (1922) & CA **17**, 1147 (1923)

[1-Phenyl(3-α-"ethylpropionate"), 4-carboxamide]-tetrazene(1). *Note:* α-ethylpropionate (or more correctly, in the opinion of the editor, α-ethylpropionatyl) is the proper name for the radical $-CH(CH_3).CO_2.C_2H_5$, derived from α-propionic acid ethyl ester.

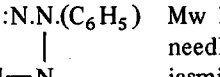
$(C_6H_5).N:N.N[CH(CH_3).CO_2.C_2H_5].NH(CO.NH_2)$, mw 279.34, N 25.08%, crysts from aq alc, mp (melts with expln ca 125°)

Was prepd by Bailey and Knox (Ref 2) from benzenediazonium chloride and α-semicarbazino-propionic acid ethylester (Beil **4**, 557)

Sol in alc, ethyl acetate & chlf; sl sol in eth; insol in benz & petr eth

Refs: 1) Beil **16**, 747 2) J.R. Bailey & L. Knox, JACS **29**, 884 (1907)

[2-Phenyl, 5-methyl]-tetrazole (Was called 1-Phenyl-4-methyl-tetrazol by Dimroth, Ref 2).

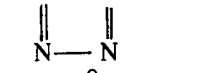


$(CH_3).C:N.N.(C_6H_5)$
$N=N$

Mw 160.20, N 34.98%, needles from gasoline, jasmine odor, bp 140° at 15mm. Can be prepd by treating 2,4,6-tribrom-1-azidobenzene with acetaldehyde phenylhydrazone in Na ethylate soln. Sol in eth and fuming nitric acid. Decomps explosively on distn at atm press

Refs: 1) Beil **26**, (110) 2) O. Dimroth & S. Merzbacher, Ber **43**, 2903 (1910)

5-Picrylaminotetrazole. Mw 296.19, N 37.84%,



$C_6H_2(NO_2)_3.NH.C.NH.N$
$N—N$

pale yel crysts, mp 224°. Can be prepd by heating 5-aminotetrazole with picryl chloride in acet acid soln under reflux for 2 hours. Sl sol in w and alc, easily sol in acet, nearly insol in eth

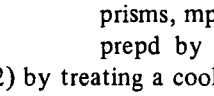
It forms salts, some of which are expl:

Silver salt. On treating a soln of picrylaminotetrazole in acet acid with a small excess of aq Ag nitrate soln, a yel ppt is obtained which corresponds to the formula $C_7H_3O_6N_8Ag$, N=27.89%. It is insol in nitric acid and difficultly sol in ammonia. It detonates violently on heating in a sealed tube or on impact

Its Cu and Pb salts were also prepd, but not analyzed. Both of them expld on heating in a sealed tube or on impact, and seem to be suitable for use as initiating agents (Ref 2)

Refs: 1) Beil—not found 2) R. Stollé & O. Roser, JPraktChem **139**, 63–4 (1933) 3) F.R. Benson, ChemRevs **41**, 7 (1947)

Pyrido-1′,2′:4,5-tetrazole. (Called 1,2,3,9-Benzoisotetrazole by Fargher & Furness (Ref 2), and Pyridotetrazole by Benson (Ref 3); 1,2,3-Triaza-indolizin or Benzisotetrazol in Ger).



$HC:CH.C:N.N$
$HC:CH.N—N$

Mw 120.13, N 46.65%, prisms, mp 159°. Was prepd by Fargher and Furness (Ref 2) by treating a cooled acet acid soln of 2-pyridylhydrazine with an aq soln of Na nitrite. Nearly insol in cold w and eth, sol in alc and acet. Explds when touched with a hot wire

Refs: 1) Beil **26**, (111) 2) R.G. Fargher & R. Furness, JCS **107**, 689 & 695 (1915) 3) F.R. Benson, ChemRevs **41**, 5 (1947)

Phenyltriazene. $C_6H_5.N:N.NH_2$, mw 121.16, N 34.69%, colorl crysts, mp 50° with rapid

decompn. Can be prepd by reduction of azidobenzene, using Sn chloride, as described in Ref 2. It is very unstable, even at room temp. Forms salts, some of which are expl:

Copper salt. $C_6H_5.N_3HCu$; yel crysts; deflagrates on heating without melting

Silver salt. $C_6H_5.N_3HAg$; deflagrates on standing at room temp

Refs: 1) Beil **16**, 685–6 2) O. Dimroth, Ber **40**, 2378–9 (1907)

1-Phenyl-1-oxy-III-benzenesulfonyl-triazine (3-Benzolsulfonyl-1-phenyltriazen-(1)-oxyd-(1) in Ger). $C_6H_5.(O:)N:N.NH.SO_2.C_6H_5$, mw 277.32, N 15.15%, needles, mp decomps 102°. Can be prepd from N,N′-dibenzolsulfonylhydrazine and nitrobenzene in the presence of alkali. It explds very violently on rapid heating or on impact

Refs: 1) Beil **16**, (414) 2) A. Angeli, Atti-AccadLinceiRend (5), **24**, I, 1098 (1915); JCS **108** (Abs 1), 847 (1915)

1-Phenyl-III-p-phenylmercaptotolyl-triazine (N′-Phenyl-N-p-phenylmercaptotolyl-triazine). $C_6H_5.N:N.NH.C_6H_4.S.C_6H_4.CH_3$, mw 319.45, N 13.16%; yel crysts from aq alc; mp 85°; bp, puffs off on rapid heating. Sol in alc and eth. Was prepd from the benzenediazonium hydrochloride, Na acetate, and [4-aminophenyl]-p-tolylsulfide (Beil **13**, 534). It explds on rapid heating above its mp

Refs: 1) Beil **16**, 720 2) A. Heiduschka & E. von Meyer, JPraktChem **68**, 275–6 (1903)

Phenylbenzotriazoles. See under Benzophenyltriazole and Derivatives in Vol **2**, B78-R to B79-R

1-Phenyl-4-nitro-5-nitraminobenzotriazole. See under Aminobenzotriazoles and Derivatives in Vol **1**, A190-R

Phenyltoluidines. See under Anilinotoluene; Diphenylmethylamines and Derivatives in Vol **1**, A438-L ff

Phenylurea and Its Nitrocompounds. See under Urea

Phermex. A 20-MeV, high intensity, high current flash radiographic app which was designed and built to complement other hydrodynamic facilities of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico. See Vol **4**, D342-R for further information and a schematic diagram

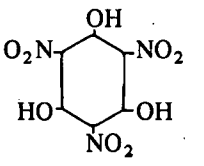
Ref: D. Venable and T.J. Boyd, Jr, "PHERMEX Applications to Studies of Detonation Waves and Shock Waves", 4th ONRSympDeton (1965), 639–47 (29 refs are included)

Phlegmatization of Explosives. See under Desensitization (Phlegmatization) of Explosives in Vol **3**, D88-L to D90-L, and Microencapsulation in this Vol

Phloroglucinol (1,3,5-Trihydroxy benzene, 1,3,5-Trioxy-benzol in Ger). $C_6H_3(OH)_3$, mw 126.11, white to yellowish crysts; mp 200–209° when heated slowly; 212–217° when heated rapidly; bp, sublimes with decompn. Sl sol in w, sol in alc and eth. Combustible. Can be prepd by fusion of resorcinol with caustic soda, or by reduction of trinitrobenzene. It is highly toxic by ingestion, inhalation and skin absorption, and is a strong irritant to skin and mucous membranes

Refs: 1) Beil **6**, 1092, (545) & [1075] 2) Merck (1968), 822-L 3) CondChemDict (1971), 685-R

Trinitrophloroglucinol (sym-Trinitrotrihydroxybenzene. $(O_2N)_3C_6(OH)_3$, mw 261.11, N 16.09%, OB to CO_2 –27.6%; yel needles with 1 mole H_2O from w; mp 167° (hydrate), 187° (with decompn for anhydr salt). Easily sol in hot w, alc, eth or benz. Explds when heated above its mp



Sorm and Drapalova (Ref 8) prepd it by boiling 1,3,5-trichloro-2,4,6-trinitrobenzene (or triaminotrinitrobenzene) with an alc NaOH soln.

Can also be prepd by treating phloroglucinol triacetate with nitric acid, or by other methods (see Ref 1)

It forms metallic salts which are more or less expl, such as Ba, Cd, K, Na and Pb, the last of which is described separately below

Refs: 1) Beil **6**, 1106–7 & [1080] 2) R. Benedikt, Ber **11**, 1376 (1878) 3) R. Nietzki & F. Moll, Ber **26**, 2185 (1893) 4) L. Jackson, AmChemJ **16**, 32 (1894) 5) J.J. Blanksma, Rec **21**, 262 (1902) and **27**, 35 (1908) 6) E. von Herz, GerP 377269 (1923); ChemZtr **1923**, IV, 622 7) E.L. Holmes, JCS **1928**, 3044 8) F. Sorm & C. Drapalova, ChemObzor **12**, 153–6 (1937) & CA **31**, 8520 (1937) 9) W.B. Woodring, USP 2206652 (1940) & CA **34**, 7610 (1940) [Primer compn contg Pb, Na or Cd salts of trinitrophloroglucinol with Pb Styphnate and other ingredients] 10) R. Schmitt, SS **38**, 149 (1943) [Quant estimation of trinitrophloroglucinol by pptn with phenyladridine soln] 11) P.J. Pearch & R.J.J. Simkins, ERDE Rept 1/R/63 (1963) [Prepn and props of trinitrophloroglucinol]

Trinitrophloroglucinol, Lead Salt of (Lead Trinitrophloroglucinate, Blei-trinitrophloroglucinat in Ger, Trinitroglucinate de plomb in Fr). $[C_6(NO_2)_3O_3]_2.Pb_3.H_2O$, after drying at 145–150°; Pb 53.77%; d 4.15g/cc at 30°; mp explds at about 210° (Ref 7)

Ficheroulle and Kovache (Ref 8) prepd the Pb salt by dissolving 2g of trinitrophloroglucinol in 50ml of w and adding, under mechanical agitation, 0.85g of NaOH. After bringing the soln to a boil, a soln of 3.80g of Pb nitrate in 50ml of w was gradually added while agitating. The soln was then cooled with agitation and the ppt sepd by vacuum filtration, washed with w and dried, first in air at room temp, and then at 145–150°

Solubility (in percent at about 18°). Water 0.12, methanol 0.05, pyr 0.06 & amyl acetate 0.04. Practically insol in benz, petr eth, chlf, trichloroethylene, carbon tetrachloride, carbon disulfide, eth and acet

Lead trinitrophloroglucinol is an expl, comparable in sensitivity to MF. According to Rathsburg (Ref 6), the impact sensitivity for the product contg 54.5% Pb using a 100g wt was 10cm (1 detonation in 6 trials) vs 12cm for MF. For a product with 53.77% Pb, Ficheroulle and Kovache (Ref 8) reported 30% detonations for a 2kg wt falling from a height of 70cm

Friction Sensitivity. Required a load of 15kg/cm^2 for a steel surface, and 20kg/cm^2 for a procelain surface (corresponding figures for MF were 12–13kg and 15kg, respectively)

Effect of heat. When anhydrous, it detonates at about 210°. The material with one H_2O deflagrates about 230°, when heated slowly, as compared to 275–290° for Pb Styphnate. Contact with flame or a red-hot wire results in immediate detonation if the material is dry, but when wet it is difficult to detonate or ignite

Thermal stability and volatility. No loss in wt was observed when stored for 300 days at 50°; for 150 days at 70°, or 50 days at 90°

Hygroscopicity. More hygroscopic than Pb Styphnate. When stored at 90% RH for 10 days it absorbed 0.24% moisture, and for 20 days, 0.90% moisture

Compatibility with metals. Moderately moist material does not attack metals; it resembles Pb Styphnate in this respect

Compatibility with explosives. Mixts with equal parts of TNT, PA, RDX, PETN, Tetryl, AN and Sb sulfide, stored for 40 days in a dry atm at 50°, remained unchanged

Uses. Pb trinitrophloroglucinol has been proposed as an ingredient of priming compns, and for use in percussion caps and detonator formulations (Refs 2, 3, 4, 5, 7 & 9)

Refs: 1) Beil **6**, [1080] 2) H. Rathsburg, BritP 190215 (1921) & CA **17**, 3101 (1923) 3) Ibid, USP 1470104 (1923) & CA **17**, 3920 (1923) 4) W. Friederich, BritP 192830 (1921) & CA **17**, 3255 (1923) 5) E. von Herz, GerP 377269 (1923) 6) H. Rathsburg, ZAngChem **41**, 1284 (1928) 7) W.B. Woodring, USP 2206652 (1940) & CA **34**, 7610 (1940) 8) H. Ficheroulle & A. Kovache, MP **31**, 11–12 & 25 (1949) 9) S. Takenaka, JapanP 6298 (1953) & CA **48**, 12410–11 (1954)

Phoenix Powders. Safety expls patented in 1899 by Sprengstoffe Dr Nahsen & Co, Hamburg, Ger. One of the newer formulations contd NG 30, Na nitrate 32, and flour 38%. Its expln temp was 2125° and its Q_c was 780cal/g (Ref 1).

Naoûm (Ref 2) states that Phoenix Powders were a variety of Brit "Carbonites" (see Vol **2**, C61-R) contg NG 28–31, K nitrate or chlorate 30–34, NC 1, and woodmeal 33–37%
Refs: 1) Daniel (1902), 449–50 [under Nahsen] 2) Naoûm, NG (1928), 402 & 440

Phorone (Diisopropylidene acetone, 2,6-dimethyl-2,5-heptadien-4-one).
$(H_3C)_2.C:CH.CO.CH:C(CH_3)_2$, mw 132.80; yel liq or yellowish green prisms; mp 28°, bp 198–199°, flash pt 185°F, d 0.885g/cc at 20/4°, vap press 0.38mm at 20°, RI 1.4968. V sol in w, sol in eth or alc. Combustible. Can be prepd by methods given in Refs 1 & 2. It has been used as a solvent for NC

When treated with ozone, it yields a very expl diozonide which ignites at room temp (Ref 2)
Refs: 1) Beil **1**, 751, (389) & [810] 2) C. Harries & H.O. Turk, Ann **374**, 338 (1910) 3) Merck (1968), 823-L 4) CondChemDict (1971), 686-L 5) Sax (1975), 1020-R

Phosgene (CG, Carbonyl or chloroformyl chloride, Carbon oxychloride). $COCl_2$, mw 98.92; colorl, highly toxic gas; suffocating odor; when much diluted with air there is an odor reminiscent of moldy hay; fr pt −127.76°, bp 8.2°, d 1.392g/cc at 19/4°. Sl sol in w and slowly hydrolyzed by it; freely sol in benz, toluene, gl acet acid, and most liq hydrocarbons. Can be prepd by passing a mixt of carbon monoxide and chlorine over activated carbon, or by other methods described in Refs 1 & 8

Phosgene was used tactically as a delayed or immediate action casualty gas. It was first employed by the Germans in WWI (Dec, 1915) in cylinders under the name D-Stoff. The French later (1916) employed phosgene as an artillery shell filler (Collingite). During the remainder of the war it was the Allies' principal war gas, used also in trench mortars, bombs, and projector drums (Ref 2)
Vapor pressure. 1173mm Hg at 20°; 555mm at 0°; 365mm at −10°
Volatility. 442,000mgs/m^3 at −40°; 2,200,000 mgs/m^3 at −10°; 6,370,000mgs/m^3 at 20°
Flashpoint. None
Decomposition temperature. 800°
Latent heat of vaporization. 60cal/g
Rate of hydrolysis. Not readily hydrolyzed under usual field conditons; however, rain destroys its effectiveness. Heavy vegetation, jungle, and forests cause considerable loss of CG by hydrolysis on leaf surfaces
Median lethal dosage. 3200mg-min/m^3
Median incapacitating dosage. 1600mg-min/m^3
Toxicology. In the presence of moisture, phosgene decomps to form HCl and CO. This action takes place within the body, when the gas reaches the bronchioles and the alveoli of the lungs. There is little irritant effect upon the respiratory tract, and the warning properties of the gas are therefore very slight. The liberation of HCl in the lung tissues results in the development of pulmonary edema, which may be followed by bronchopheumonia, and occasionally lung abscess. Degenerative changes in the nerves have been reported as later sequelae. Concns of 3 to 5ppm of phosgene in air cause irritation of the eyes and throat, with coughing; 25ppm is dangerous for exposure lasting 30 to 60 minutes, and 50ppm is rapidly fatal after even short exposure

There may be no immediate warning that dangerous concns of the gas are being breathed. After a latent period of 2 to 24 hours, the subject complains of burning in the throat and chest, shortness of breath and increasing dyspnea. Where the exposure has been severe, the development of pulmonary edema may be so rapid that the subject dies within 36 hours after exposure. In cases where the exposure has been less, pneumonia may develop several days after the occurrence of the accident. In subjects who recover, no permanent residual disability is thought to occur (Ref 12)
Disaster hazard. Phosgene is highly dangerous. When heated to decompn, or on contact with w or steam, it will react to produce toxic and corrosive fumes (Ref 12). Powdered Al burns in its vapor (Ref 3)

In the formation of tert-butyl azidoformate by the addition of phosgene to alcohols followed by the addition of Na nitride or hydrazoic acid in the presence of pyridine, reaction of phosgene with the azide can cause the formation of expl carbazide (Ref 9)

Phosgene and 2,4-hexadiyn-1,6-diol react to form 2,4-hexadiyn-1,6-bischloroformate, which

is shock sensitive (Ref 11)

The reaction between isopropyl alcohol and phosgene forms isopropyl chloroformate and HCl. In the presence of Fe salts thermal decompn can occur, which in some cases can become expl (Ref 7)

Mellor (Ref 5) reports that a mixt of K and phosgene explds when subjected to shock, and that vapors of Na and phosgene react with luminescence at about 260° (Ref 4)

The requirements of the US Armed Forces for phosgene are covered in specification **MIL-P-10455A** (18 Apr 1951), which covers two grades; Grade A – for use in munitions, max free chlorine 1.0%, and Grade B – for use in chemical manuf, max free chlorine 0.05%. Both grades are required to have a purity of 98.0% min, acidity (calcd as HCl) of 0.50% max, and residue on evaporation of 0.50%

Refs: 1) Beil **3**, {31} 2) Bebie (1943), 121 3) Mellor **5**, 214 (1946–47) 4) Ibid **2**, Supp 2, 470 (1961) 5) Ibid **2**, Supp 3, 1568 (1963) 6) Anon, "Military Chemistry and Chemical Agents", **TM3-215** (1963), 12–13 7) I.I. Konstantinov, TrKhimiKhimTechnol **10** (2), 171–4 (1967) 8) Merck (1968), 823-L 9) Anon, ChemPharBull **18** (4), 850–51 (1970) & CA **73**, 14099 (1970) 10) CondChemDict (1971), 686-L 11) P.E. Driedger & H.V. Isaacson, C&EN **50** (12), 51 (1972) 12) Sax (1975), 1020-R 13) Anon, "Toxic and Hazardous Industrial Chemical Safety Manual", The International Technical Information Institute, Tokyo (1975), 412

Phosphine (Hydrogen phosphide, Phosphorus trihydride). PH_3, mw 34.00; colorl gas, disagreeable, garlic-like odor; mp –133.5°, bp –85°, autoignition temp 100°F; d 1.185g/cc. Sparingly sol in cold w, insol in hot w, sol in alc and eth. Can be prepd by boiling yel P with an aq alkali hydroxide, or by the action of acids or w on metallic phosphides (Refs 8, 9 & 11)

Pure phosphine does not spontaneously ignite in air below 150° unless it is thoroughly dried, when it ignites in cold air. The presence of traces (0.2%) of diphosphane (P_2H_4) in phosphine as normally prepd causes it to ignite spontaneously in air, even at below –15° (Ref 5). Pure phosphine is rendered flammable by a trace of dinitrogen trioxide, nitrous acid, or similar oxidant (Ref 2)

Phosphine, generated by the action of w on Ca phosphide, was dried by passage thru towers packed with the latter. Soon after refilling the generator (but not the towers) and starting purging with argon, a violent expln occurred. This was attributed to the air, displaced from the generator by argon, reacting explosively with dry phosphine present in the drying towers, possibly catalyzed by the orange-yellow polyphosphine which forms on the surface of Ca phosphide (Ref 6)

Ignition occurs on contact with chlorine or bromine or their aq solns (Ref 3). The passage of phosphine into concd Ag nitrate soln causes ignition or expln, depending on the gas rate. Hg(II) nitrate soln gives a complex phosphide, expl when dry (Ref 4). Phosphine is violently decompd by concd nitric acid, and flame is produced. Warm fuming nitric acid, dropped into a container of phosphine gas, produces an expln (Ref 1). Even small amts of oxygen present in phosphine results in an expl mixt, in which autoignition occurs at low pressure (Ref 7)

Phosphine is highly toxic by inhalation and is a strong irritant. Tolerance 0.3ppm in air (Refs 10 & 11)

Refs: 1) T. Graham, EdinRoySoc **13**, 88 (1835) 2) Mellor **8** (1940), 811 & 812 3) Ibid, 812 4) Ibid **3** (1941), 471 & **4** (1940), 993 5) N.V. Sidgwick, "The Chemical Elements and their Compounds", Oxford Univ Press (1950), 729 6) H.A.C. McKay, Chem&Ind **1964**, 1978 7) E.O. Fischer et al, AngChem(Intern-Ed) **7**, 136 (1968) 8) Merck (1968), 823-R 9) CondChemDict (1971), 687-L 10) Sax (1975), 1021-R 11) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 413

Phosphorescence. See under Fluorescence, Luminescence and Phosphorescence in Vol **6**, F124-R

Phosphorus (Red). $P_{4(vapor)}$, mw 123.92; violet red, amorph or cryst powder; mp 597°, subl at 416°; d 2.34g/cc; autoignition temp

about 260°, burns with formation of the pentoxide. Can be obtained from white P by heating at 240° with a catalyst. Insol in w, caustic alkali, CS_2, eth and ammonia soln (Refs 5 & 6)

Red P has been employed as an ingredient of pyrotechnic smoke, delay and safety match formulations (Refs 1, 2, 3 & 4). White smoke consisting of small droplets of phosphoric acid have been widely used for military purposes. These droplets result from the reaction of P pentoxide, formed by the burning in air of the P vapor (produced by the evaporation of Red P in a fuel-oxidant mixt) and w vapor in the air:

$P_4 + 5O_2 \rightarrow 2P_2O_5$

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

$H_3PO_4 + nH_2O \rightarrow H_3PO_4$ (dilute)

P vapor is extremely toxic and causes bone decay; however, it is not present after the smoke is formed. P pentoxide and phosphoric acid are not toxic in small concns, although they may be irritating to the eyes, respiratory tract and skin (Ref 3)

Red P is used in burning-type munitions mainly for signaling purposes. Compns consisting of red P and certain oxidants or fuels are relatively slow-burning and are sometimes used in sea markers. The chemical reactions may be quite involved. For example, the main reaction for a burning mixt of Ca sulfate and red P appears to be:

$30CaSO_4+19P_4 \rightarrow 6Ca(PO_3)_2+12Ca_2P_2O_7+10P_4S_3$

The heat produced by this reaction vaporizes the remaining Red P contained in the smoke mixt. The P vapor burns on contact with air. Some sulfur dioxide is formed when the P_4S_3, produced in the above reaction, burns along with the P vapor:

$P_4S_3+8O_2 \rightarrow 3SO_2+2P_2O_5$ (Ref 3)

In the presence of moisture and air, there is a tendency for red P to slowly oxidize due to the presence of small quantities of Cu and Fe. This may result in ignition difficulty and an overall decreased performance of the smoke item. *Stabilized* red P has been produced which is not only low in Fe and Cu, but particles of less than 10 microns are mostly removed, and 2.5% of alumina is added as a stabilizer (Refs 3 & 4)

Red P is poisonous on inhalation or ingestion, but slower acting than white P. The lowest published lethal dose in man by oral ingestion is 1.4mg/kg (Ref 7). It should never be allowed to come in contact with the eyes. Red P, while less reactive than white P, is a dangerous fire hazard. It is easily ignited by spark or friction and is dangerous when in contact with organic materials or oxidizers. It can ignite spontaneously in air, and emits highly toxic fumes when heated (Ref 2)

The requirements of the US Armed Forces for red P are covered in two specifications, **MIL-P-211B** (18 June 1969) for Phosphorus, Red, Technical, and **MIL-P-670A** (18 Feb 1966) for Phosphorus, Red, Stabilized

MIL-P-211B covers two classes of material, Class 1 – fine granulation, and Class 2 – extra fine granulation. Chemical and physical requirements are detailed in Table 1 below:

Table 1
Phosphorus, Red, Technical

	Percent by weight			
	Class 1		Class 2	
Characteristic	Min	Max	Min	Max
Red phosphorus	99.0	–	99.0	–
White phosphorus	–	0.02	–	0.02
Acidity(as H_3PO_4)	–	0.10	–	0.10
Moisture	–	0.20	–	0.20
Particle size:				
Retained on a No 40 (420 micron) sieve	–	0.1	–	–
Retained on a No 100 (149 micron) sieve	–	–	–	2.0

MIL-P-670A covers one grade of aluminated red P furnished in powdered form, with the following requirements:

Granulation. Before alumination – based on a selective sedimentation test, the phosphorus shall contain a max of 3% of particles of less than 10 microns in diameter. After alumination the powder shall pass thru the following sieves:

Thru US Standard Sieve No	Percent
100	98.0 min
140	85.0 min
325	50 ± 20

Oxidation. Based on the Norma-Hoff max oxidation bomb test, the phosphorus shall show the following oxidation characteristics: Induction period – the minimum induction period shall be 20 hours. Oxidation rate – the maximum

decrease in pressure per hour for a 5 gram sample shall be 1.4psi for the visual method
Copper and iron. The maximum content of either copper or iron shall be 50 parts per million. The product of the copper content and iron content, each expressed in parts per million, shall not exceed 125
Total phosphorus. Shall be a minimum of 93 percent
White phosphorus. Shall be a maximum of 0.01 percent
Alumina. Shall be 2.5 ± 0.5 percent calculated as $Al(OH)_3$

The phosphorus, red, stabilized powder shall be free flowing and free from lumps
Refs: 1) Bebie (1943), 122 2) Anon, EngrDesHndbk, "Military Pyrotechnics Series. Part III – Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963), 223–27 3) Anon, EngrDesHndbk, "Military Pyrotechnics Series. Part I – Theory and Application", **AMCP 706-185** (April 1967), 7–21 & 7–22 4) Ellern (1968), 19, 50, 56, 66, 68, 74, 112, 120, 202 & 304 5) Merck (1968), 824-R 6) CondChemDict (1971), 689-L 7) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975)

Phosphorus (White or Yellow, WP). P_4(vapor), mw 123.92; colorl or yellowish, transparent, cryst solid, darkens on exposure to light; mp 44.1° (vap press 0.181mm); bp 280° (vap d corresponds to formula P_4); d (solid, 20°) 1.82g/cc, (liq, 44.5°) 1.745g/cc. When exposed to air in the dark, emits a greenish light and gives off white fumes. Ignites at about 30° in moist air; the ignition temp is higher when the air is dry. Can be produced in an electric furnace from phosphate rock, sand and coke. The P vapor is driven off and condensed under w. Almost insol in w (1p in 300,000ps); v sl sol in abs alc (1g/400ml); sl sol in abs eth (1g/102ml); sol in chlf (1g/40ml); sol in benz (1g/35ml); v sol in CS_2 (1g/0.8ml) (Refs 5 & 6)

Ellern (Ref 4, pp26–7 & 65–6) reports that Paracelsus (1490–1541), physician and philosopher on the nature of man and the origin of sickness, seems to have been the first to discover "the element of fire" in the residue of the pyrogenic decomposition of urine. More than a century later (1669), the alchemist Brandt discovered the waxy material that miraculously glowed without heat in the dark and that caught fire on the slightest provocation. After the latter accidental discovery, better methods of manufacture were found, but the material, at a price of 50 guineas per ounce, remained a mere curiosity until another hundred years had passed. In 168C with the laborious manufacture of white phosphorus (WP) by Hankwets in London and the application by Robert Boyle of the then enormously expensive material to ignite a sulfur tipped wood splint, the story of its use in matches began. Between 1780 and 1830, numerous contrivances approaching the shape of an individual match were introduced, leading eventually, from about 1835 on, to real matches as we know them now. The poisonous qualities of WP matches showed themselves rarely in use except when the tips were chewed by children or swallowed by people wishing to commit suicide. Workers exposed during the manufacture of the matches to the fumes of WP, which entered the body mainly thru defective teeth, were subjected to an uncurable destruction of the jaw bones, the so-called phosphorus necrosis. With the awakening of social conscience in the protection of workers, all civilized countries either eventually prohibited use of WP in matches or taxed them out of existence

WP was largely used by the Allies in WWI for screening smokes in hand grenades and mortars. It was also suggested for use in incendiary bullets, and these proved to be very effective against H_2-filled aircraft, such as Zeppelins, used during WWI. During WWII it was also employed in incendiary and anti-personnel applications (Ref 1). More recent applications include the following. When scattered by the force of a burster charge, such as the *Igniter AN-M9*, the substance will easily ignite in air and, in turn ignite various fillings of incendiary bombs. Similarly, it will ignite when dispersed from items such as the *WP Smoke Shell M302* for 60mm mortars, the *M105* for 155mm howitzers, the *WP Smoke Hand Grenade M15*, or the *Navy Smoke Bomb AN-M47A4* with either 100 lbs of WP or 74 lbs of plasticized WP (PWP-see below) (Ref 4, pp 26–7)

As indicated above, WP is widely used in

bursting-type munitions to produce smoke screens for ground-combat operations, and for signaling and spotting purposes. Slow-burning fragments of WP, produced and spread by an explosive burster, are incendiary while burning. Since burning WP produces flesh burns which are slow to heal, it is an excellent harassing agent

WP is the most efficient smoke producer on a weight basis; however, the screening effectiveness of WP in bursting-type munitions is slight. Most of the charge burns within seconds following the burst, resulting in a smoke concn many times that required for effective screening. In addition, the temp rise in the cloud immediately surrounding the burst is sufficient to produce a strong thermal updraft which rapidly lifts the cloud from the ground so that the smoke cloud pillars. This may be helpful for signaling purposes but generally reduces the effectiveness of WP as a screening smoke. Two general ways to improve smoke-producing efficiency are possible. The first involves reduction of the heat of combustion, which can be accomplished only by using different P compds. The second method, which is more attractive, involves controlling the rate of combustion by reducing the fragmentation of the WP. Several methods for controlling the fragmentation of WP have been tried, including the addition of mechanical reinforcement such as steel wool, asbestos, plastic tubes, wire screens, and other devices, causing ejection of the WP in pieces of predetermined size. Other methods attempted involved the alteration of the physical properties of WP so as to produce a plastic mass with low shattering characteristics (Ref 3)

Plasticized white phosphorus (PWP) was found to be the most promising development for control of the fragmentation of P and pillaring of the smoke. It consists of an intimate mixt of granulated WP in a viscous rubber soln. The material burns more slowly and the particles do not disintegrate by melting. As a result, pillaring is reduced and the effective screening time is greatly prolonged. Test results have indicated that PWP produces distinctly better smoke screens than similar P-filled rounds. The anti-personnel incendiary action of PWP is as good as that of WP (Refs 3 & 4, p 149)

WP dissolves easily in carbon disulfide. If such a soln is soaked into filter paper or cotton cloth and exposed to air, the highly volatile solvent evaporates readily, and finely dispersed P residue bursts spontaneously into flame. Addition of gasoline or toluene to the P soln delays the spontaneous ignition because of slower evapn rate of the added vehicles (Ref 4, p 27)

The spontaneous flaming of WP in air can also be made more reliable when a eutectic mixt of 55% WP with 45% phosphorus sesquisulfide (P_4S_3) is formed. This material (mp 40°, d 1.84g/cc) was used in WWII in one-shot flame throwers designed to protect tanks against suicide attacks by infantry *(E1 Antipersonnel Tank Protector)* (Ref 4, p 27)

WP is considered a very dangerous expln and fire hazard, not only because of its spontaneous ignition in air, but because it can react vigorously with oxidizing materials. Ref 7 details documented instances of fire and/or explns with 100 different chemical compds. Containers or ammo contg WP should be kept below its mp (44.1°), as pressure may rupture the container. WP is preferably stored under w in sealed metal vessels enclosed in wooden boxes or metal drums. Use w to fight a WP fire (Ref 2, p 227)

WP is highly toxic with a lethal dose for man of less than 1mg/kg. High concns of the vapors evolved by burning are irritating to the nose, throat and lungs as well as the skin, eyes and mucous membranes. If P is ingested, it can be absorbed from the gastrointestinal tract or thru the lungs. The absorption of toxic quantities of P has an acute effect on the liver and is accompanied by vomiting and marked weakness. The long-continued absorption of small amts can result in necrosis of the mandible or jaw bone. Long-continued absorption, particularly thru the lungs, and thru the gastrointestinal tract can cause a chronic poisoning. This gives rise to a generalized form of weakness, attended by anemia, loss of appetite, gastrointestinal weakness and pallor. WP, when it comes into external contact with the eyes, can cause conjunctivitis (Refs 8 & 9)

No US Military Specification currently exists for WP

Refs: 1) Bebie (1943), 123 2) Anon, Engr-DesHndbk, "Military Pyrotechnic Series. Part III – Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (Oct 1963),

223–27 3) Anon, EngrDesHndbk, "Military Pyrotechnic Series. Part I – Theory and Application", **AMCP 706-185** (April 1967), 7–21 4) Ellern (1968), 26–7, 42, 66, 67, 77, 80, 148ff & 218ff 5) Merck (1968), 824-R 6) CondChemDict (1971), 688-R 7) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, Natl Fire Protection Assoc, Boston (1975), **491M**, 314 to 320 8) Sax (1975), 1023 9) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 420–22

Phosphorus Oxychloride (Phosphoryl chloride). $POCl_3$, mw 153.35; colorl, clear, strongly fuming liq; pungent odor, mp 1.2°, bp 107.2°, d 1.67 g/cc, RI 1.460 (25/D). It is decompd by w and alc with evolution of heat. Prepd from P trichloride, P pentoxide and chlorine (Refs 11 & 13)

P oxychloride and B triiodide react vigorously (Ref 2). The disposal of a benz soln of P oxychloride into a waste drum contg C disulfide and other solvents caused an instantaneous reaction, with the probable evolution of hydrogen chloride (Ref 6). Poor stirring during formulation of 2,5-dimethylpyrrole with a preformed complex of dimethylformamide with P oxychloride caused eruption of flask contents. Reaction of the complex with a local excess of the pyrrole may have been involved (Ref 12). The interaction of P oxychloride and 2,6-dimethylpyridine n-oxide in the absence of a diluent caused an expln (Ref 7). An expln occurred immediately after pouring and capping of the P oxychloride recovered from the prepn of ferrocene-1,1-dicarbonyl chloride. The storage bottle contained P oxychloride recovered from similar prepns, which had been stored for about three months (Ref 5). Dimethyl sulfoxide decomps violently on contact with P oxychloride (Refs 3 & 8); gaseous Na reacts with luminescence at 270° (Ref 4). Zn dust ignites in contact with a little P oxychloride, and the subsequent addition of w liberates phosphine which ignites (Ref 1). When w reacts with P oxychloride there is little warning; first a little bubbling and then a rapid acceleration and pressure increase. Small quantities of P oxychloride were emptied into a scrap Ni drum contg about 28 lbs of w. After a delay of 15 to 30 minutes, the drum expld (Refs 9 & 10)

P oxychloride is highly toxic by inhalation and ingestion, and a strong irritant to skin and tissue (Refs 14 & 15)

Refs: 1) Mellor **8**, 1025 (1940) 2) Ibid **5**, 136 (1946–47) 3) Anon, C&EN **35** (9), 87 (1957) 4) Mellor **2**, Suppl 2, 463 (1961) 5) C.S. Marvel, C&EN **40** (3), 55 (1962) 6) Anon, ABCM QuartSafetySumm **35**, 24 (1964) (Assn of Brit Chem Manuf, London) 7) Anon, C&EN **43** (47), 40 (1965) 8) Anon, ChemInd **40**, 1706–07 (1967) 9) Anon, MCA Case History No **1274** (1967) 10) Anon, Chem Safety Data Sheet **MCA SD-26** (1968) 11) Merck (1968), 825-L 12) Anon, "Case Histories of Accidents in the Chemical Industry", MCA Case History No **1460** (1968) (Manufg Chem Assn, Washington) 13) CondChemDict (1971), 689-L 14) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 414 15) Sax (1975), 1025-L

Phosphorus Pentachloride (Phosphoric chloride, Phosphorus perchloride). PCl_5, mw 208.27; white to pale yel, fuming, deliq, cryst mass; pungent, unpleasant odor; mp (under press) 148°; ordinarily sublimes without melting at 160–165°. Sol with decompn and liberation of much heat in w or alc; sol in C disulfide or tetrachloride. Can be prepd by the action of chlorine on P or P trichloride (Refs 9 & 10)

P pentachloride causes ignition on contact with Al powder (Ref 2), while contact with a mixt of chlorine and chlorine dioxide usually results in expln, possibly due to formation of the more sensitive chlorine monoxide (Ref 5). Interaction with diphosphorus trioxide is rather violent at ambient temp (Ref 3); treatment with fluorine causes the entire mass to become incandescent (Ref 1). Ignition occurs when hydroxylamine is mixed with P pentachloride (Ref 6), while mixts with Mg oxide react with brilliant incandescence (Ref 7). The residue from interaction of P pentachloride and anilide in benz and removal of solvent and phosphoryl chloride in vacuo expld violently on admission of air (Ref 12). A soln of P pentachloride in nitrobenzene is stable at 110°, but begins to de-

comp with accelerating violence above 120°, with evolution of nitrous fumes (Ref 13). A mixt with K produces a very violent expln on impact (Ref 8); molten Na can ignite or expld when in contact with P pentachloride (Ref 11). Interaction with w in limited quantities is violent, and the hydrolysis products may themselves react violently with more w (Ref 4)

P pentachloride is an irritant to skin and eyes; tolerance, 1mg per cubic m of air (Refs 14 & 15)

Military specification **MIL-P-51269**, "Phosphorus Pentachloride, Analyzed Reagent" (14 May 1968) is mandatory for use by all Departments and Agencies of the Department of Defense. The chemical requirements are given below:

Characteristic	Maximum percent by weight
Insoluble matter	0.005
Residue after ignition	0.05
Sulfur compounds (as SO_4)	0.020
Heavy metals (as Pb)	0.002
Iron (Fe)	0.002

Refs: 1) H. Moissan, "Le Fluor et ses Composés", Paris (1900), 134 2) E. Berger, CR **170** (1920), 29 3) Mellor **8** (1940), 898 4) Ibid, 1012 5) Ibid **2** (1941), 281; **8** (1940), 1013 6) Ibid **8** (1946–47), 290 7) Ibid **8** (1946–47), 1016 8) Ibid **2**, Suppl 3 (1963), 1571 9) Merck (1968), 825-L 10) CondChemDict (1971), 689-R 11) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, Natl Fire Protection Assn, Boston (1975), **491M**-374 12) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 701 13) Ibid, 702 14) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 415–16 15) Sax (1975), 1025-R

Phosphorus Pentoxide (Phosphoric anhydride, Phosphoric oxide, Diphosphorus pentoxide). P_2O_5, mw 141.96; a soft, white powder; absorbs moisture from the air with avidity, forming meta-, para-, or orthophosphoric acid, depending upon amt of w absorbed and upon conditions of absorption; mp 580–585°, bp subl at 300°, d 2.387g/cc. Sol in w and alc with evolution of much heat and acrid white fumes. It is prepd commercially by burning P in a current of dry air (Refs 5 & 8)

P pentoxide reacts violently with ammonia (Ref 4); with Ca oxide, Na hydroxide or Na carbonate when initiated by local heating (Ref 7); and with hydrogen fluoride at even 19.5° (Ref 6). A violent expln occurs if a soln of perchloric acid in chlf is poured on P pentoxide (Ref 1). Interaction with warm Na or K is incandescent, and is expl with heated Ca (Ref 2). Interaction with w is very energetic and highly exothermic. The increase in temp may be enough to ignite combustible materials if present and in contact (Ref 3)

Refs: 1) Anon, JACS **23** (1901), 444 2) Mellor **8** (1940), 945 3) Ibid, 944 4) Ibid, Suppl 1 (1964), 331 5) Merck (1968), 825-R 6) G. Gora, ProcRoySoc **17** (1969), 256 7) Mellor **8**, Suppl 3 (1971), 406 8) CondChemDict (1971), 688-L

Phosphorus Trichloride (Phosphorous chloride). PCl_3, mw 270.73; colorl, clear fuming liq, mp −111.8°, bp 76°, d 1.547g/cc. Decomps rapidly in moist air. Dissolves in w or alc with decompn and liberation of much heat. Sol in benz, chlf, eth and C disulfide. Prepd by passing a current of dry chlorine over gently heated P, which ignites. The trichloride, admixed with some pentachloride, distills over. A small amt of P is added and the whole distilled (Refs 9 & 10)

P trichloride is highly toxic, and a strong irritant to skin and tissue. It is a dangerous fire risk in contact with w. Tolerance, 0.5ppm in air (Refs 12 & 13)

Several laboratory explns have occurred when using the reaction between P trichloride and acetic acid to form acetyl chloride. Poor heat control probably caused formation of phosphine (Ref 2). Two later explns may have been due to ingress of air and combustion of traces of phosphine (Ref 8). Al powder burns in P trichloride vapor (Ref 4); K ignites and molten Na explds on contact (Ref 3). Each drop of chromyl chloride added to well-cooled P trichloride produces a hissing noise, incandescence, and sometimes an expln (Ref 5). It reacts with fluorine with incandescence (Ref 1), and with ignition

when mixed with hydroxylamine (Ref 6). An expln occurs when P trichloride is brought in contact with nitric or nitrous acid (Ref 7). Its reaction with w is exothermic and immediately violent, and is accompanied by liberation of some diphosphane which ignites (Ref 11)

The requirements of the US Armed Forces for P trichloride are covered in two specifications, **MIL-P-10398B** (11 Feb 1969) for Phosphorus Trichloride, Technical, and **MIL-P-51300** (12 March 1969) for Phosphorus Trichloride, Analyzed Reagent

MIL-P-10398B contains the following requirements for physical characteristics:

Table 1
Phosphorus Trichloride, Technical

Characteristic	Minimum	Maximum
Color	Water white	
Specific gravity, 15.5/15.5°C	1.582	1.588
Distillation range (°C):		
Initial boiling point	74.5	–
Dry point	–	79.0
Total range	–	3.0

MIL-P-51300 contains the following requirements for physical and chemical characteristics:

Table 2
Phosphorus Trichloride, Analyzed Reagent

Characteristic	Minimum	Maximum
Specific gravity	1.54	1.60
Boiling range, °C	75.0	76.0
Sulfate (SO_4), percent by weight	–	To pass test
Heavy metals (as Pb), percent by weight	–	0.001
Iron (Fe), percent by weight	–	0.0015

Refs: 1) H. Moisson, "Le Fluor et ses Composés", Paris (1900), 134 2) R.D. Coghill, JACS **60**, 88 (1938) 3) Mellor **8**, 1006 (1940); **2**, 470 (1941) 4) Ibid **5**, 214 (1946–47) 5) Ibid **11**, 395 (1946–47) 6) Ibid **8**, 290 (1946) 7) Ibid **8**, 827, 1004 & 1038 (1946–47) 8) T.A. Peacocke, SchoolSciRev **44** (52), 217 (1962) 9) Merck (1968), 825-R 10) CondChemDict (1971), 690-L 11) Anon, Chemical Safety Data Sheet **SD-27**, Manufg Chemists' Assoc, Washington (1972) 12) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 419–20 13) Sax (1975), 1027-L

Phosphorous Trioxide (Diphosphorus trioxide). P_2O_3, mw 109.95, transparent monocl crysts, mp 23.8°, bp 173.1° in nitrogen atm, d 2.135 g/cc. Exists as P_4O_6 when in vapor phase or in benz soln. Disproportionates into red P and P_2O_4 when heated above 210°. Sol in benz and C disulfide. When placed in cold w, H_3PO_3 is formed. Prepd by treating PCl_3 with tetramethylammonium sulfite in liq SO_2, or from the elements (Ref 6). It is highly toxic (Ref 7)

The interaction of ammonia and molten P trioxide under nitrogen is rather violent, and the mixt ignites (Ref 2). Its interaction with disulphur dichloride is very violent (Ref 5); it ignites in contact with excess chlorine gas, and reacts violently, usually igniting, with liq bromine (Ref 2). Interaction with air or oxygen is rapid and, at slightly elevated temps in air or at high oxygen concn, ignition is very probable, particularly if the P trioxide is molten or distributed as a thin layer. The solid in contact with oxygen at 50–60° instantly ignites with a flame of almost blinding brilliance (Ref 3). The reaction between P trioxide and P pentachloride is violent at ordinary temps (Ref 1); sulfur monoxide reacts with great violence (Ref 2). Interaction of a mixt of S and P trioxide under inert atm above 160° to form P oxysulfide is violent on anything but a small scale (Ref 2). The addition of sulfuric acid to P trioxide causes violent oxidation, and ignition if more than 1–2g is used (Ref 5). Its reaction with cold w is slow, but with hot w, violent, the evolved phosphine igniting. With more than 2g of P trioxide, violent explns occur (Ref 4)

Refs: 1) T.E. Thorpe et al, JCS **57**, 545 (1890) 2) Ibid, JCS **59**, 1019 (1891) & Mellor **8**, 897–8 (1946–47) 3) W.E. Downey, JCS **125**, 347 (1924) & Mellor **8**, 897–8 (1940) 4) Mellor **8**, 897 (1940) 5) Ibid, 898 6) Merck (1968), 826-R 7) Sax (1975), 1027-L

Photochemistry of Explosives. The addition of radiant energy to a chemical system produces electronically excited molecules that are capable of undergoing chemical reactions. An organic molecule in which all the electrons are in stable orbitals is said to be in the ground electronic state. These orbitals may be either bonding or nonbonding. If a photon of the proper energy collides with the molecule, ie, the photon is absorbed, one of the electrons is promoted (excited) to an unoccupied orbital of higher energy—an antibonding molecular orbital. Electronic excitation results in spatial redistribution of the valence electrons with concomitant changes in internuclear configurations. Since chemical reactions are controlled to a great extent by these factors, an electronically excited molecule undergoes chemical reactions that may be distinctly different from those of its ground-state counterpart

The energy of the photon is defined in terms of its frequency or wavelength:

$E = h\nu = hc/\lambda$

where E is energy; h is Planck's constant (6.6×10^{-27} erg-sec); ν is the frequency of the radiation (sec^{-1}); c is the speed of light; and λ is the wavelength of the radiation. When a photon is absorbed, all of its energy is imparted to the absorbing species. The primary act following absorption depends on the wavelength of the incident light. Photochemistry studies photons whose energies lie in the ultraviolet region (1000–4000Å) and in the visible region (4000–7000Å) of the electromagnetic spectrum; such photons are primarily a cause of electronically excited molecules. When this energy is released as chemical energy, fragmentation, free-radical formation, isomerization, and addition reactions may take place (Ref 6)

Many photochemical studies have been conducted over the past 40 years on materials of ordnance interest. The major studies are annotated below in chronological sequence:

Schultz and Ganguly, in 1925, noted that the surface of pulverized TNT became colored on exposure to sunlight. They concluded that tautomeric quinoximes were formed thru an unstable intermediate. In acetone, a stable intermediate formed (Ref 1). Gray, Bonomo and Denner (Ref 8) could not repeat their results

Leighton and Lucy studied o-nitrobenzaldehyde, 2,4-dinitrobenzaldehyde and 2,4,6-trinitrobenzaldehyde as solids and in acet and ligroin soln, on exposure to radiation between 2654–4040Å. For o-nitrobenzaldehyde, quantum yield was independent of wavelength, oxygen and state. The product was o-nitrosobenzoic acid (Ref 2)

Shelegova irradiated nitrobenzene vapor with various light sources. In the 2160–2900Å region the products were phenol and NO_2; in the 1850–2160Å region, phenol and polynitrobenzenes (Ref 3).

Gorislavets (Ref 4) claimed that the nitration of benzene or nitrobenzene with nitrogen dioxide readily occurred on irradiation with rays of certain definite wavelengths which activate NO_2. Thus, benzene was nitrated quantitatively at 4000–7000Å at a temp of 55–60°. The highest yield of dinitrobenzene was obtained at 1800–2900Å. These results were not confirmed by Hastings and Matsen (Ref 5) who reported nitrosobenzene and p-nitrophenol as the main products from the mercury arc irradiation of nitrobenzene vapor. They concluded that the absorption led to the release of an O atom from the NO_2 group which inserted itself in the parent molecule

Lippert and Vogel (Ref 7) asserted, on the other hand, that on irradiation with high intensity ultra-violet light, nitrocompds undergo dissociation into free radicals:

$ArNO_2 \rightarrow Ar. + .NO_2$

Margerum et al (Ref 9) photolyzed solns of aromatic nitrocompds in 95% alc using an unfiltered 400 watt mercury lamp. No compd was found to be phototropic which did not have a nitrogroup ortho to a benzyl hydrogen. They hypothesized that an intramolecular process involving an H-atom transfer was operative.

Wettermark (Refs 10, 11 & 12) studied o-nitrotoluene and dinitrotoluene, flash photolyzed in w and alc. He observed transients, and noted that the absorption spectra was a function of pH. He concluded that intramolecular H-atom transfer was involved

Tench and Coppens (Ref 13) photolyzed o-nitrobenzaldehyde, nitrobenzene, and nitrobenzoic acid with light > 3500Å. ESR measurements revealed the presence of radicals for o-nitrobenzaldehyde (in solns and powder), with no radicals observed with nitrobenzene and

nitrobenzoic acid. They concluded that the photoradical occurred as a side reaction, and was not the intermediate in the conversion of the nitro to the nitrosocompd

Morrison and Migdalof (Ref 14) irradiated o-nitrotoluene and p-nitrotoluene with a Pyrex-filtered mercury lamp using D_2O and p-dioxane as solvents. C-D bonds formed with o-nitrotoluene, with no C-D formation for p-nitrotoluene

Ward (Ref 15) and Brown and Williams (Ref 16) studied nitrobenzene with radiation > 3300Å using tetrahydrofuran (THF) as solvent in degassed solns. The effects of low temp were also studied. An ESR signal, attributed to the $C_6H_5N(\dot{O}_2)H$ radical, was obtained with THF as solvent. No ESR signal was obtained when perfluoronaphthalene was added. They concluded that the triplet state of nitrobenzene was an intermediate

B. Suryanarayana, J.R. Autera and R.J. Graybush (Ref 16a), during a study of solid phase transitions in the four polymorphic forms of HMX utilizing differential thermal analysis (DTA) techniques, found that prior irradiation with 2537Å light caused the β to δ transformation to occur approximately 15° below the transition point of unirradiated material. A similar but smaller effect, a decrease of 5°, was observed after irradiation of β-HMX with 3100–3400Å light. They hypothesized the involvement of a free radical or a trapped charge

Hurley and Testa (Ref 17) exposed nitrobenzene in isopropyl alcohol, degassed and in air, to a mercury lamp at 3660Å. Products in the absence of air were acetone and phenylhydroxylamine (PHA). In air PHA was oxidized to nitrosobenzene which couples with PHA to form azoxybenzene. They hypothesized that the triplet molecule abstracted H-atoms from the solvent; no effect was noted with benzene as solvent. They also worked with nitrobenzene in isopropyl alcohol-water mixts containing HCl with a mercury lamp at 3660Å (Ref 18), and found that the quantum yields depended on pH and isopropyl alcohol content, but were independent of oxygen with acid present. Their conclusion was that the quantum yield consisted of two parts, H abstraction by the triplet, and protonation of the triplet

Strom and Weinstein (Ref 19) used an unfiltered 200 watt mercury lamp on degassed solns of o-nitrocumene and o-nitrotoluene. The former yielded radicals, while with the latter the yield was markedly lower. The radicals were stable for days and could also be formed in the presence of oxygen. No radicals were formed with corresponding parasubstituted compds. It was thought that the reaction proceeded via an intramolecular step

Baltrop and Bunce (Ref 20) employed a variety of radiation wavelengths, nitrocompds and solvents. For wavelengths less than 2900Å, aniline was the main product, while above 2900Å, bimolecular species such as azobenzene predominated. Since oxygen had little effect on aniline production, expts were performed in the presence of oxygen. For nitrobenzene in isopropyl alcohol, no azoxybenzene was produced as with Hurley and Testa (See above Ref 17). They concluded that the excited state abstracts H-atoms, and suggest that the nitrobenzene triplet is in π, π^*, and that nitrosobenzene is an unobserved intermediate

Hashimoto, Sunamoto, Fujii and Kano (Ref 21) used a 130 watt mercury lamp to irradiate isopropyl alcohol-HCl-nitrocompd solns. The effect of oxygen was also studied. They found that in the absence of HCl, nitrobenzene produced phenylhydroxylamine. When HCl was present, it produced aniline and other products. No explanation of mechanism was given

Weller and Hamilton (Ref 22) irradiated solns of nitrobenzene and alkanes with a 450 watt mercury lamp using different glass filters. Good yields of alcohols and carbonyl compds were observed. They concluded that the oxidation involved an H-atom abstraction by nitrobenzene

Ayscough, Sealy and Woods (Ref 23) irradiated nitroso- and nitrobenzene in isopropyl alcohol and other solvents with an incident wavelength greater than 3000Å, and performed ESR studies on the solns. They found a stable radical, $C_6H_5N\dot{O}H$, and concluded that participation of a triplet state was not involved with nitroso-compds, and not firmly established with nitrocompds

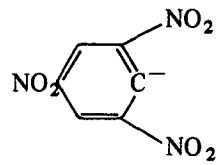
Sandus and Slagg (Ref 24) performed flash and continuous photolysis expts at 2537Å ($\pi \rightarrow \pi^*$ transitions) on nitrocompds in soln. Flash photolysis revealed intermediates for o-nitrotoluene and its nitroderivatives. The

spectrum and mean lifetime of the intermediate for flashed TNT were detd. Continuous photolysis expts revealed that all the aromatic nitrocompds had disappearance quantum yields of the order of 10^{-3}, implying that the most important reaction occurring was the deactivation to the ground state of the original molecule. The presence or absence of oxygen did not appear to be significant. Product analyses suggested that aromatic nitrosocompds and nitrophenols were the main products. However, the observed products did not conform in a simple manner to the constraints of the isosbestic points observed in all the photolyses. It appeared that other products were present, some of which could have low extinction coeffs in the spectral range studied

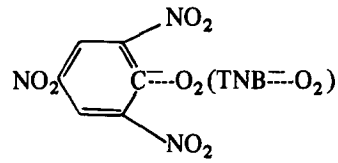
The photolysis of solid dimethylnitramine with 2537Å light resulted in the formation of dimethylnitrosamine as a major product (Ref 25). The mechanism of bond-breaking was investigated via a ^{15}N tracer technique, and showed that the nitrosamine arose from the nitramine as a result of an N–O bond cleavage, and that the nitrosamine after being formed underwent an almost 100% light-induced rearrangement involving the bond between the two N-atoms

Nanosecond flash photolysis studies of α-nitronaphthalene in polar and nonpolar solvents led to the detection of the triplet-triplet absorption spectrum of this nitrocompd (Ref 26). A large red shift observed in polar solvents was indicative of the intramolecular charge transfer character of the triplet state. The change of dipole moment accompanying the transition $T_1 \rightarrow T_n$, as well as rate constants for electron and proton transfer reactions involving the T_1 state of α-nitronaphthalene, were determined. The lower reactivity in polar solvents was attributed to a reduced n-π^* and increased charge transfer character of the triplet state

The flash photolysis of s-trinitrobenzene (TNB) aerated solns in alcohols generated a transient species with absorption maxima at 430 and 510nm (Ref 27). The yield of the transient was a function of oxygen concn, and its rate of formation was viscosity dependent. In deaerated solns, instead of the transient, a brown permanent product, identified as a charge transfer (CT) complex with absorption maxima at 470 and 550nm, was produced. These species were formed only in polar solvents with relatively high proton affinity. The data suggested an intermolecular proton transfer, from electronically excited TNB to the solvent forming the anion



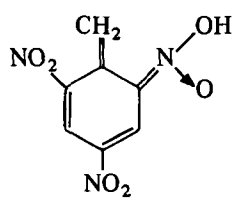
The anion thereby produced interacts with oxygen in aerated alcohols to form the transient attributed to CT complex



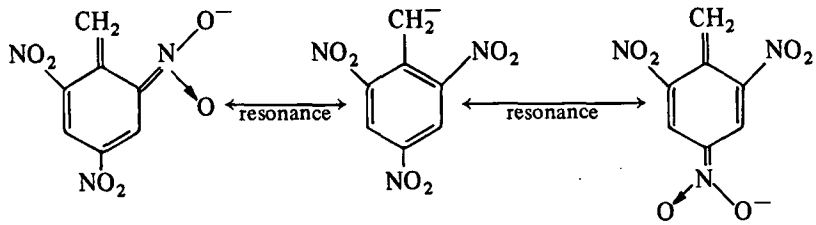
while in deaerated alcohols the anion reacted with the solvent to produce RO^-, which led to the CT complex RO⁻⁻⁻TNB

Capellos and Suryanarayanan (Ref 28) described a ruby laser nanosecond flash photolysis system to study the chemical reactivity of electrically excited state of aromatic nitrocompds. The system was capable of recording absorption spectra of transient species with half-lives in the range of 20 nanoseconds (20×10^{-9} sec) to 1 millisecond (10^{-3} sec). Kinetic data pertaining to the lifetime of electronically excited states could be recorded by following the transient absorption as a function of time. Preliminary data on the spectroscopic and kinetic behavior of 1,4-dinitronaphthalene triplet excited state were obtained with this equipment

The flash photolysis of 2,4,6-trinitrotoluene solns (TNT) indicated a photochemically induced isomerization leading to the aci-quinoid isomer



with an absorption maximum at 460nm in nonpolar solvents, or the conjugate base



of the aci-quinoid isomer with absorption maxima at 500, 540, and 630nm in polar solvents. Both species, the quinoid isomer and the conjugate base, had transient existence and their identification was based on detailed spectroscopic and kinetic studies. The magnitude of the negative charge on the transient conjugate base was detd with salt effect expts and found to be equal to unity (Ref 27)

Nanosecond flash photolysis of b-nitronaphthalene in nonpolar and polar solvents showed a transient species with maximum absorption and lifetime dependent on solvent polarity. In deaerated n-hexane the absorption maximum and lifetime were 425nm and 530nsec, while in deaerated ethanol the corresponding values were 470nm and 1.7μsec. This transient absorption was attributed to the triplet excited state of b-nitronaphthalene, and the observed red shift as well as its longer lifetime in polar solvents were considered to be indicative of the intramolecular charge transfer character of this state. The change of dipole moment accompanying the transition $T_1 \rightarrow T_n$, as well as rate constants for electron and proton transfer reactions involving the T_1 state of b-nitronaphthalene were detd. Spectroscopic and kinetic data obtained indicated that the triplet state of b-nitronaphthalene behaved like a n-π^* state in nonpolar media, while in polar solvents the n-π^* character of the state was reduced with a simultaneous increase in the charge transfer character (Ref 30)

Nanosecond flash photolysis of 1,4-dinitronaphthalene in aerated and deaerated solvents showed a transient species with absorption maximum at 545nm. The maximum of the transient absorption was independent of solvent polarity and its lifetime seemed to be a function of the hydrogen donor efficiency of the solvent. The transient absorption was attributed to the lowest excited triplet state of 1,4-dinitronaphthalene. Based on spectroscopic and kinetic evidence, the triplet state of 1,4-dinitronaphthalene behaved as an $n \rightarrow \pi^*$ state in nonpolar solvents, while in polar solvents the state is predominantly $n \rightarrow \pi^*$ with a small amount of intramolecular charge transfer character (Ref 31)

The most recent researches of Capellos and Suryanarayana on the triplet excited states of 1,2- and 1,8-dinitronaphthalenes, and those of Capellos and Lang on the triplet excited states of 4-nitronaphthalene and 4-nitro-N,N-dimethylnaphthalene have been accepted for publication by the International Journal of Chemical Kinetics

Refs: 1) G. Schultz & K.L. Ganguly, Ber **58**, 702 (1925) 2) P.A. Leighton & F.A. Lucy, JChemPhys **2**, 756 & 760 (1934) 3) O.M. Shelegova, JExptlTheoretPhysUSSR **9**, 1527 (1939) 4) I.O. Gorislavets, ZhFizKhim **17**, 102 (1943) 5) S.H. Hastings and F.A. Matsen, JACS **70**, 3514 (1948) 6) Kirk & Othmer **15** (1956), 331 7) E. Lippert & W. Vogel, ZPhysChem **9**, 133 (1956) 8) D.N. Gray, F.S. Bonomo & R.I. Denver, "Study on the Effect of Temperature Cycling of High Explosives", AFSWC Report **TDR 62-16**, Contract No AF 29 (601) 2671 (March 1962) 9) J.D. Margerum, L.J. Miller, E. Saito, M.S. Brown, H.S. Mosher and R. Hardwick, JPhysChem **66**, 2434 (1962) 10) G. Wettermark, Nature **194**, 677 (1962) 11) Ibid, JPhysChem **66**, 2560 (1962) 12) G. Wettermark & R. Ricci, JChemPhys **39**, 1218 (1963) 13) A.J. Tench and P. Coppens, JPhysChem **67**, 1378 (1963) 14) H. Morrison & B.H. Migdalof, JOrgChem **30**, 3996 (1965) 15) R.L. Ward, JChemPhys **38**, 2588 (1963) 16) J.K. Brown & W.G. William, Chemical Communications, 495 (1966) 16a) B. Suryanaryana et al, MolecularCrysts **2**, 373–77 (1967) 17) R. Hurley & A.C. Testa, JACS **88**, 4330 (1966) 18) Ibid, JACS **89**, 6917 (1967) 19) T. Strom & J. Weinstein, JOrgChem **32**, 3705 (1967) 20) J.A. Baltrop & N.J. Bunce, JCS (C), 1467 (1968) 21) S. Hashimoto, J. Sunamoto, H. Fugii & K. Kano, BullChemSocJapan **41**, 1249 (1968) 22) J.W. Weller & G.A. Hamilton, ChemCommunications, 1390 (1970) 23) P.B. Ayscough,

R.C. Sealy & D.E. Woods, JPhysChem **75**, 3454 (1971) 24) O. Sandus & N. Slagg, PATR **4385** (1972) 25) K. Suryanarayanan & S. Bulusu, JPhysChem **76**, 496 (1972) 26) C. Capellos & G. Porter, JCS Faraday Trans II **70**, 1159 (1974) 27) C. Capellos & K. Suryanarayanan, IntJChemKinetics **5**, 305 (1973) 28) C. Capellos & K. Suryanarayanan, PATR **4445** (1973) 29) K. Suryanarayanan & C. Capellos, IntJChemKinetics **6** (1), 89–102 (1974) 30) C. Capellos & K. Suryanarayanan, IntJChemKinetics **8**, 529–39 (1976) 31) Ibid **8**, 541–48 (1976)

Photoflash Compositions. See under Pyrotechnics, Military in this Vol

Photography in Ballistic and Aerodynamic Investigations. See under Cameras, High-Speed Photographic in Vol **2**, C13-L to C19-R

PH-Salz (PH-Salt). Ger designation for Ethylenediamine Dinitrate (EDD, EDDN, EDAD or DIAMIN). See in Vol **6**, E236-L to E237-R

In Ger, PH-Salz was prepd by treating ethylenedichloride with ammonia and Na hydroxide, followed by nitration with nitric acid not stronger than 50%. Although PH-Salz has a high mp (185°), it has the property of depressing the mp of other high mp compds. For this reason, the Germans used it to obtain castable expl mixts during WWII. For example, a mixt of 45% PH-Salz and 55% AN melts at 105° and can be cast-loaded. Such a mixt has an expl power equal to that of TNT or Amatol, but has the disadvantage of shrinking considerably on cooling. The addition of aq Ca nitrate to this mixt practically eliminates shrinkage and results in a very good cast. The following mixts contg PH-Salz were used for filling shells as a substitute for TNT:

Ammonit. AN 46, PH-Salz 46 & $Ca(NO_3)_2 \cdot 4H_2O$ (tech) 8%; d of fragments 39–40m (see Fragment Concentration Test in Vol **3**, D84-L)

Ammonit. AN 55, PH-Salz 10, $Ca(NO_3)_2 \cdot 4H_2O$ 10, RDX 20 & Na nitrate 5%; d 1.53g/cc; casting temp 108°, d of fragments 40m (Ref 3)

H-5 (Ammonit). AN 50, PH-Salz 10, $Ca(NO_3)_2 \cdot 4H_2O$ 15 & RDX 20% (Ref 2)

S-16. AN 32, PH-Salz 10, Na nitrate 6 or 8, K nitrate 2 or 0 & Al powder 40% (Ref 2)

S-22 (Hexo). AN 45, PH-Salz 14, Na nitrate 9, K nitrate 3, RDX 14 & Al powder 15% (Ref 2)

S-22 (Hexa). AN 45, PH-Salz 14, Na nitrate 9, K nitrate 3, HNDPhA 14 & Al powder 15% (Ref 2)

Amatol 41. AN 52, PH-Salz 30, $Ca(NO_3)_2 \cdot 4H_2O$ 6, RDX 10 & Montan wax 2% (Ref 3)

Compns contg Al were particularly suitable for underwater ordnance because they possessed high blast effect. PH-Salz could also be used straight or slightly phlegmatized. In the latter case, it was particularly suitable for use in anti-concrete shells, called Be-Granate (Be is an abbreviation for Beton = concrete)

Refs: 1) PB (Publication Board of the US Office of Technical Services) Rept No **925** (1945), 24 2) PB Rept No **1820**, 29 3) PBL Rept No 85–160 (1946), 23 4) B.T. Fedoroff et al, PATR **2510**, Ger 131–2 (1958)

Phthalic Acids and Derivatives

$C_6H_4(COOH)_2$, mw 166.13

o-Phthalic Acid (Phthalic Acid, Benzoldicarbonsäure-(1,2) in Ger). Monocl crysts, mp 191°, d 1.593 g/cc at 20/4°. Prepn & other properties given in Beil **9**, 791–8, (349–50) & [580–84]

m-Phthalic Acid (Isophthalic Acid, Benzoldicarbonsäure-(1,3) in Ger). Needles from hot w or alc, mp 347–8°, bp sublimes. Prepn & other properties given in Beil **9**, 832–4, (371) & [608–9]

p-Phthalic Acid (Terephthalic Acid, Benzoldicarbonsäure-(1,4) in Ger). Cryst or amorph powder, mp 425° (starts to sublime above 300°). Prepn & other properties given in Beil **9**, 841–3, (373–4) & [611–12]

Note: The exothermic nitration of phthalic acid or phthalic anhydride by a fuming nitric acid-sulfuric acid mixt may give mixts of the potentially expl phthaloyl nitrates or nitrites or their nitro derivatives. Formation of these compds can be avoided if the nitrating mixt is

extensively diluted with sulfuric acid and if a small (1.5 mole equiv) of nitric acid is present (Anon, Chem&Ind **17**, 664 (1972); Ibid **20**, 790 (1972)

Mononitrophthalic Acids

$O_2N.C_6H_3(COOH)_2$, mw 211.13, N 6.63%

3-Nitro-o-phthalic Acid. Pale yel prisms or plates from w; mp dec 207–230°. Prepn and properties are given in Refs

Refs: 1) Beil **9**, 823–4, (367) & [605] 2) O. Miller, Ann **208**, 240 (1881) 3) F.C. Whitmore, Ed, OrgSynth **7** (1927), 70

It forms salts, some of which are expl, eg:

Basic Lead Salt. $PbC_8H_3O_6N$, mw 416.32, N 3.36%. Insol in w. For prepn and properties, see Ref 2. Was proposed by Brün for use as a component of ammo priming mixts (Ref 3)

Refs: 1) Beil **9**, 825 2) A. Faust, Ann **160**, 57–59 (1871) 3) W. Brün, USP 1971030 (1934) & CA **28**, 6314 (1934)

Silver Salt. $Ag_2C_8H_3O_6N$. Insol in w; puffs off on heating. Prepn and properties are given in Ref 2

Refs: 1) Beil **9**, 825 2) A. Laurent, Ann **41**, 112 (1842)

4-Nitro-o-phthalic Acid. Needles from eth, mp 162–64°. Easily sol in w & alc; sol in hot AcOH; diff sol in cold AcOH; fairly sol in eth; insol in chlf, benz, petr eth & C tetrachloride. Prepn and properties are given in Refs

Refs: 1) Beil **9**, 828, (370) & [606] 2) J.R. Johnson, Ed, OrgSynth **16**, 56 (1936)

It forms salts, some of which are expl, eg:

Basic Lead Salt. $PbC_8H_3O_6N$, mw 416.32, N 3.36%. Was proposed by Brün for use in mixts with Pb Styphnate, Pb nitrate, etc, in expl compns (Ref 3)

Its **potassium** salt was reported to be a mild expl (Ref 2), as are probably its **silver** and **barium** salts

Refs: 1) Beil **9**, 828–30 & [606–7] 2) O. Miller, Ann **208**, 230–2 (1881) 3) W. Brün, USP 2205116 (1940) & CA **34**, 7112 (1940)

2-Nitro-m-phthalic Acid. Prisms from methanol, mp 310–315° (begins to brown ca 287°). Sl sol in w, easily sol in alc or eth. Its **barium** salt, which is very sol in w, is probably expl (Ref 2)

Refs: 1) Beil **9**, 839, (373) & [610] 2) E. Noelting & C. Grachot, Ber **39**, 73 (1906) 3) C.W. James et al, JCS **117**, 774 (1920)

4-Nitro-m-phthalic Acid. Crysts, mp 255–60°. Diff sol in cold w, v sol in hot w, alc & eth. Forms numerous salts of which the **silver** salt was reported to be expl

Ref: Beil **9**, 839, (373) & [610]

5-Nitro-m-phthalic Acid. Colorl crysts from alc, mp 255–56°. V sol in alc, eth or hot w; sl sol in cold w. Forms numerous salts of which the **silver** salt was reported to be expl

Ref: Beil **9**, 839–40 & (373)

2-Nitro-p-phthalic Acid (Nitroterephthalic Acid). Only one isomer is possible. Crysts, mp 268–70°. Easily sol in alc or eth, sol in hot w. Can be prepd by nitration of terephthalic acid or by other methods given in the Refs. Some of its salts are probably expl

Refs: 1) Beil **9**, 851, (377) & [614] 2) G.A. Burkhardt, Ber **10**, 145 (1877) 3) M.A. Soderman & T.B. Johnson, JACS **47**, 1393 (1925)

Dinitrophthalic Acids

$(O_2N)_2.C_6H_2(COOH)_2$, mw 256.14, N 10.94%

3,5-Dinitro-o-phthalic Acid. Prisms from eth, mp 225–6°. Very sol in w, alc & eth; insol in ligr, C disulfide and benz. Can be prepd by the oxidation of 5,7-dinitro-1,2,3,4-tetrahydro-naphthalene with 30% boiling nitric acid or by other methods given in the Refs. The **barium** salt, $C_8H_2(NO_2)_2O_4.Ba$ is expl

Refs: 1) Beil **9**, 831, (370) & [607] 2) F. Beilstein & A. Kurbatow, Ann **202**, 226–7 (1880) 3) G. Schroeter, Ann **426**, 46 (1922)

3,6-Dinitro-o-phthalic Acid. Needles from eth, mp 200–202°. Easily sol in w, alc or eth. Can be prepd by heating 1,5-dinitronaphthalene with mixed nitric-sulfuric acid. Its **barium** salt (Refs 2 & 3) is expl
Refs: 1) Beil **9**, 831–2 2) V. Merz & W. Weith, Ber **15**, 2725 (1882) 3) W. Will, Ber **28**, 369 (1895)

2,5 (or 4,5) -Dinitro-m-phthalic Acid. Crysts from w with $5H_2O$; loses it when heated to 100°; mp 215°. Sl sol in w, sol in alc, nearly insol in eth. Can be prepd by heating 1 p of isophthalic acid with 5p of fuming nitric acid in a sealed tube at 150–180° for 6 hrs. Forms salts, some of which (**silver** salt) are expl
Refs: 1) Beil **9**, 840 & [611] 2) A. Claus & S. Wyndham, JPrChem [2] **38**, 316 (1888)

2,3-Dinitro-p-phthalic Acid (2,3-Dinitroterephthalic Acid). Glassy crysts from hot w; mp > 290° with decompn; explds on rapid heating. Can be prepd by treating 2,3-dinitro-p-tolylic acid with concd nitric acid in a sealed tube at 170°
Refs: 1) Beil **9**, 853 2) C. Haeussermann & E. Martz, Ber **26**, 2982–85 (1893)

2,5-Dinitro-p-phthalic Acid (2,5-Dinitroterephthalic Acid). Prisms from w; mp ≥ 280° with decompn; explds when heated rapidly. Sol in w. Can be prepd by heating 2,5-dinitro-p-phthalic acid with concd nitric acid in a sealed tube at 140°. Forms expl salts such as $BaC_8H_2O_8N_2$
Refs: 1) Beil **9**, 853 2) C. Haeussermann & E. Martz, Ber **26**, 2984 (1893)

2,6-Dinitro-p-phthalic Acid (2,6-Dinitroterephthalic Acid). Crysts from hot w; mp ca 255° with decompn; explds on rapid heating. Difficultly sol in w. Can be prepd by treating p-phthalic acid with mixed nitric-sulfuric acid, or by heating 2,6-dinitro-p-cymol with fuming nitric acid in a closed tube at 140°. Forms an expl **barium** salt
Refs: 1) Beil **9**, 853 & [615] 2) C. Haeussermann & E. Martz, Ber **26**, 2983 (1893) 3) A.S. Wheeler & C.R. Harris, JACS **49**, 497 (1927)

2,4,6-Trinitro-m-phthalic Acid (2,4,6-Trinitroisophthalic Acid). $(O_2N)_3.C_6H(COOH)_2$, mw 301.14, N 13.96%. Crysts from w, mp 196–7° with decompn. Can be prepd by oxidation of 2,4,6-trinitro-m-xylene with chromium oxide in concd sulfuric acid at 80–90°. Its **silver** salt, yel cryst, explds on heating
Refs: 1) Beil **9**, [611] 2) M. Giua, Gazz **52** (I), 186 (1922); JCS **122** (I), 534 (1922)

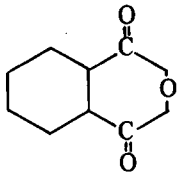
Phthalic Acids – Azides and Diazides

3-Nitrophthalic Acid Azide [3-Nitrophthalsäureazid (1), in Ger]. $HO_2C.C_6H_3(NO_2).CO.N_3$, mw 236.16, N 23.73%. Scales from eth & petr eth, mp explds on heating. Can be prepd by treating the hydrazide of 3-nitrophthalic acid with nitrous acid under cooling conditions
Refs: 1) Beil **9**, (370) 2) T. Curtius & A. Semper, Ber **46**, 1162 & 1167 (1913)

Isophthalic Acid Diazide (m-Phthalic Acid Diazide). $C_6H_4(CO.N_3)_2$, mw 216.18, N 38.88%. Prisms from acet, mp 56°, explds on further heating. Easily sol in acet or eth. Can be prepd by treating isophthalic acid hydrazide hydrochloride with Na nitrite in cold aq soln
Refs: 1) Beil **9**, 837 2) E. Davidis, JPrCh [2] **54**, 77 (1896)

Terephthalic Acid Diazide. $C_6H_4(CO.N_3)_2$, mw 216.18, N 38.88%. Plates from acet, mp 110°, explds on further heating. Easily sol in eth or acet. Can be prepd by treating terephthalic acid hydrazide hydrochloride with Na nitrite in cold aq soln
Refs: 1) Beil **9**, 847 & (376) 2) E. Davidis, JPrCh [2], **54**, 84 (1896)

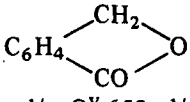
Phthalic Anhydride. $C_8H_4O_3$, mw 148.11, wh cryst needles, mp 131.16°, bp 285°, sublimes below bp, flash pt 152°, combustible, autoignition temp 584°, flammable limits 1.7–10.5%. Sol in alc, sl sol in eth and hot w. Prepd by the catalytic oxidn of naphthalene or ortho-xylene



Attempts to follow a published method for nitration of phthalic anhydride in sulfuric acid at 80–100° with fuming nitric acid caused an eruptive decompn to occur after a 2 hr delay (Ref 3). It was found that this hazard could be eliminated thru use of a smaller excess of nitrating acid at 55–65° (Ref 4). Possible causes of the delayed eruption were suggested as the formation of potentially expl mixts of phthaloyl nitrates or nitrites, or their nitro derivatives

Refs: 1) Merck (1968), 827-L 2) CondChemDict (1971), 692-L 3) J.H.P. Tyman et al, Chem&Ind **17**, 664 (1972) 4) R.K. Bentley, Ibid **20**, 767 (1972) 5) L. Bretherick, Ibid **20**, 790 (1972) 6) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 422

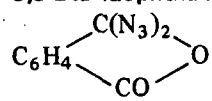
Phthalide (Isobenzofuranone, 1-Phthalanone, 1-Oxo-phthalan in Ger). $C_8H_6O_2$, mw 134.13, needles from w, mp 73° (65°), bp 290°, d 1.164 g/cc at 99/4°, Q_c 6470 cal/g, Q_f^v 653cal/g, Q_f^p 671cal/g. V sol in w, sol in alc. Can be prepd by reducing phthalimide, $C_6H_4(CO)_2NH$, with Zn dust in aq Na hydroxide or by other methods (Ref 1). Was proposed by Parodi-Delfino et al as a gelatinizer and stabilizer for NC in smokeless powd. It was claimed that in double-base proplnt, it was superior to Centralite (Ref 2). Allison (Ref 3) used it as a deterrent for coating proplnt grains



Refs: 1) Beil **17**, 310, (161) & [332] 2) L. Parodi-Delfino et al, CongrInternQuimPuraApplicada **4**, 447 (1934) & CA **30**, 3237 (1936); USP 1609303 (1926) & CA **21**, 325 (1927) 3) E.R. Allison, USP 2267261 (1941) & CA **36**, 2725 (1942) 4) P. Tavernier, MP **38**, 308 & 329 (1956)

Phthalide forms an expl diazide:

3,3-Diazidophthalide. $C_8H_4N_6O_2$, mw 216.18, N 38.9%, mp 56° (decomp), detonates when heated rapidly. Can be prepd from phthalyl chloride and Na azide in aq acet under cold conditions



Refs: 1) Beil **17**, [334] 2) H. Lindemann & W. Schultheis, Ann **464**, 249 (1928)

Phthaloylperoxide (Phthalylsuperoxyd in Ger). $(C_8H_4O_4)_x$, mw $(164.12)_x$, crysts, mp 133.5° with decomp, puffs off at about 136°. Insol in the usual organic solvents. Was prepd by von Pechmann and Vanino by shaking phthalylchloride with a soln of Na peroxide in 10% aq Na acetate under cooling. Explds on rapid heating or when brought into contact with concd sulfuric acid

Refs: 1) Beil **9**, 804 2) H. von Pechmann & L. Vanino, Ber **27**, 1511–12 (1894)

PHX. Code letters for 1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. See Vol **1**, A52-L

PIAT. Acronym for *p*rojector *i*nfantry *a*nti*t*ank. A Brit WWII weapon based on the shaped charge effect. It fired a rocket-propelled charge weighing 3 lbs which could pierce 4-inch armor plate

Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw Hill, NY (1973), 349

Picarmite. A plastic military Dynamite, developed at PicArsn about 1949, contg 70 RDX, 15 talc, 9 di(2-ethylhexyl) sebacate, 3 polyisobutylene, and 3% SAE 10 motor oil. It had a wt strength equivalent to 47% straight Dynamite, a rate of detonation of 6625m/sec at its max d of 1.40g/cc when initiated with a Corps of Engineers Special Blasting Cap, and a brisance at the above d that was 1/3 to 1/2 that of **Composition C-3** (see Vol **3**, C484-R). It had the consistency of bread dough, was plastic at −70°F and remained flexible below this temp, was odorless, non-toxic, non-tacky, stable in

storage at 170°F, w-resistant, non-hygroscopic, and could be furnished in any color desired for camouflage purposes. It was superseded in 1950 by **Composition C-4**, also called **Harrisite** (see Vol **3**, C485)

Ref: K.G. Ottoson, "Development of Military Explosives Equivalent to Commercial Dynamites", PATR **1760** (1950)

Picatinny Arsenal. A US Army Armament Command (USAARMCOM) installation located near Dover, Morris County, New Jersey

USAARMCOM Regulation 10-10 assigns Picatinny Arsenal its mission, major functions and materiel assignments within the Armament Command. The following is an extract from that regulation:

Mission. To perform research, design development, engineering, integrated logistic support, maintenance support, procurement, fabrication, and product assurance of assigned materiel

Major Functions.

(1) Conduct research, development, test and evaluation with respect to assigned materiel and perform specialized research and technology in the following fields:

(a) Energetic materials
(b) Safing, arming, and fuzing
(c) Nuclear weapons
(d) Non-metallic materials excluding rubber, greases, lubricants, corrosion preventatives and fuels
(e) Munitions/Ammunition

(2) Conduct exploratory and engineering activities in the methods and technology of manufacture as applied to assigned commodities and their components, materials and ancillary equipment except projectile metal parts which are the responsibility of Frankford Arsenal, and specified elements of chemical items which are the responsibility of Edgewood Arsenal. This is to include support of plant/facilities modernization within ARMCOM, abatement of environmental contamination caused by manufacturing processes and exploitation of automation techniques

(3) Perform total system safety management throughout life cycle of all assigned systems, subsystems and equipment

(4) Perform in-house fabrication and pilot plant manufacture of prototypes and preproduction evaluation quantities; and emergency production of limited quantities of assigned critical items to fill in supply gap until industry can meet needs

(5) Conduct exploratory development for packaging of munitions which are assigned to ARMCOM

(6) Perform cataloging, standardization, new equipment training, and design of training devices, and provide technical assistance to users, as required by HQ, ARMCOM

(7) Perform design, product, process, maintenance, and value engineering, and related product assurance for assigned materiel

(8) Perform mobilization planning (general mobilization, continuity of operations, and industrial preparedness) to include utilization of pilot line fabrication and shop capabilities to provide assigned materiel in short supply until such time as industry can assure quantity production

(9) Develop, publish, and maintain supporting emergency plans in accordance with AMC guidance and the ARMCOM Civil Disturbance, Force Mobilization, War Emergency, and Disaster Control Plans

(10) Operate the Department of Defense Plastics Technical Evaluation Center

(11) Execute the technical management of the ARMCOM Weapons Vulnerability Program including Penetration Aids

(12) Provide technical support to the Federal Bureau of Investigation for operation and maintenance of the National Bomb Data Center

(13) Provide technical support to, and membership in, the Army Nuclear Weapons System Safety Committee

(14) Perform, as directed, maintenance and repair on nuclear weapons, radar, and inertial fuzes, Permissive Action Link Devices, ADM Firing Systems, and Adaptation Kits

(15) Operate the Department of the Army repository of drawing information pertaining to nuclear components received from the Atomic Energy Commission and its contractors

(16) Operate technical activity in support of DA hazardous munitions countermeasures program and technical escort program including explosives ordnance disposal (EOD) for all items assigned to the Army, including foreign surface munitions

(17) Perform surveillance testing on all standard US Army gun propellant and rocket propellants to support and advise field surveillance activities of the safe life potential and/or possible degradation of both bulk stored material and items using these propellants
(18) Provide guidance and assistance to the Navy and Air Force relative to Army requirements for EOD technical publications and tools and equipment developed and maintained by those services, and to be used by Army EOD units. Operate the US Army Technical Detachment
(19) Provide national procurement of nuclear munitions and of selected non-nuclear commodities as assigned
(20) Develop, prepare, and publish demilitarization procedures for assigned materiel
(21) Perform malfunction/deficiency investigations for assigned materiel
(22) Maintain direct contact with users to monitor design engineering and quality assurance potential problems for newly fielded items

Materiel Assignments.

(1) Nuclear and non-nuclear munitions (to include mines, grenades, demolition devices, explosives, explosive devices and initiators) except chemical and smoke munitions assigned to Edgewood Arsenal
(2) Artillery and tank ammunition (nuclear and non-nuclear)
(3) Recoilless rifle ammunition including rocket assisted types
(4) Aircraft dispersed munitions except for chemical items assigned to Edgewood Arsenal
(5) Nuclear and non-nuclear rocket and missile warhead sections, and assigned rocket motors
(6) Propellants and pyrotechnics, less smoke and tracers
(7) Safing and arming devices and fuzes except proximity and those assigned to Frankford Arsenal
(8) Non-metallic cartridge cases
(9) Other assigned equipment pertinent to mission items

Background. Picatinny Arsenal is a development Arsenal concerned with research and engineering of military propellants, explosives and hardware for Army weapons of all kinds and for the adaption of nuclear and non-nuclear warheads to missiles

The Arsenal is located in the central portion of northern New Jersey, near the town of Dover. This places it at the outer rim of the New York metropolitan area. It occupies a ten mile long valley, lying between mountain ridges which serve as natural barricades. The valley also has a natural water supply which, even today, is adequate. These are the three attributes for which the site was selected: nearness to the world of commerce; means of protection of the surrounding area from the hazards inherent in its work; and the availability of the one extremely vital natural resource – water

In approximate size, the Arsenal covers 6500 acres. Its activities are conducted in over 1500 buildings which are serviced by 85 miles of roads and 31 miles of railroad. Within its boundaries are two artificial lakes, three widely separated test-firing ranges, and two remote areas for the extremely hazardous activities

As to the dollar-value of the Arsenal, its facilities are valued at over $500,000,000. The nature of these facilities varies, from the conventional to the nuclear. Conventional ammunition production lines, control laboratories and inspection systems are maintained in stand-by and are occasionally used in experimental or pilot-lot production. Nuclear weapons ammunition, components and devices are developed and produced in the necessarily special research laboratories, proof-testing facilities and production and pilot assembly lines

History. Picatinny, or "water-by-the-hill", was the name given by the Lenape Indians to the brook flowing under what is now called Picatinny Peak. Thus, two of the essentials for the manufacture of ammunition are implied by its name

In the mid-eighteenth century a migrant blacksmith, Jonathan Osborne, was attracted by this plentiful water, by the supply of iron ore being mined over the mountain to the east, and by the inexhaustible forest of chestnut for his charcoal fires. At the foot of Picatinny Peak he built one of the first forges in New Jersey

A few decades later this Middle Forge, as it was called, entered the ordnance picture. With the coming of the American Revolution, when the Continental Army fought its way across New Jersey, it was used to produce solid cannon

shot. At that time the plant had been taken over by a liberty-loving ironworker named Jacob Faesch, who had emigrated from Switzerland to help the hard-pressed Americans

Early records fail to note the amount of ammunition produced. That it was considerable for that age may be inferred from the following known facts. To meet the demands, General Washington detailed 250 Hessian prisoners of war to augment the 440 workers assembled by Faesch from the scant local labor market. This working force of about 700 men turned out shot sufficient for waging a successful campaign; and for this, Faesch was made an American citizen by a special act of Congress

Even in Revolutionary days, the valley was the scene of multiple ammunition activity. Faesch also manufactured fuzes made of wood. As was specified for such components, his men moistened the powder "with a good grade of whisky" before tamping it into the fuze well

Following the Revolution, the iron forge and powder mill in the Picatinny Valley shared the changes of fortune of the country's industries. Except for brief periods of boom activity, particularly during the War of 1812 and the Civil War, they operated in comparative obscurity

In 1879, Congress appropriated funds for the establishment of a powder depot near New York. Major F.H. Parker of the Ordnance Department inspected nine possible sites within 100 miles of Manhattan. On the basis of those attributes already mentioned, the Picatinny Valley site was chosen. On September 6, 1880, the War Department purchased 1866 acres in the valley for $62,750. The Secretary of War designated the reservation as the Dover Powder Depot. Four days later he issued an order changing the name to the Picatinny Powder Depot. Six days later, on September 16, 1880, Major Parker was named the first Commanding Officer. In June 1883, the name was again changed to the U.S. Powder Depot

For more than a decade, Picatinny (as variously named) was merely a storage and powder depot. The initial building, a magazine 200 by 50 feet, was built at a cost of $51,700. Four other magazines followed rapidly, as did officers' quarters, stables for the horses and the necessary service buildings

The first phase of the development of the Arsenal extended to the year 1902, and the history of the depot was one of gradual construction with the ultimate idea of an establishment for the storage of powder. However, a few years before the Spanish American War, the depot began assembling powder charges for cannon. This propellant charge loading, Picatinny's first production activity, has never ceased

In 1902, the need was felt for the storage of a war reserve of sodium nitrate, of armor-piercing projectiles and of high explosives. The second phase of Picatinny's development began. Six projectile sheds and some nitrate buildings were erected. A year later, a temporary plant was installed for filling projectiles with Maximite and several thousand armor-piercing projectiles were filled with this explosive

The third phase of the Arsenal's development began with an appropriation in 1906 of $165,000 for the erection and equipage of a powder factory. This work was undertaken by Major B.W. Dunn, Jr, the inventor of Explosive "D", which replaced Maximite for armor-piercing shell. In 1907 this, the Army's first powder factory, was constructed. It was at this time also, and in line with its expanding activities, that the name was finally changed to Picatinny Arsenal

Subsequent Commanding Officers supervised the powder factory and in the ensuing eight years, production increased from 3,000 to 9,000 pounds of cannon powder a day. Under the command of Major O.C. Horney, the Arsenal added other factories, including one for Explosive "D" and one for the manufacture of .30 caliber powder. In addition, an officers training school was established for instruction in the chemistry of explosives and interior ballistics

At the outbreak of World War I, Picatinny was producing all sizes of propellants from .30 caliber up to 16-inch; for weapons from the rifle to the sea-coast gun. But possibly more important was the knowledge the Army obtained thru its development work. Quality was constantly improved and costs were constantly lowered. The investment in the training school was repaid many times in the preparation of the Ordnance officers to face difficult situations in action

In the years following World War I, Picatinny started the melt-loading of projectiles on a production basis, and the development and manufacture of pyrotechnic signals and flares. This

latter research took pyrotechnics out of the "fireworks" class which had proved so ineffective during the war. It designed and produced an entirely different and effective group of pyrotechnics. In these years also, experimental plants were set up for the manufacture of more modern propellants, high explosives, fuzes and metal components. The manufacture of fuzes on a production scale was started

The modern Picatinny Arsenal dates from July 10, 1926, the Saturday afternoon when lightning struck a tree overhanging a magazine at the neighboring Naval Powder Depot at Lake Denmark. The detonation of the depth bombs stored in that magazine, and minutes later, of two neighboring magazines, laid waste much of Picatinny. Since Saturday noon was, at that time, the end of the work-week, the loss of life was extremely limited for such a major disaster, with 18 fatalities (See Vol **6**, E374-R to E377-R)

The Board of Officers investigating the disaster recommended not only the Arsenal's immediate reconstruction, but urged that more land and facilities be added, to the end that a bigger, better, and safer manufacturing and development Arsenal should result. The recommendation was followed. Within a few months, activities were resumed, the rubble was pushed back and the single-story brick magazines, which had survived the blasts, were reroofed and rewindowed. In these makeshift buildings the plans were drawn for the administration building and the laboratory group, which were the nucleus of the present facilities

The subsequent story of Picatinny is revealed thru its accomplishments:

Long before World War II, the Axis powers were boosting their stockpiles of arms. By 1938, following the now infamous Munich Pact, President Roosevelt began to call for increased armament production in the U.S. When the Germans pushed the Allies into the sea at Dunkirk, Picatinny Arsenal was the only plant in the U.S. capable of producing large quantities of artillery ammunition and bombs, high explosives and pyrotechnics, fuzes and other essential ordnance

It was no accident that Picatinny was ready. While the U.S. has no military ammunition industry in peace times, Congress always has permitted the Army certain funds for research and engineering work, which is the primary mission of Picatinny. As such, it always has been the Arsenal's function to be prepared to advise private industry on new and better ways to manufacture ordnance when the time comes. An all-important phase of this activity was the manufacture of munitions on a pilot plant basis

The Ordnance Corps' sensitivity to the urgent demand for war material kept pace with the swift-moving events in Europe. Thus, most of the pilot plant operations at Picatinny were expanded to all-out assembly line production before Hitler overran the Low Countries

At the time of the Japanese attack on Pearl Harbor, no other plant existed in the U.S. capable of making anything larger than small arms ammunition. There was no knowledge elsewhere; there were no detailed plans for whole industries elsewhere. Without the industrial "know-how" developed at Picatinny, the rapid conversion of commercial concerns to mass ammunition manufacture would have been impossible

While waiting for private industry to convert its assembly lines for ammunition production, Picatinny filled the gap. Between July 1939 and September 1952, more than 7,500,000 bomb fuzes, almost 20,000,000 boosters, 44,000,000 artillery primers, 39,000,000 artillery fuzes, and countless millions of other items were turned out

With the outbreak of war, Picatinny immediately set to the task of training workers. During the conflict, more than 8,000 men and women were trained in the highly specialized techniques peculiar to the mass production of all munitions other than small arms. In addition, almost 20,000 persons involved in munitions work visited Picatinny

To illustrate the value of these efforts: in one year the job training methods, research projects and improved work developments originating at Picatinny, and passed along to outside plants, saved the Government more than $30,000,000. This accomplishment was recognized by Lt. Gen. Brehon Somervell, Chief of the Army Service Forces, and Maj Gen L.H. Campbell, Jr, Chief of Ordnance, in letters to the Commanding Officer

Thus was proved the Army's foresight in maintaining Picatinny during the years of peace.

Only because of the Arsenal's ever awake research and development program was the United States able to turn to a ready source to meet the demands for information when the need arose

To Picatinny's accomplishments in meeting the urgent needs for masses of ammunition and aid to industry must be added two others: the production of new types of ammunition to meet specific needs; and delivering them in time

In 1944, the Navy needed 200 special bomb fuzes. Over one weekend the fuze parts were received from a firm in Milwaukee, the fuzes loaded and assembled, and delivered to a carrier-based plane from the Saratoga, then far out at sea in a task force on its way to Murmansk

Still another illustration of Picatinny's problem-solving ability: Ammunition manufacturers had long depended exclusively on silk for cartridge cloth. Because of its high tensile strength and low ash content it made an ideal container for propellant load charge. America could not rely on silk as it did not control the supply. Cotton would be ideal from the standpoint of supply and low price, but was objectionable because of its high ash content and the danger of resulting embers in the gun barrel

This was a problem to all the Allies: but it was a Picatinny researcher who solved it. Thru patient burning of samples of cotton cloth, for burning time and amount of residual ash, he narrowed down the fabrics to a few good possibilities. Then he traveled to cotton mills in New England and the South to seek still better cloth. Finally a cotton fabric was developed as a suitable substitute for silk

The Ploesti oil fields were a vital source of petroleum for Hitler's forces. Special bombs were needed to blow up those fields. Picatinny Arsenal supplied these and the Ploesti installations vanished into thin air

Other special bombs were needed to blow up dams on the Dnieper River in Russia and thus immobilize 600,000 Germans. The Arsenal planned the bombs, made them and shipped them. They did the job

Still another illustration involves the English fog. American airmen there, in their around-the-clock bombing of German targets, suffered heavier casualties in landing on the fog-bound runways than during combat missions. A flare was needed which would develop 800,000 candle power, burn for at least five minutes, be able to penetrate mist and fog, develop little or no smoke, have a mount suitable for installation on new runways and be easy to ignite under the most adverse weather conditions. Picatinny's pyrotechnics engineers produced an even better flare; and the first 250 of them were flown to England, all within 60 days after the request was received

During the Battle of the Bulge alone, these flares were credited with preventing more than 100 bombers from crashing

Other problems of the airmen were solved at Picatinny. In 1943, the introduction of skip-bombing brought a special request. Because of the low altitude at which the bombing plane had to fly, a bomb with a delay fuze was required to permit the plane sufficient time to get away from the effective range of the explosion. In many instances, bombs were to be dropped from as low as 25 feet. Again, Picatinny came up with the answer: a fuze which would delay detonation of the bomb eight to eleven seconds.

Another instance of aid to the Air Corps involved its radio IFF System (Identification, Friend or Foe) to protect fighter and bomber planes against enemy attack from the rear when returning from a mission. More than 100 heavy bombers were grounded in the U.S. until Picatinny came thru with a vitally needed item. The situation was this: The IFF System was based on a combined radio transmitter-receiver in each plane, tuned to a secret wave length. When a plane came up behind the U.S. Aircraft, the pilot of the pursued plane knew immediately whether the one behind him was a friend or foe. As long as the enemy never put his hands on one of the transmitter-receivers, the secret would be safe. Air Corps Commanders knew, however, that sooner or later a U.S. plane would go down behind enemy lines and the secret would be no more. Picatinny was sent an "emergency" order to design, develop and produce a controlled explosive which, housed inside the trans-receiver, would blast the radio beyond restoration upon receiving any jar greater than that experienced in normal landing operations. The order was phoned from Washington and immediately the resources of the Arsenal were swung behind the assignment. The Technical

Division – operating behind sealed doors because the job was top secret – came up with the answer: a short, serrated metal tube containing just enough explosive to shatter the inside of the radio set without causing any damage to the plane. The development of this item was spiked with troubles. An essential part of the design was a plastic plug at one end of the tube. This required top precision machining of the mould for the plastic; when this was half ground, the two machinists were simultaneously drafted into the Army. In a rare adjustment to emergency, the discharge of the men was effected and 48 hours later they were back on the job. Without revealing the reason for the urgency, the grinders were pressured to speed up the job. It looked then as if they might complete it in less than six weeks instead of the estimated two months. Toward the end of the period the Arsenal received a demand: 150 "destructors" within three days. This was on Sunday night. On Tuesday evening, 200 destructors were aboard a dispatch plane at Newark Airport

These and hundreds of other difficult assignments were handled by Picatinny; and with similar dispatch. The civilian employment rose to 18,000, of whom 10,000 were women

Buildings were expanded and new construction went on continuously. At a press visit to the Arsenal in 1941, Col W.E. Larned, Commanding Officer, told reporters: "We don't need new buildings. We need ammunition. We can make it in tents, if necessary." Unexpected realism was given this statement. Workers reporting to a new components building, not yet completed, found it weather-proofed with huge tarpaulins; but the miniature parachutes for flares rolled out on a 24-hour, three-shift basis

In addition to producing ammunition, the Arsenal had to help get it to the front on time – and in good condition. Picatinny saw to it that the items were well packed. Packaging engineers were imported to supplement the Arsenal's staff to develop better methods of packing bombs, explosives and ammunition. Engineers from private industry came to Picatinny to learn the science of packaging

The close of this period of great war activity was marked by V-J Day. It also marked, faintly and hesitatingly at first, the beginnings of a new era – the establishment of Picatinny Arsenal as a modern research, development and engineering center. Gradually the installation converted its primary role to that of research and engineering of new ordnance to provide the Army with the most modern and effective means of combat

The outbreak of hostilities in Korea belied the theory that the A-bomb would put an end to all wars, and it proved once more the importance of Picatinny's role. When the North Koreans began using Russian-made T34 medium tanks in the middle of July 1950, the U.S. 8th Army's toe-hold on Taejon began to slip. Even the reliable Bazooka, the rocket launcher that had stopped Rommel's Tank Corps in Africa, could not stop the massive, heavier T34's imported from Soviet Siberia. In the United States, a new and more powerful 3.5-inch Bazooka had just been perfected. At Picatinny, rocket shell for the improved weapon were produced on a pilot lot plant test basis. Immediately General MacArthur issued a dramatic call for the new Bazooka. If he was to be successful in fighting a delaying action until more troops arrived, he had to have the best ordnance available – if possible, better than the enemy's. In less than 24 hours the test plant was expanded to full-scale assembly line production. As finished rockets came off the line, they were trucked to nearby Morristown Airport where waiting Army cargo planes loaded them for the trip to the other side of the world. Seven days after General MacArthur radioed his urgent demand for the heavier Bazookas, seven Red tanks were knocked out of the war. In a matter of a month the tanks no longer were a major menace

When the hordes of bugle-blowing North Koreans attacked U.S. positions, our troops found existing battlefield illumination unsatisfactory. To more effectively combat the enemy forces, they needed a pyrotechnic item which would illuminate the attackers from the rear, thus silhouetting them to make better targets for our riflemen. With typical GI ingenuity, they attached trip flares to tail fin assemblies which normally were used to launch conventional fragmentation grenades from rifle launchers. A make-shift arrangement, it was not the most efficient system. Picatinny's pyrotechnics experts stepped into the picture. Within a matter of weeks, a new illuminating rifle grenade was developed and delivered to front line troops,

increasing the accuracy of our infantrymen during the nighttime raids

Thus, during the Korean conflict, Picatinny reassumed its mission: meeting emergencies on time, and the mass production of the ordnance it had designed and developed

In subsequent years, the Arsenal achieved one of its most notable achievements: the development of a nuclear shell which was capable of being fired from an artillery gun. This gave the United States its first nuclear artillery weapon, the 280mm Cannon. Picatinny's success in producing the first nuclear shell inevitably led to the development of other sizes of atomic shell. To meet the need for a smaller, more mobile weapon than the 280mm, the Ordnance Corps in August 1952 called for an 8-inch nuclear shell capable of being used in both Army and Navy weapons. With the Korean Conflict still on and the future uncertain, a crash program was ordered. Though the 1953 armistice ended the fighting in Korea, work on the 8-inch shell continued to completion at a rapid pace. Besides, at that time, being the smallest package of nuclear ammunition achieved, the 8-inch shell was also notable because it was the first shell of any kind to use the lightweight, high strength metal, titanium

Another application of nuclear energy to weaponry was in the nuclear demolition munition or "ADM". These are pre-positioned nuclear warheads to which are linked firing devices that set off the explosion at the desired time. An ADM is easily transported and can provide as much blast effect as 500 railroad box cars of TNT. ADM's may be emplaced above or below ground or underwater. The early ADM's were simply nuclear bombs converted into time bombs. Later developments scaled down their size to the point where components of low-yield ADM's could be man-carried to the emplacement site. The bulk and weight of larger yield ADM's were also considerably reduced. One of Picatinny's chief contributions to the ADM program was the development of a Universal Firing Device. This UFD, more compact and rugged than any of its predecessors, can convert any of the Army's present or future nuclear warheads into a nuclear demolition munition

A nuclear weapon created for infantrymen – the Davy Crockett – was developed under the technical direction of Picatinny. This weapon could be hand carried and fired from a tripod by two or three men. A heavier launcher with longer range was mounted on a jeep or armored personnel carrier and fired by two men. The lighter model was also vehicle-mounted. Great as was the destructive force of the Davy Crockett, its effective radius was kept small enough to protect the using forces as well as other friendly troops and civilian population from blast danger. The danger from radioactive fallout was thus minimized

In the field of support devices, the Daisy photoflash cartridge was developed by Picatinny's pyrotechnics experts. It was used in the optical tracking of intermediate and long-range missiles. Such tracking is for the purpose of evaluating the performance of the guidance and control mechanisms in missiles, thereby helping to improve the accuracy and reliability of these mechanisms. The tracking was achieved by affixing to the missiles a set of photoflash cartridges which fired at intervals while the missile was in flight and photographed by two or more ballistic cameras set at prefixed positions on earth. Since the firings were made at night, these cameras photographed not only the man-made star – the Daisy – but also the natural stars. With the positions of these natural stars as established reference points, the track of the Daisy was determined with great accuracy. This accuracy was greater than could be achieved by electronic means because it made tracking independent of any errors arising from the missile system itself and of distortions caused by the ionosphere. The Daisy cartridge weighed only two ounces but produced 20 million candlepower, visible at a distance of 1000 miles or more.

Another contribution of Picatinny's pyrotechnics engineers was the development of the infrared decoy, used by planes to divert enemy missiles which are attracted to the plane's infrared exhaust emanations. These decoys consist of high-efficiency infrared flares which are ejected by the plane at the appropriate time, attracting the missiles to the decoys and away from the plane

Still another development of the pyrotechnic engineers was a nuclear timer, more accurate and rugged than any mechanical timer. Depending for its power on a nuclear battery, the

timer, in addition to its use in missile research, gave technicians the capability of pinpointing the location of nose cones thru sound tracking

Among the missile systems to whose development Picatinny has contributed were the various members of the Nike family. The Nike-Ajax was the country's first supersonic air defense guided missile fired from the ground to intercept and destroy enemy planes. The Nike-Hercules, capable of much longer ranges and higher altitudes, could carry a nuclear warhead. The Nike-Zeus was the first weapon designed to intercept inter-continental ballistic missiles. Picatinny designed the "business end" of these weapon systems, the warhead section, which includes the explosive payload plus its fuzing, safing and arming devices. Ancillary handling and checkout equipment is also designed and developed by the Arsenal

To defend against low-flying aircraft, Picatinny developed the warhead for the Hawk, which can be used not only to defend fixed installations but which can be carried by fast-moving combat troops in the field

The Corporal, equipped with either a nuclear or conventional high-explosive warhead, gave the field commander a weapon with which he could hit tactical targets 75 miles away. Succeeding the Corporal came the Sergeant, which was air-transportable and could be quickly emplaced and fired by a relatively small crew under almost any weather or terrain conditions

The Honest John, with the range of medium to long-range artillery, was designed to provide close-fired support in land combat operations. With a single round the Honest John could deliver as much demolition effect as several hundred artillery shell. The Lacrosse was another general support weapon that was not only powerful but was so accurate that it could be used to destroy small fortifications

The Redstone was designed to deliver its nuclear or high explosive payload a distance of more than 150 miles. Its successor, the Pershing, is much smaller, lighter, and more mobile

The Lance system enables the fielding of a nuclear capability with improved field readiness and greater versatility over the Sergeant, Honest John and Little John systems

Although missiles and other nuclear items were the new weapons of the post-Korean period, the need for the older conventional gun-type weapons had not disappeared. Existing missiles were not as accurate or reliable as artillery guns and did not provide their rate of fire and responsiveness. For many uses, missiles were also much more expensive than gun artillery

Picatinny Arsenal's contributions to the recent military effort in Southeast Asia were substantial. The timely and quantitative production of bombs and other standard items of ammunition was accomplished until industry could regear to resume that role. The Arsenal also responded to the need for the development of new and improved munitions during this period, including more effective fuzes and safing and arming devices

The development of a family of 40mm ammunition for helicopter and infantry was a typical example. Because of the broad spectrum of industrial facilities and processes which support the munitions program on a nation-wide basis, a major effort at Picatinny in terms of manpower and technology effort is being expended to support a multi-billion dollar Plant Modernization Program for improvement of GOCO facilities to insure production operations that are modern, economical, safe, automated and non-polluting. A concomitant to the progress of Arsenal technology is an ever increasing awareness and application of the latest industrial pollution abatement technologies and a priority concern with environmental protection

In the highly versatile 175mm gun, for which Picatinny developed the ammunition, the Army has a weapon superior to any World War II cannon. Picatinny also streamlined the 81mm and 4.2-inch mortar shell to provide greater accuracy and longer range. The lethality of the shell was considerably increased. Increased range was provided for the 105mm and 155mm howitzers

Another weapon system which was developed and engineered for production by the Arsenal for Southeast Asia was Beehive ammunition of varying calibers which dispense great numbers of tiny, lethal steel darts. This type of ammunition proved effective in Southeast Asia since it lends itself to use against troops in frontal mass assault as well as those entrenched behind the cover of heavy jungle brush

Historically, mines have been defensive wea-

pons. Their use has required time consuming operations to lay a field in expected avenues of enemy approach. In an effort to overcome this problem, the Arsenal conducted studies to determine the feasibility of rapidly emplacing mine fields from aircraft. During the height of the Southeast Asia conflict, such a system was designed, developed, produced in quantity and utilized in the field

Advancing technology as well as this demonstration of potential utility of Mass Scatterable Mines led the Army to revise mine warfare doctrine and establish new requirements for a family of Scatterable Mines that could be rapidly and remotely emplaced by a variety of delivery systems. This requirement called for both Anti-Tank and Anti-Personnel Mine Systems. To this end, two first generation systems are well advanded in development. These are: the XM56, a helicopter delivered Anti-Tank Mine System and the XM692, an artillery delivered Anti-Personnel Mine System. Other second generation systems which add increased versatility and capability are scheduled to follow

Presently the Arsenal's scientists and engineers continue to explore ways and means of developing new and improved versions of existing munitions which would be required to meet the challenge of another time and a confrontation of a different nature. This it does thru its comprehensive and continuing program of research, in the nuclear as well as the non-nuclear field. Such efforts include missile warhead programs, aircraft weaponization, rocket assisted projectiles, tank weaponry, flare development, and similar projects, all of which are aimed at making the American soldier the world's best equipped fighting man

Effective July 1973, the U.S. Army Armament Command was established as a Major Command of the U.S. Army Materiel Command, located at Rock Island, Illinois. Effective 30 September 1973, the U.S. Army Munitions Command and the U.S. Army Weapons Command were disestablished and merged into the operational command of this new Armament Command. Picatinny Arsenal, as a Commodity Center, presently reports organizationally to the U.S. Army Armament Command

Refs: 1) N.F. Ramsey, ArOrdn **7**, 1–8 (1926) (Historical background) 2) F.H. Miles, ibid, 9–12 (1926) (The Picatinny Arsenal Powder Factory) 3) G.C. Hale, ibid, 13–18 (1926) (Research activities at Picatinny Arsenal) 4) H.H. Zornig, ibid, 19–22 (1926) (Organization and administration of development work at Picatinny Arsenal) 5) J.P. Harris, ibid, 40–48 (1926) (Loading ammunition at Picatinny Arsenal) 6) C.J. Bain, ibid, 49–52 (1926) (High explosives at Picatinny Arsenal) 7) F. Olsen, ibid, 53–57 (1926) (The relation of Picatinny Arsenal to field service) 8) W.H. Tschappat, ibid, 131–34 (1926) (The Lake Denmark explosion; its effect on Picatinny Arsenal)

Picramates. Salts of Picramic Acid. See in Vol **1**, A242-L to A243-L

Picramic Acid. See under 4,6-Dinitro-2-aminophenol in Vol **1**, A241-R

iso-Picramic Acid. See under 2,6-Dinitro-4-aminophenol in Vol **1**, A243-R

Picramide. See under 2,4,6-Trinitroaniline in Vol **1**, A409-R

PICRATES

The salts and additive compds of Picric Acid (PA) are usually included under picrates. For convenience, inorganic and organic picrates will be described separately

PICRATES, INORGANIC

PA attacks all the commonly used metals except Al and Sn, with the formation of salts known as picrates. These salts can also be prepd by the action of PA on hydroxides or carbonates, or by other methods. Nearly all picrates are expl, and are usually more sensitive than PA. Some picrates, eg, Pb Picrate, can serve as initiating agents. Many picrates detonate with such

violence that they can initiate an indefinite amt of PA; even wet PA can thus be expld (Ref 7)

The hazardous nature of the picrates is underscored in Urbański's description of the construction of PA driers (Ref 11):

"The construction of pciric acid driers presents certain difficulties because of the ready formation of picrates. Having this in mind, wood is mostly used as the construction material for driers, and any metal parts (screws, nails) should be made either of metals that form picrates with difficulty such as copper or aluminum, or of tinned metals or stainless steel. Floors should be made of wood covered with linoleum or concrete coated with asphalt. At the beginning of World War I when concrete floors were commonly in use, picric acid would with time form picrates with cationic constituents of the concrete: calcium, magnesium, sodium and iron. Washing the floor created conditions favourable for the penetration of picric acid into the concrete, and after several months a thick layer of picrates used to form. Any friction, as for example, by moving a bench around or any sort of blow, initiated an explosion of picrates all over the floor, causing fire or explosion in the drier. The inside walls should be plastered with plaster of Paris, since gypsum, being the salt of a strong acid, yields calcium picrate only with difficulty. Lining the walls of the drier section with white glazed wall-paper is recommended. Heaters for heating the drying air should not be placed inside the drying premises. Workman who have to enter the drying section should put on protective wooden-soled shoes with no nails in them. The floor should be swept frequently and washed with water."

Although metallic picrates have been known since as early as 1795 (Ref 4), there is still much confusion in regard to their compn and properties. The first application of picrates as expls seems to have been made in 1869 by Designolle of Fr, who proposed the use of K picrate, K nitrate and charcoal in various proportions. Fontaine proposed a mixt of K picrate and K chlorate, while Brugere and Abel, independently, and about the same time (1869), proposed the use of mixts of Amm Picrate and K nitrate (Ref 7)

The first systematic study of metallic picrates seems to have been done in 1901 by Dupré (Ref 2). This was followed by Will in 1906 (Ref 3), Silberrad and Phillips in 1908 (Ref 4), and Kast in 1911 (Ref 5). More recently (1938), Hopper of PicArsn (Ref 6) detd and described the expl properties of the following metallic picrates: Al, Cd, Cr, Cu, Fe^{+3}, Fe^{+2}, Na, Ni and Zn. In general, he prepd the salts as cryst hydrates from aq solns by methods outlined by Silberrad & Phillips, and Kast. These were then dehydrated by heating at temps of 80 to 150°, depending on the ease with which the w of crystn could be driven off, to obtain the desired degree of hydration

The salts were identified by their metallic content, which was detd by standard lab methods. Their expln temps were detd by the method originated by H. Weber (Bull US Bureau of Standards **9**, 119 (1913) and modified at PicArsn [PATR **1401** (1944)]. The sensitivity to impact was detd using the PicArsn app, described by H.S. Deck [ArmyOrdn **7**, 34 (1926)], using a 2kg wt

According to Hopper, the relative sensitivity of metallic picrates depends largely upon the amts of w of crystn present. The highly hydrated forms are very insensitive, the lower hydrates are in general more sensitive, and the anhydr forms most sensitive. The anhydr salts, with the exception of Na, Amm, Al and Fe^{+2}, are more sensitive to impact than PA. Anhydr Cu, Zn and Cd picrates are only slightly more sensitive, while anhydr Ni picrate is especially sensitive, lying in the sensitivity range between MF and Tetryl

According to Thorpe's (Ref 7), the order of impact sensitivity of some of the metallic picrates is as follows; Pb > Fe > Co > Ni > Ba > Cu > Mn > Zn > Ca and Na, with Amm picrate being among the least sensitive

The sensitive anhydr salts are obtained with difficulty by prolonged heating of the hydrated forms at temps above 100°

The picrates prepd by Hopper, as well as other expl picrates, are described below

Refs: 1) Beil **6**, 275–78, (134–35) & [262–65] 2) A. Dupré, MP **11**, 92 (1901) 3) W. Will, SS **1**, 209 (1906) 4) O. Silberrad & H.A. Phillips, JCS **93**, 474–89 (1908) (Metallic picrates, with numerous refs, beginning in 1795) 5) H. Kast, SS **6**, 8–9, 31–33 & 67–70 (1911) (Metallic picrates) 6) J.D. Hopper, JFrankInst

225, 219–25 (1938) (Prepn and expl properties of some metallic picrates) 7) Thorpe's **4**, 482–3 (1940) 8) E.E. Sancho, "Quimica de los Explosivos", A. Aguado, Madrid (1941), 158–59 9) Davis (1943), 165–69 10) Vivas, Feigenspan & Ladreda **2** (1946), 255–58 11) Urbański **1** (1964), 518 12) Kirk & Othmer **8** (1965), 618

List of Inorganic Picrates

Most of the salts described below can be prepd by interaction of PA with the corresponding inorganic salt or base. Inasmuch as PA is only sparingly sol in w, it is advisable to dissolve the metallic salt (or base) in w, and then introduce the PA in a finely divided state. For example, the Ksalt (see below) can be prepd by saturating a hot K carbonate soln with powdered PA; $2C_6H_2(NO_2)_3OH+K_2CO_3 \rightarrow 2C_6H_2(NO_2)_3OK+H_2O+CO_2$. When the liq is cooled, pale yel acicular crysts separate out

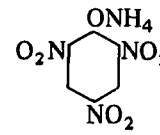
Aluminum Picrate. $[C_6H_2(NO_2)_3O]_3Al$; mw 711.31; N 17.73%; mp, fuses above 100° and explds on further heating. Can be prepd by the prolonged heating of one of its hydrates (such as di-, tetra-, deca-, or hexadeca-hydrate) to 100°. Its impact sensitivity is 16″ vs 14″ for TNT, as detd with the PicArsn app with a 2kg wt. The dihydrate, $[C_6H_2(NO_2)_3O]_3Al.2H_2O$, obtained by heating the decahydrate to 80°, is comparable in sensitivity to the anhydr salt, while the decahydrate is very insensitive. The expln temp is about 360°

Refs: 1) Beil **6**, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS **93**, 483 (1908) 3) J.D. Hopper, JFrankInst **225**, 224 (1938) 4) Davis (1943), 165

Aluminum Picrate (Basic). $[C_6H_2(NO_2)_3O]_2$. $AlOH.7H_2O$; mw 530.35, N 15.85%; reddish to pale yel needles which, when heated to 80°, change to the tetrahydrate, a pale yel powd which, on heating, decomps without explding

Ref: Colver (1938), 331

Ammonium Picrate (Explosive D, Dunnite, Ammonium trinitrophenolate). $C_6H_2(NO_2)_3.ONH_4$;



mw 246.14; N 22.77%; OB to CO_2 –52%; exists in stable yellow and metastable red forms of orthorhombic crysts; mp, decomps without melting >265°; d 1.717g/cc (it can be pressed to a d of 1.64g/cc at 100,000psi); RI at 20°, a_o 1.508, b_o 1.870 & c_o 1.907; Q_f 395cal/g; Q_e 800cal/g; Q_c 2745cal/g

History. Amm Picrate was first prepd in 1841 by Marchand, but it was not until 1869 that it was used by Brugère (see Vol **2**, B318-R), in admixt with K nitrate, as a proplnt for the Chassepot rifle. Later, in 1888, it was patented by A. Nobel for use in Dynamites. It was adopted as a mil expl by the US Army in 1901, and the US Navy in 1907. Its importance as an expl was based on its relative insensitivity to impact and friction, making it ideal for use in armor-piercing (AP) projectiles, even though it was slightly inferior to TNT in expl strength. For several years it was used mainly in conjunction with BlkPdr in projectiles. The usual loading consisted of Explosive D in the nose section with BlkPdr in the rear, however, from 1917 thru WWII, the Navy used it for AP common and high capacity projectiles of practically all calibers, as well as AP and common rocket warheads and AP aircraft bombs. The demand for Explosive D during WWII was quite high, increasing from 1,500,000lbs/month in 1942 to 6,500,000 lbs/month in 1944. During the last year of WWII, Composition A-3 (see Vol **3**, C474-R) began to replace Explosive D in smaller anti-aircraft (AA) projectiles. However, the development of Jet-Assisted-Take-Off (JATO) units, which used a mixt contg 50% Explosive D, counterbalanced its replacement in AA missiles (Ref 11). Currently, Explosive D is no longer used as a bursting-charge expl in shells, having been displaced by more modern expls of greater strength

General Properties. Chemically, Explosive D is not very reactive. It is decompd into PA and ammonia by strong alkalies. At 0°, it absorbs one molecule of ammonia, but loses this at 26°. When maintained at its mp, it decomps

As stated above, Explosive D is remarkable chiefly for its insensitivity to shock, which

permits its use in AP projectiles. It has a relatively low expln temp test value, and is slightly sensitive to frictional impact as indicated by friction pendulum and rifle bullet impact test results (see below). It is relatively insensitive to initiation, as it cannot be detonated completely in the sand test by Pb Azide or MF alone, but it can be detonated by DDNP. When stored at 50° for two years, Explosive D is sensitized so that it can be detonated with MF alone. Subsequent storage at ordinary temp restores its previous insensitivity

Explosive D is approx 80% as brisant as TNT, as indicated by sand tests, but fragmentation tests in shell have shown it to be about 95% as brisant. Both expls have about the same rate of detonation at a d of 1.56g/cc; hence, approx equality of brisance would be expected. The rate of detonation of Explosive D has been found to be somewhat affected, particularly at lower loading densities, by the granulation of the material, but this effect is not pronounced. Its expl strength is 98% that of TNT, as evidenced by the ballistic pendulum test (see below)

As judged by vacuum stability test data (see below), Explosive D is of a very high order of stability. The material has been found to withstand storage at ordinary temps for a period of twenty years with no evidence of deterioration, and at 50° for more than five years without marked deterioration

Explosive D should not be exposed to moisture, since w reduces its strength and sensitivity to detonation. Moisture also increases its reactivity with metals such as Pb, K, Cu, Fe, etc, to form extremely sensitive compds. This reactivity requires that all projectiles loaded with this material must have contact areas covered with acid-proof paint

When Explosive D is ignited in an unconfined state, it burns slowly, emitting dense black smoke without detonation. When confined and heated to its ignition temp, it will expld. When detonated completely, it emits a dense cloud of black smoke with a sooty deposit and an odor of ammonia. When an incomplete detonation is obtained, a yel smoke is observed, together with unburned particles of Explosive D

Explosive D which has been pressed into and removed from projectiles or other ammo is much more sensitive to shock than new or unused material. Therefore, reclaimed material should not be pressed or loaded into ammo items until it has been recrystd (Ref 12)

The destruction of Explosive D can be accomplished by chem decompn by dissolving the expl in thirty times its wt of a soln made from one p of Na sulfide in six p of w (Ref 13)

Preparation. Explosive D is manufd by suspending PA in hot w and neutralizing it with gaseous or liq ammonia. As the picrate is formed, it goes into soln; on cooling, it ppts out. An excess of ammonia leads to formation of the red form of Amm Picrate, and should be avoided. The separated crysts are washed with cold w to remove any excess ammonia, and dried

Solubility. In gms/100gms of solvent:

	Temperature, °C						
	0	10	20	30	50	80	100
Water	–	0.70	1.02	–	–	–	75
Alcohol	0.51	0.69	–	1.05	1.89	3.62	–
Ethyl Acetate	0.29	0.30	–	0.38	0.45	0.56	–

Brisance. Sand Test, 200g bomb: 37.5 to 39.5g sand crushed vs 48.0g for TNT (78 to 82.5% TNT). Plate Dent Test: Method A for pressed confined charge, 91% of TNT at d 1.50g/cc

Explosion Temperature.

Seconds	°C
0.1 (no cap used)	405
1	367
5	318 (decomps)
10	314
15	299
20	295

Friction Pendulum Test. Steel shoe, unaffected

Heat of Combustion. 685kcal/mole at C_v (Ref 1, [262]); 2890cal/g at C_v [Ref 1 (134)]; 2745cal/g at C_p

Heat of Explosion. 800cal/g

Heat of Formation. 395cal/g or 97.04kcal/mole

Hygroscopicity. At 100% RH and 25°, gains 0.1% to equil

Impact Sensitivity. PicArsn app, 2kg wt, 16-17″ vs 12-14″ for TNT

Initiation Sensitivity. Min charge of MF to initiate 0.4g of Explosive D loaded at 200atm/sq inch in detonator cap is 0.85g vs 0.26g MF necessary to initiate 0.4g TNT

Loading Density.

d, g/cc	psi
1.33	3,000
1.41	5,000
1.47	10,000
1.49	12,000
1.51	15,000
1.53	20,000
1.64	100,000

Power. Ballistic Mortar, 99% TNT

Pressure. Max theoretical; when expld adiabatically at C_v, 8956kg/cm^2 at d 1.5g/cc and 9553 kg/cm^2 at 1.6g/cc. These are 113% of the corresponding values for TNT

Rifle Bullet Sensitivity. 10 trials, 7 unaffected, 3 partly burned

Sensitivity to Electrostatic Discharge. Thru 100 mesh material, confined 6.0 joules, unconfined 0.025 joules (Ref 10)

Stability. Vacuum Stability Test, 5g sample:

°C	100	120	150
cc gas/40 hrs	0.2	0.4	0.4

100° Heat Test: % loss 1st 48 hrs, 0.1; % loss 2nd 48 hrs, 0.1; expln in 100 hrs, none

130° Heat Test: No expln and not acid in 300 min

Toxicity. Explosive D is not markedly toxic, but it discolors the skin and may cause a dermatitis in some cases. Inhalation of the dust should be minimized, and frequent baths and changes of clothes are desirable for those working with the material in quantity (Ref 14)

Velocity of Detonation. 4750m/sec at d 1.0g/cc, and 7040m/sec at d 1.60g/cc with a 2.5x40cm unconfined charge; 6850m/sec at d 1.55g/cc for a 1.0 inch charge diameter. It can be calcd approx from the formula, V=960+3800d, where d is density in g/cc, and charge diameter of 1.0 inch is employed

The requirements of the US Armed Forces are described in Military Specification **MIL-A-166C** (6 January 1975) entitled, "Ammonium Picrate (Explosive D)". It covers one grade of material, representing two classes with respect to granulation. Class 1 material (coarse) is intended for use in the press-loading of shells, while Class 2 (fine) is used for the manuf of Picratol and other compns. The requirements are as follows:

Table 1
Requirements for Ammonium Picrate (Explosive D)

Property	Requirement Class 1	Class 2 *
Surface moisture and volatiles content, %, maximum (max)	0.10	–
Total moisture content, % max	–	0.20
Ammonium picrate purity, %, min	99.0	99.0
Sulfates (as sulfuric acid), %, max	0.10	0.10
Chloroform soluble impurities, %, max	0.10	–
Water insoluble material, %, max	0.10	0.10
Irritant contaminants (as chlorine) parts of chlorine per million, max	50 **	–
Ash, %, max	0.1	0.1
Acidity and alkalinity (as picric acid or ammonia), % max	0.025	0.025
Color	Yel to Orn	Yel to Orn

* The picric acid used to make Class 2 ammonium picrate shall be made by the nitration of phenol and shall contain no material salvaged from trimmings or from loading operations. Class 2 ammonium picrate shall contain no reworked ammonium picrate made by way of any process other than the phenol nitration process

** Not applicable to ammonium picrate made from picric acid produced by the nitration of phenol

The color requirement is intended to cover the unavoidable presence of a small amt of the red form of Explosive D in admixt with the yel form. The requirement with respect to irritant contaminants represents a control of the purity of PA used in manuf when this is made by the dinitrochlorobenzene process. The chloroform soluble impurities requirement also represents a control of the nature of impurities present in PA manufd by a process other than the nitration of phenol

The granulation of the applicable class of Amm Picrate shall be as specified in Table 2

Table 2
Granulation Requirements for
Ammonium Picrate (Explosive D)

US Standard Sieve No	Percent by Weight	
	Class 1	Class 2
Thru No 12, min	99.9	–
Thru No 40, min	–	99.5
Retained on No 70, min	60.0	–
Retained on No 70, max	–	20.0
Thru No 200, max	5.0	–

Bulk density (applicable to Class 1 only). The bulk density of the Amm Picrate shall be 0.82 g/cc min. In order to comply with this requirement on recrystd Amm Picrate, the manufacturer shall be allowed, if necessary, to recryst all such material solely from w, and, in addition, may use as many w washes as required for the resulting material to pass the requirement

Refs: 1) Beil **6**, 276, (134) & [262] 2) Marshall **2**, 746–7 (1917); **3**, 174 (1932) 3) R. Datta & N. Chatterjee, JCS **115**, 1006 (1919) 4) J.E. Crawshaw, JFrankInst **189**, 607 (1920) 5) C.A. Taylor & W.H. Rinkenbach, BurMines Rept **2513** (1923) 6) G.C. Hale, SS **21**, 87 (1926) (Rotes und Gelbes Ammoniumpikrat) 7) W.M. Dehn & A.A. Wagner, ArmyOrdn **8**, 35 (1927) 8) J.D. Hopper, JFrankInst **225**, 219 (1938) (Explosive characteristics of certain metallic picrates) 9) Davis (1943), 167–8 10) F.W. Brown, D.H. Kusler & F.C. Gibson, "Sensitivity of Explosives to Initiation by Electrostatic Discharge", BurMines Rept **RI 3852** (1946) 11) Anon, "U.S. Navy Bureau of Ordnance in World War II", Rept **202-203**, US Printing Office, Washington (1953) 12) Anon, "Ammunition Ashore, Production and Renovation", BuOrd **OP-5**, Vol **2** (1955), 62.6, 69.2, 69.9–69.51 13) Anon, EngrDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 138–9 14) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 37

Barium Picrate. $[C_6H_2(NO_2)_3O]_2Ba$, mw 594.64, N 14.14%, yel powd which explds with moderate violence at 333–37°. Can be obtained by heating its pentahydrate, $[C_6H_2(NO_2)_3O]Ba.5H_2O$; yel prismatic needles which cryst from a concd aq soln. The anhydr salt explds at 403°, but is fairly insensitive to impact and friction (Ref 3)

Refs: 1) Beil **6**, 277, (135) & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 480 (1908) 3) C.A. Taylor & W.H. Rinkenbach, JFrankInst **204**, 374 (1927)

Barium-Picrato-Acetate. $[Ba_2(CH_3.CO_2)_2]\cdot(C_6H_2O_7N_3)_2$, with $4H_2O$ or $7H_2O$; yel crysts, expld on heating

Refs: 1) Beil **6**, [264] 2) R. Weinland & A. Hendricksen, Ber **56**, 529, 533–4 (1923)

Cadmium Picrate. $[C_6H_2(NO_2)_3O]_2Cd$, mw 569.70, N 14.76%, yel powd which explds violently at 336–41°. Was obtained by heating one of its hydrates at 80–150°. Silberrad and Phillips (Ref 2) reported on the hepta- and pentahydrates, while Hopper (Ref 3) reported on the octahydrate. Sensitivity of the anhydr salt is 12″ vs 14″ for TNT, as detd with the PicArsn app using a 2kg wt. The value for the octahydrate is 35″, making it less sensitive than BlkPdr dust

Refs: 1) Beil **6**, 277 & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 482 (1908) 3) J.D. Hopper, JFrankInst **225**, 223 (1938)

Calcium Picrate. $[C_6H_2(NO_2)_3O]_2Ca$, mw 497.38, N 16.90%, yel powd which explds violently at 323–28°. It is obtained when the decahydrate is heated to 80°

Refs: 1) Beil **6**, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS **93**, 479 (1908)

Cerium Picrate. $[C_6H_2(NO_2)_3O]_3Ce$, mw 824.45, N 15.29%, brown powder which explds violently at 306–13°. Can be prepd by heating either its trihydrate or undecahydrate

Refs: 1) Beil **6**, 277 2) O. Silberrad & H.A. Phillips, JCS **93**, 485 (1908)

Cesium Picrate. $C_6H_2(NO_2)_3OCs$, mw 361.01, N 11.64%, yel needles; explds with moderate violence at 277–87°. It has been used to surface seed RDX charges used in expl driven magneto-hydrodynamic generators (Ref 3)
Refs: 1) Beil **6**, 276 & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 476 (1908) 3) J.S. Malcolm, Jr, "Fundamental Research in Explosive Magnetohydrodynamics", AFOSR **TR-76-0435**, Jones (Malcolm) Associates, Inc, Corona Del Mar, Calif, Contract F44620-75-C-0017 (Feb 1976), AD-A023-135

Chromium Picrate. $C_{30}H_{10}O_{36}N_{15}Cr.27H_2O$, mw 1695.09, N 12.04%. Green crysts of this basic salt were prepd by Silberrad and Phillips (Ref 2) by mixing equiv quantities of Ba picrate and Cr sulfate, and evapg the filtrate in vacuo over sulfuric acid. It yields an anhydr salt when heated to 150°. Hopper (Refs 3 & 4) claimed to have prepd the salts with $13H_2O$ and $1H_2O$; both expld at about 330°. The impact sensitivity of the $13H_2O$ salt (PicArsn app with 2kg wt) was 36″ vs 8″ for the $1H_2O$ salt (TNT=14″)
Note: The violet form of Cr sulfate was used in the double decompn reaction with Ba picrate, since the sulfate ion of the green form was not completely ppt by Ba compds
Refs: 1) Beil **6**, 278 2) O. Silberrad & H.A. Phillips, JCS **93**, 486 (1908) 3) J.D. Hopper, PATR **764** (1936) 4) Ibid JFrankInst **225**, 224 (1938) 5) Davis (1943), 165

Cobalt Picrate. $[C_6H_2(NO_2)_3O]_2Co$, mw 371.03, N 22.66%, brown powder which explds with moderate violence at 320–25°. Can be obtained by heating any of its hydrates to 150°
Refs: 1) Beil **6**, 278 & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 487 (1908)

Copper Picrate (Cupric Picrate).
$[C_6H_2(NO_2)_3O]_2Cu$, mw 520.85, N 16.14%, greenish-yel powder, very hygroscopic. Explds violently at 282–87° (Ref 2) and 373° (Ref 3). Can be prepd by heating any of its hydrates to 80–150°. Its impact sensitivity is 12″ vs 14″ for TNT, using the PicArsn app with a 2kg wt (Ref 4). Hopper claimed to have prepd the trihydrate, which expld at 300°; its impact sensitivity was 19″ (Ref 4)
Refs: 1) Beil **6**, 276, (134) & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 478 (1908) 3) C.A. Taylor & W.H. Rinkenbach, JFrankInst **204**, 374 (1927) 4) J.D. Hopper, Ibid **225**, 224 (1938)

Ferric Picrate. $[C_6H_2(NO_2)_3O]_3Fe.11H_2O$, mw 938.4, N 13.44%, yellowish-red needles. Was prepd in 1911 by Kast by treating a hot satd soln of ferric sulfate with Ba picrate (Ref 1). Hopper (Ref 2) prepd several hydrated ferric picrates of unknown w content which expld at 295°. Their impact sensitivity ranged from 6″ (for material dried at 150°), to 36″ (for material dried at 25°) (PicArsn app with 2kg wt)
Refs: 1) Beil **6**, (135) 2) J.D. Hopper, J-FrankInst **225**, 224 (1938)

Ferrous Picrate. $[C_6H_2(NO_2)_3O]_2Fe$, mw 513.15, N 16.38%, dark green powder which expld feebly at 315–20°. It was obtained by drying the octahydrate in a vac dessicator over sulfuric acid. Its impact sensitivity was 14–15″ (vs 14″ for TNT). The octahydrate was obtained by treating a hot concd aq soln of ferrous sulfate with Ba picrate; yel hexagonal prisms which turned brown on standing; impact sensitivity 36″
Note: According to Thrope (Ref 3), the anhydr ferrous salt is very sensitive; in 1901, it caused a fire at Huddersfield
Refs: 1) Beil **6**, (135) 2) O. Silberrad & H.A. Phillips, JCS **93**, 487 (1908) 3) Thorpe **4**, 482 (1949)

Lead Picrate. $[C_6H_2(NO_2)_3O]_2Pb$, mw 663.41; N 12.67%; yel crysts; mp, explds violently at 270–81°. Can be obtained by heating either the monohydrate or tetrahydrate to 150°. The tetrahydrate is obtained in the form of silky yel needles when an aq soln of PA is treated with Pb carbonate. The Ger method of prepn is given under Bleipikrat in Ref 9

The impact sensitivity of the anhydr salt is, according to Taylor and Rinkenbach, 4cm when using a 500g wt. This means that it is more

sensitive than MF (24cm). When detd on the Pic-Arsn app using a 2kg wt, its sensitivity was 2″ vs 14″ for TNT. Its friction sensitivity, as detd by the Friction Pendulum Test, was also high (Ref 3)

Pb picrate monohydrate was patented in Fr in 1872 for use in caps and primers (Ref 4). It was used in Ger (Refs 5 & 6) for the prepn of ignition mixts in "fusehead" manuf. Belcher (Ref 10) reported that during the usual qual inorganic analytical procedure, samples contg the Pb and salicylate radicals can lead to the formation and possible detonation of Pb picrate. This arises during evapn of the filtrate with nitric acid, after pptn of the Cu-Sn group metals with hydrogen sulfide. Salicylic acid is converted under these conditions to PA, which in presence of Pb, gives expl Pb picrate. An alternative scheme is described which avoids this possibility

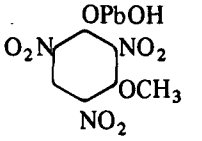
Refs: 1) Beil **6**, 278, (135) & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 485 (1908) 3) C.A. Taylor & W.H. Rinkenbach, JFrankInst **204**, 374 (1927) 4) Davis (1943), 63 5) G. Ashcroft et al, BIOS, Final Rept No 833, Item No 2, London, HMSO (1946); PB Rept 63877 6) Anon, "Allied and Enemy Explosives", Aberdeen Proving Ground, Md (1946), 98 7) Anon, PB Rept No 95613 (1947), Section D 8) Thorpe's **4**, 482 (1949) 9) B.T. Fedoroff et al, PATR **2510** (1958), Ger 13 10) R. Belcher, JRInstChem **84**, 377 (1960)

Note: Several expl basic Pb picrates are listed in Beil, such as:

(1) $2Pb(C_6H_2O_7N_3)_2+3PbO+8H_2O$; pale yel, microscopic crysts which expld violently ca 180°; (2) $Pb(C_6H_2O_7N_3)_2+4PbO$; dark yel, microscopic plates; explds on impact or when brought in contact with a flame. It was prepd by A.G. Lignose (Refs 1 & 3) from 2 moles of PA and 5 moles of Pb oxide in hot w. It is insol in hot w. Friederich (Ref 2) prepd the basic salt by adding an alkaline soln of PA dropwise to a soln of a Pb salt while the latter was agitated. He proposed its use in primers, percussion caps and detonators

Refs: 1) Beil **6**, 278 & [264] 2) W. Friederich, BritP 192830 (1923) & CA **17**, 3255 (1923) 3) A.G. Lignose, GerP 407416 (1925); Ibid, ChemZtr **1925**, I, 2484

Lead Methoxy Picrate. $C_7H_5N_3O_9Pb$, mw 482.35, N 8.71%, dark yel polycryst solid; mp, when heated it decomps with a loud crack; on slow decompn in a DSC app, the thermogram displayed a small endotherm at 207° and a prominent exotherm at 247° which marked its decompn; impact sensitivity, 4″ (10% value, PicArsn app, 2kg wt); expln temp (5 sec value), 264°; brisance (crushed sand), 28.6g; Q_c 1555.9cal/g; Q_e 405.4cal/g; insol in w, sol in dimethyl sulfoxide and dimethyl formamide



Prepd by treating methoxy picric acid with Pb hydroxide. It loses its OCH_3 group thru hydrolysis to form normal Pb Styphnate. The OPbOH group displays acidic behavior in soln. The expl properties of Pb methoxy picrate are similar to those of n-Pb Styphnate

Refs: 1) Beil–not found 2) T. Richter, E. Sowinski & M. Warman, "Lead Salts of Trinitro Phenols. I. Preparation and Properties of Methoxy Picric Acid and Lead Methoxy Picrate", PATR **3344** (1966)

Lithium Picrate. $C_6H_2(NO_2)_3O.Li$; mw 235.05; N 17.88%; pale yel powder which rapidly reabsorbs one mole of H_2O; mp, explds with moderate violence at 318–23°, d 1.724–1.740 g/cc at 20°. Can be prepd by heating its hydrates

Refs: 1) Beil **6**, 276 & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 474 (1908)

Magnesium Picrate. $[C_6H_2(NO_2)_3O]_2Mg$; mw 481.60, N 17.45%; explds feebly at 367–72°. Can be prepd by heating one of its hydrates to 150°

Refs: 1) Beil **6**, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS **93**, 474 (1908)

Manganese Picrate. $[C_6H_2(NO_2)_3O]_2Mn$, mw 512.23; N 16.41%; yel powder, explds violently at 325–30°. Can be obtained by heating any of its hydrates to 150°

Refs: 1) Beil **6**, 278 2) O. Silberrad & H.A. Phillips, JCS **93**, 486 (1908)

Nickel Picrate. $[C_6H_2(NO_2)_3O]_2Ni$; mw 516.01; N 16.29%; green powder, explds at 335–40°. Can be prepd by heating one of its hydrates. Hopper (Ref 3) gives the expln temp for the hexahydrate as 390°, and the impact sensitivity for the anhydr salt as 4″ vs 14″ for TNT using the PicArsn app with a 2kg wt
Refs: 1) Beil **6**, 278 2) O. Silberrad & H.A. Phillips, JCS **93**, 488 (1908) 3) J.D. Hopper, JFrankInst **225**, 223 (1938)

Platinum Base Picrates. Some compds contg Pt and PA are expl, for example:
$[Pt(CH_3.S.CH_3)_4]$ $[C_6H_2O_7N_3]_2$; N 9.32%; yel scales; explds on heating;
$[Pt(C_2H_5.S.CH_2.CH_2.S.C_2H_5)_2]$ $[C_6H_2O_7N_3]_2$; N 8.8%; yel solid; explds on heating
Refs: 1) Beil **6**, (135) 2) L. Tschugaeff & W. Chlopin, ZAnorgChem **86**, 251, 253 (1914)

Potassium Picrate. $C_6H_2(NO_2)_3.OK$; mw 267.20; N 15.73%; reddish yel or green rhombic crysts; mp, explds with moderate violence at 310–16°; d 1.852 at 20°. It was first prepd in an impure state in the 17th century by J.R. Glauber (1603–1668) by dissolving wood in nitric acid, and neutralizing the resulting mixt with potash. K picrate is prepd by neutralizing a hot aq soln of K carbonate with a hot PA soln, and filtering off the crysts that separate when the soln cools. It is sol in w to the extent of 0.5g/100g at 15°, and 25g/100g at 100°; in alc, 0.2g/100g at 25°. Q_c^v is 621.8kcal/mole; impact test, 2″; expln temp test value, 370°. K picrate is of the same order of stability as Explosive D, but it is less brisant. When subjected to contact with a flame, it deflagrates with a loud report (Ref 6). Mixts of K picrate with oxidizing agents, such as K nitrate, only burn when ignited, but are sensitive to shock (Ref 7)

According to Sarrau and Vieille (Ref 4), K picrate of d 0.5g/cc decomps on expln as follows:

$$16C_6H_2(NO_2)_3OK \rightarrow 4KCN+6K_2CO_3+21CO_2+52CO+22N_2+6CH_4+4H_2+7C$$

Based on this equation, its "caractéristique théoriques" values were: v_o (vol of gas at 0° and 760mm), 549ℓ/kg; f (force specifique), 6352; t (temp of expln), 2779°; α (covolume), 0.658; P (action explosive), 332 T.m.

K picrate was used as early as 1869 in expls, such as poudres Designolles (K picrate + K nitrate + charcoal) and poudres Fontaine (K picrate + K chlorate). It has also been used in pyrotechnic whistle compns (Ref 8), proplnts such as Ballistite, and in some primer mixts, ie, K picrate, Pb picrate & K chlorate (Ref 4)
Refs: 1) Beil **6**, 276, (134) & [263] 2) E. Sarrau & P. Vieille, MP **2**, 151 (1884) 3) O. Silberrad & H.A. Phillips, JCS **93**, 476 (1908) 4) Vennin, Burlot & Lécorché (1932), 453 5) T. Tucholski, RocznikiChem **18**, 840–9 (in Ger 849–50) (1938) & CA **33**, 6691–2 (1939) (Thermal decompn of K picrate) 6) Davis (1943), 63, 72, 293 & 417 7) Anon, "Military Explosives", **TM9-1910** (1955), 167–8 8) Ellern (1968), 183 9) Z.G. Szabb & J. Száva, "Factors which Influence Thermal Decomposition of Potassium Picrate", 8th Symp Combstn (1962), 863–72

Rubidium Picrate. $C_6H_2(NO_2)_3.ORb$; mw 313.58; N 13.40%; yel needles which expld with moderate violence at 300–15°; also expld on impact
Refs: 1) Beil **6**, 276 & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 476 (1908)

Silver Picrate (also called Pikratol in Ger). $C_6H_2(NO_2)_3.OAg$; mw 335.98; N 12.51%; fine yel needles; mp, 315° with decompn; bp, expld ca 335°, or when brought in contact with an open flame; was not ignited or detonated by the spit of a fuse when compressed in a detonator cap. Can be prepd by dissolving Ag oxide in a hot satd PA soln (Ref 3)

Ag picrate was prepd in 1809 by Chevreul, and recognized by Liebig in 1888 as an expl. Silberrad and Phillips (Ref 2) established its formula, and stated that it explds feebly at 336–44°. Solubility in 100g of solvent at 25°: H_2O, 1.61; eth, 0.019; acet, 3.117; & 95% alc, 0.978g

According to Taylor & Rinkenbach (Ref 4), the sensitivity to impact with a 500g wt is 34cm vs 24cm for MF and 43cm for LA. It is fairly insensitive to friction, as detd by the Friction Pendulum app

Refs: 1) Beil **6**, 276, (134) & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 477 (1908) 3) C.A. Taylor & E.P. Buxton, ArmyOrdn **7**, 68 (1926) 4) C.A. Taylor & W.H. Rinkenbach, JFrankInst **204**, 374 (1927)

Silver Ammonia Picrate. $[Ag(NH_3)_2]$-$[C_6H_2(NO_2)_3.O]_2$; mw 682.23; N 28.75%; yel crysts; explds violently when heated above its mp
Refs: 1) Beil **6**, [263] 2) E. Ephraim, Ber **54**, 404 (1921)

Sodium Picrate. $C_6H_2(NO_2)_3.ONa$; mw 251.10; N 16.74%; yellowish needles, which expld on being heated to 310–15° (Ref 2). Sol in w and alc. Can be prepd by heating its monohydrate to 150°; which in turn can be prepd by the action of Na carbonate on an aq soln of PA

According to Hopper (Ref 3), the monohydrate explds at 360°, and its impact sensitivity is 17″ vs 15″ for anhydr Na picrate, vs 14″ for TNT (PicArsn app with a 2kg wt)

Na picrate deflagrates on flame contact, and retains this property when mixed with other materials. It has been used in expl and pyrot compns in lieu of K picrate (Ref 5)

Note: **Sodium Picrate, Double Salts of.** When an aq soln of Na picrate (3 moles) is stirred and heated with 3 moles of finely powdered Ba or Pb picrate, the resulting double salts are less sensitive to impact than the single salts (and for this reason are less dangerous to handle). The same can be said for other picrate double salts (Ref 4)

Refs: 1) Beil **6**, 276, (134) & [263] 2) O. Silberrad & H.A. Phillips, JCS **93**, 475–6 (1908) 3) J.D. Hopper, JFrankInst **225**, 223 (1938) 4) Colver (1938), 327 5) Davis (1943), 63 & 165

Strontium Picrate. $[C_6H_2(NO_2)_3.O]_2Sr$, mw 544.92; N 15.43%; yellow salt, explds fairly violently at 340–45°. Can be prepd by heating any of its hydrates to 200°. The monohydrate is a yel powd which explds at the same temp as the anhydr salt

Refs: 1) Beil **6**, 277 2) O. Silberrad & H.A. Phillips, JCS **93**, 479–80 (1908)

Thallium Picrate. $C_6H_2(NO_2)_3.OTl$, mw 432.48; N 9.72%; yel needles; mp, explds feebly at 273–75°. Can be prepd by dissolving Tl carbonate in aq PA, and partially evapg the filtrate. Explds on heating or by impact

Refs: 1) Beil **6**, 277& (135) 2) O. Silberrad & H.A. Phillips, JCS **93**, 484 (1908)

Thorium Picrate. $Th(C_6H_2O_7N_3)_4.10H_2O$, mw 1324.68; N 12.69%; yel needles; mp 52–53°; explds on contact with a flame

Refs: 1) Beil **6**, (135) 2) G. Karl, Ber **43**, 2068 (1910)

Zinc Picrate. $[C_6H_2(NO_2)_3O]_2Zn$; mw 522.67; N 16.08%; brownish-yel powd; mp, explds violently at 350–55°. Can be prepd by heating one of its hydrates to 150°. According to Colver (Ref 3), its impact sensitivity, as detd with a 2kg wt, is 60cm, which is comparable to that of PA

Refs: 1) Beil **6**, 277, (135) & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 481 (1908) 3) Colver (1938), 334

Zirconium Picrate. $[C_6H_2(NO_2)_3O]_4Zr$; mw 1003.66; N 16.75%; yel needles; mp, explds at 317–22°. Can be prepd by adding Zr carbonate to aq PA

Refs: 1) Beil **6**, 278 & [264] 2) O. Silberrad & H.A. Phillips, JCS **93**, 484 (1908)

PICRATES, ORGANIC

These compds can be prepd, in general, by dissolving the respective organic compds (hydrocarbons, nitrohydrocarbons, amines, phenols, etc) in warm alc solns of PA, boiling the mixt, and then cooling it to cryst out the resulting picrate

Organic picrates are usually more stable than PA, less sensitive to shock or heat and less corrosive to metals

Some organic picrates of nitrocompds are described in Beilstein under these compds, and this system is followed herein. Following is a

selected list of compds, taken primarily from the section on PA in Beilstein, which are more or less expl. The expln temps of many of the listed organic picrates were detd by R.J. Datta and N.R. Chatterjee, JCS **115**, 1007–8 (1919):

Acenaphthene Picrate. $C_{12}H_{10}+C_6H_3O_7N_3$; orange-red prisms; mp 161–62°; explds at 412° (Beil **6**, 273, (132) & [260])

Allylamine Picrate. $C_3H_7N+C_6H_3O_7N_3$; lemon yel needles; mp 140–41°; explds at about 270° (Beil **6**, 283)

Aniline Picrate. $C_6H_2(NO_2)_3OH+C_6H_5NH_2$; yel crysts; mp, decomps at 165°, explds at 398° [Beil **12**, 120 & (143)]

Atropine Picrate. Plates; mp 173–75°; explds at about 460° (Beil **21**, 30)

Azidoguanidine Picrate. $N_3.C(:NH).NH_2.HOC_6H_2(NO_2)_3$; explds on heating but not on impact [CanNatlResCouncil Rept (Feb 17, 1942)]

Cinchonidine Picrate. Explds at about 260° [R.J. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919)]; $2C_{19}H_{22}ON_2+3C_6H_3O_7N_3$; yel crysts; mp 194–95°; explds at about 268° (Beil **23**, 430)

Guanidine Picrate. $CH_5N_3+C_6H_3O_7N_3$; yel crysts; explds at about 498° (Beil **6**, 279 & [265])

Hexamethylenetetramine Picrate. $C_6H_{12}N_4+C_6H_3O_7N_3$; yel needles; mp, explds at about 360° (Beil **1**, 586)

Hydrazine Picrate. $N_2H_4+C_6H_3O_7N_3$; yel needles from alc; mp, 201.3° (184°), explds at about 385° (R.J. Datta & N.R. Chatterjee, JCS **115**, 1007 (1919) & Beil **6**, 276 & [263])

Indene Picrate. $C_9H_8+C_6H_3O_7N_3$; golden yel needles; mp 98°; very expl in the dry state; decomps slowly in air (Beil **6**, 271 & [259])

d-Lysine Picrate. $C_6H_{14}O_2N_2+C_6H_3O_7N_3$; crysts; mp, explds on slow heating [Beil **6**, 287 & (139)]

Naphthalene Picrate. $C_{10}H_8+C_6H_2(NO_2)_3OH$; golden yel needles; forms eutectic mixts with PA; mp 149–151.5°; explds at 484° (Beil **6**, 272, (132) & [259])

α-Naphthol Picrate. $C_{10}H_8O+C_6H_3O_7N_3$; yel orange needles; mp 189–90°; explds at about 458° [Beil **6**, 605 & (306)]

β-Naphthol Picrate. $C_{10}H_8O+C_6H_3O_7N_3$; orn-red needles; mp 155–57°; explds at about 469° (Beil **6**, 640, (312) & [597])

Phenanthrene Picrate. $C_{14}H_{10}+C_6H_3O_7N_3$; golden yel needles; mp 143–45°; explds at 478° (Beil **6**, 273, (133) & [261])

Pyridine Picrate. $C_5H_5N+C_6H_3O_7N_3$; golden yel needles; mp, 165–66°; explds at 432° (Beil **20**, 208)

Quinidine Picrate. Explds at 280° [R.J. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919)]

Semicarbazide Picrate. Explds at 474° [R.J. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919)]

Strychnine Picrate. Explodes at about 290° [R.J. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919)]

o-Toluidine Picrate. Pale yel crysts; mp 185°; explds at about 400° (Beil **12**, [433])

Urea (or Carbamide) Picrate. $CH_4ONO_2+C_6H_3O_7N_3$; yel needles; mp 142° (decompn); explds at about 489° [Beil **6**, 279 & R.J. Datta & N.R. Chatterjee, JCS **115**, 1008 (1919)]

Picrate Whistles. According to Davis (Ref 1), an intimate mixt of finely powdered K picrate and K nitrate (60/40 by wt), rammed tightly into paper or bamboo tubes from 1/4" to 3/4" in diameter, burns with a loud whistling sound

In WWII, the Germans used picrate whistles as a psychological adjunct to bombs, and they also used pyrotechnic whistles as gas alarms

Because the above mixt is extremely sensitive to shock and dangerous to handle, non-picrate whistle compns such as those contg gallic acid and K chlorate are currently utilized (Ref 2)

Refs: 1) Davis (1943), 72–73 2) Ellern (1968), 183 & 376–77

Picratol. A mixt of TNT/Ammonium Picrate (48/52% by wt) developed in the USA during WWII to replace pure Ammonium Picrate (Explosive D) in AP and SAP projectiles and bombs. OB TO CO_2 –63%, to CO –19%

Prior to WWII, armor-piercing projectiles were press-loaded with Explosive D. This required the application of pressures of the order of 10,000 to 12,000psi to successive increments of the charge and was a slow and expensive operation. The development of armor-piercing bombs necessitated the use of an insensitive expl that could be melt loaded; and for this reason,

Picratol was developed

Molten TNT has little or no solvent action on Explosive D, and consequently, cast Picratol consists essentially of a physical mixt of crystals of the two expls. Its d is 1.61 to 1.63g/cc, and this permits a wt of charge almost equal to that of Explosive D pressed under 10,000 to 12,000 psi. Picratol has the solubility and reactivity chracteristics of its ingredients. It is hygroscopic to the extent of only 0.02% when exposed to an atm of 90% RH at 30°

Preparation. Picratol is manufd by heating TNT to above 90° in a steam-jacketed melting kettle equipped with a stirrer. The Explosive D is added slowly, without preheating, with continuous agitation; and this is continued for a short time after all the Explosive D has been added. The thick slurry is allowed to cool to about 85° before being cast into ammo components. Like molten TNT, it undergoes marked contraction in volume on solidification; but this is much less than in the case of TNT

Sensitivity. The standard small scale impact tests indicate Picratol to be as sensitive to impact as TNT, rather than Explosive D, and large scale impact tests of cast charges confirm this. Friction pendulum tests show no difference between Picratol, TNT and Explosive D, with respect to sensitivity to friction. When subjected to the rifle bullet impact test, Picratol burns in about 40% of the trials, but undergoes no detonation. Explosive D burns in about 30% of the trials. The expl temp test value (5 sec) of Picratol (285°) is less than that of Explosive D (318°), and much less than that of TNT (475°). Picratol is as insensitive to initiation as Explosive D, having a min detonating charge value of 0.06g of Tetryl. The overall sensitivity of Picratol, therefore, is not greater than that of TNT

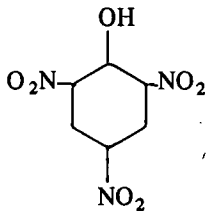
Explosive Properties. Picratol is only 94% as brisant as TNT, as judged by the sand test, but the plate dent test indicates the two to be equally brisant, and the fragmentation of shell charges show Picratol to be 102% as brisant as TNT. The rate of detonation of cast Picratol (unconfined charge, d 1.63g/cc, 1.0" diam) is 6970 m/sec, 101% that of cast TNT. Picratol and TNT are of equal power, as measured by the Ballistic Pendulum test, and have equal blast effects

Stability. The stability of Picratol is very slightly less than that of either TNT or Explosive D, as measured by Vacuum Stability tests at 100° (0.37cc/40 hrs), 120° (0.68cc) and 150° (0.70cc). These test results may be considered to indicate slight reaction between the Explosive D and the molten TNT ingredients at the elevated temps of the tests. At ordinary temps there is no evidence of such reaction, and Picratol appears to be of the same high order of stability as its ingredients

Analytical. The compn of Picratol can be detd by extracting a weighed sample with cold eth that has been satd with Explosive D. The residue is dried and weighed, and this and the loss in wt are calcd to % of Explosive D and TNT, respectively

Refs: 1) A.J. Clear, "Characteristics of 52/48 Picratol", PATR **1470** (1944) 2) O. E. Sheffield, PATR **1729** (1949) [Props of a 36/64 TNT/Amm Picrate Picratol] 3) Urbański **3**, 266 (1967) 4) Anon, EngrDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971)

Picric Acid (PA; listed as 2,4,6-Trinitrophenol in CA since 1972; Mélinite in Fr; Melinit in Russ, Lyddit in Engl; Granatfullung or Sprengkorper 88 in Ger; Pertit in Ital; Picrinit in Span, Ekrasit in Austr; TNF in Pol; Shimoza in Jap)



mw 229.11, N 18.34%, OB to CO_2 –45%, yel rhomb crysts, mp 122°, d 1.76g/cc. In recent years PA has fallen out of favor as an expl. Consequently, modern literature on PA is not voluminous and this article of necessity draws heavily upon older literature. The article is divided into the following sections: I. Historical; II. Physical Properties, Solubility and Toxicity; III. Thermochemical Data; IV. Chemical Properties; V. Specifications & Analytical; VI. Uses; VII. Preparation; VIII. Explosive Characteristics; and IX. References

I. Historical. PA is probably the earliest known nitrophenol. According to Urbański (Ref 35) it is mentioned in the alchemical writings of Glauber as early as 1742. Glauber reacted nitric acid with wool or horn and isolated PA in the

form of Pb or K picrates. A few decades later, Woulfe (Ref 1) prepared PA by treating indigo with nitric acid. In 1783, Haussmann (Ref 2) showed that PA behaves like an acid. Other early experimenters (Refs 3–5) obtained PA by nitrating various organic substances such as silk, natural resins, etc. Marchand (Ref 6) assigned it the empirical formula of $C_{12}H_6N_6O_{14}$, which is exactly double the actual formula. The correct constitution of Picric Acid was determined by Laurent (Ref 7) in 1841. He prepared it by reacting phenol with nitric acid. He was also able to isolate dinitrophenol formed in an intermediate stage of the nitration. A further improvement in the method of preparation of Picric Acid from phenol was its sulfonation prior to nitration, described by Schmidt and Glutz (Ref 8)

Some of the authors had drawn attention to the expl character of Picric Acid salts, but it was not until 1830 that Welter (Ref 3) suggested the possibility of using picrates as expls. At that time Picric Acid was prepared solely by the action of nitric acid on indigo. Marchand (Ref 6) expressed the view, which proved to be true, that it was aniline, formed as an intermediate product in the process of decompn of indigo, silk and other organic matter, that yielded Picric Acid under the influence of nitric acid

According to Urbański (Ref 35, p 473): "In the second half of the nineteenth century, Picric Acid was very widely used as a fast dye for silk and wool. The first definite suggestions as to the application of Picric Acid for the manufacture of explosives go back to the early second half of the nineteenth century. They referred to the application of Picric Acid salts, as by then the explosive properties of picrates were already well known. Thus, for example, Designolle (Ref 17) suggested K picrate, and Brugère (Ref 9) ammonium picrate as propellants, while in 1871 Abel (Ref 10) proposed ammonium picrate as a high explosive. At that time K picrate was already being used in Great Britain and in the US for filling shells

The view then prevailed, supported by such an authority as Abel, that Picric Acid itself is not an explosive, but only its salts are. Nevertheless in 1873 Sprengel (Ref 11) proved that Picric Acid could be brought to explosion by a detonator and Turpin (Ref 12) proposed applying this property of Picric Acid by utilizing it for filling shells. In Russia methods of preparation of Picric Acid and using it as a shell filling were worked out near 1894 by Panpushko (Ref 26). Eventually Picric Acid was accepted all over the world as the basic high explosive for military uses"

However during the present century TNT has been continuously replacing PA as the main military explosive. To some degree this change was accelerated by the acidic character of Picric Acid and its corrosive action on metals, resulting in the formation of salts sensitive to impact and friction. Moreover, because of its relatively high sensitiveness to impact, Picric Acid by itself is unsuitable for filling certain special purpose ammo, for example for armor piercing shells

II. Physical Properties, Solubility and Toxicity. PA crystallizes in colorl to yellowish needles or lamellae of the orthorhombic-bipyramidal system. It sublimes above its mp, and its vapor press is 2mm Hg at 195° and 50mm Hg at 255° (Ref 48). The specific gravity of liquid PA is 1.59g/cc at 124° and 1.51g/cc at 170°. In w satd air at 32° PA picks up 0.37% moisture in 48 hours (Ref 35). According to Dautriche (Ref 14), PA packing density varies with loading pressure as follows:

Pressure, kg/cm^2	Average density, g/cm^3
275	1.315
685	1.480
1375	1.614
2060	1.672
2750	1.714
3435	1.731
4125	1.740

The IR spectrum of PA is given by Levitsky et al (Ref 37)

PA is somewhat sol in w and more sol in acids. It also dissolves in a variety of org solvents. According to Dolinsky (Ref 13), its soly in w is shown in Table 1

Table 1
Solubility of Picric Acid in Water

Temp °C	Content of Picric Acid, g	
	in 100g of solution	in 100g of solvent
0	0.67	0.68
10	0.80	0.81
20	1.10	1.11
30	1.38	1.40
40	1.75	1.78
50	2.15	2.19
60	2.77	2.81
70	3.35	3.47
80	4.22	4.41
90	5.44	5.72
100	6.75	7.24

In sulfuric acid the amount of PA dissolved goes thru a min at about 18% acid (Ref 15) (Table 2)

Table 2
Solubility of Picric Acid in H_2SO_4

H_2SO_4 concn %	Picric Acid content in 100g of the solution		
	18°C	50°C	80°C
0	1.184	2.399	4.541
2.3	0.230	0.692	1.940
4.7	0.142	0.368	1.251
10.0	0.091	0.265	0.727
18.0	0.079	0.214	0.561
25.5	0.092	0.230	0.587
50.5	0.429	0.645	1.104
69.7	0.928	1.424	2.203
87.9	2.461	5.826	7.610
97.4	7.531	12.785	24.020
100.0	10.180	16.230	25.860

Drucker (Ref 20) gives the following PA solubilities in nitric acid (Table 3)

Table 3
Solubility of Picric Acid in Nitric Acid

HNO_3 concentration in mole/ℓ	Picric Acid concentration in mole/ℓ
0.00000	0.05327
0.00635	0.05095
0.02564	0.04281
0.05166	0.03493
0.0872	0.02604

In organic solvents the solubility of PA was measured by Urbański (Ref 35) (Table 4)

Table 4
Solubility of Picric Acid in Organic Solvents

Solvent	Temp °C	Amount of solvent	Amount of PA
Ethyl alcohol	25	100 ps	7.452 ps
Ethyl ether	13	100 ps	1.08 ps
Ethyl ether (water satd)	13	100 ps	4.00 ps
Benzene	6	100 ps	3.50 ps
Benzene	15	100 ps	5.9 ps
Toluene	20	100 ml soln	12.0 g
Amyl alcohol	20	100 ml soln	1.755 g

and by Duff & Bills (Ref 21) (Table 5)

Table 5
Solubility of Picric Acid

% of organic component of the soln	Grams of Picric Acid per 100g of the solvent at 25°C		
	Methyl alcohol	Ethyl alcohol	Acetone
0	1.3	1.3	1.3
30	2.4	3.1	9.5
60	7.1	10.5	46.7
80	–	13.8	–
81	–	13.8	–
85	–	13.2	–
90	16.0	12.3	–
100	21.1	8.0	43

PA forms eutectics with TNT and 2,4,6-trinitroxylene. The former contains about 33% PA and melts at 59°, while the latter contains about 78% PA and melts at 106° (Ref 35)

Toxicity. Picric Acid is more toxic than the nitro derivatives of toluene, xylene or naphthalene. It is, however, much less toxic than nitro derivatives of benzene

According to Lazarev (Ref 27) a single lethal dose for a cat is 0.5g/kg of its weight. A daily dose of 0.05–0.2g/kg causes death after 9 days

Saladini (Ref 15a) pointed out that small doses of PA cause no ill-effects in man

Koelsch (Ref 16), based on observation of 1200 workers engaged in handling PA, described the symptoms of poisoning as follows: a yellow coloration of unprotected parts of the skin and hair, irritation of the mucous membranes and of the upper parts of the respiratory tract and the digestive tract. In addition, a constant bitter taste and a lack of appetite appear

Similar results of observations, carried out at the Institute of Occupational Diseases in Leningrad, were reported by Matussevich (Ref 19)

Lebedev (Ref 22) described the signs of mild poisoning by Picric Acid as follows: Yellow coloration of the skin, the teeth, the saliva and nasal mucous, bitter taste, lack of appetite, occasionally nausea and vomiting. A decrease in the acidity of the gastric juice is also possible, as well as conjunctivitis, irritation of the upper respiratory tract and of the middle ear. Instances of perforation of the nasal wall are also known. In more severe cases an intense headache appears, as well as abnormally high temp, dizziness, spasms, disturbances of the digestive organs, anemia and more rarely kidney trouble. In women menstrual disturbances may occur. More or less severe eczema may also appear

According to Nawrooki and his co-workers (Ref 23), a concn of Picric Acid in air amounting to 1–17.5mg/m^3 may cause severe poisoning after six hours' exposure

Koelsch (Ref 16) suggested the following protective measures when working with PA: adequate ventilation to prevent the accumulation of PA dust, protective clothing including gloves and head coverings to cover as large an area of the skin as possible, and washing the face and hands and rinsing the mouth before eating. Taking meals in working quarters should be forbidden. Workers should be subjected to medical inspection at regular intervals

III. Thermochemical Data. The std heat of formation of PA is –51.3kcal/mole (Ref 41). The heat of fusion is 4.7kcal/mole (Ref 48) and the heat of vaporization is 21.0kcal/mole (Ref 25). Taylor & Rinkenbach give the following variation of specific heat with temp (Ref 18):

Temperature, °C	Specific heat, cal/g
0	0.234
20	0.250
40	0.266
60	0.282
80	0.300
100	0.318
120	0.337

There is disagreement about the coefficient and heat conductivity of PA. Belyaev & Matyshko give it as 2.4 x 10^{-4}cgs units at 1.7g/cc (Ref 24), while H.H. Licht's value (Ref 44) is 6.2 x 10^{-4}cgs units at 1.41g/cc

Urbański (Ref 35) gives the total heat of nitration as –917.4kcal/kg of phenol

IV. Chemical Properties & Thermal Decomposition. Most of the chemistry of PA is determined by its acidic nature. It is a strong acid whose ionization constant of 1.6 x 10^{-1} (Ref 31) makes it comparable in acid strength to pyrophosphoric acid and trichloroacetic acid. PA readily forms salts with bases and esters with alcohols. The salts are known as *Picrates.* Many of them are expl and will be described in a separate article in this Vol. The esters are phenol ethers, eg, *Trinitroanisole* (see Vol **1**, A450-L)

Like other polynitroaromatic compounds, Picric Acid readily forms addition products with aromatic hydrocarbons. This behavior is expecially pronounced in PA. Addition compds with phenols, aromatic ketones, acids and even with nitro compds are also known

Urbański (Ref 35) lists the following addition compds formed by Picric Acid with other substances in a 1:1 mole ratio:

Second component	Melting points, °C
Anthracene	ca 141 (non uniform melting)
Benzene	84
Fluorene	84
Naphthalene	150
Phenol	85
Resorcinol	100
Pyrocatechol	124
Guaiacol	88.6
o-Cresol	89.8
p-Cresol	ca 65.6 (non uniform melting)
Thymol	96.8
β-Naphthol	145.8
Triphenylcarbinol	138.5
Acetophenone	ca 50 (non uniform melting)
Benzophenone	27 (readily dissociates)
Cinnamic acid	106.5

Although these compds are readily formed, they are also readily decompd, eg by the addition of a solvent that dissolves one of the two constituents. The nature of these non-covalent compds is discussed by Urbański (Ref 35)

Picric Acid is not resistant to strong oxidizing agents. It is oxidized by boiling nitric acid to yield oxalic acid. Boiling with ammonium persulfate results in a complete oxidation, according to the equation:

$$C_6H_2(NO_2)_3OH \xrightarrow{(NH_4)_2S_2O_8} CO_2+HNO_3+HCN$$

When mildly reduced, for example with Na sulfide or hydrosulfite or with ferrous sulfate, PA is converted into picramic acid, a very useful intermediate in the dyestuffs industry and a starting material for the preparation of Diazodinitrophenol, a primary expl (see Vol **2**, B59-L). Stronger reduction may lead to the formation of triaminophenol

Violent boiling of PA with a concd soln of NaOH may bring about decompn of the former:

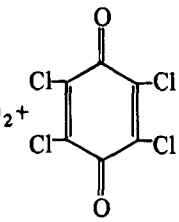
$$C_6H_2(NO_2)_3OH \xrightarrow{NaOH} NH_3+HCN+HNO_2$$

Hypochlorites decomp PA, which undergoes chlorination to form chloropicrin. The reaction is carried out with Ca hypochlorite. The Ca hydroxide formed in the reaction neutralizes the hydrochloric acid formed. This is a commercial method of preparing chloropicrin:

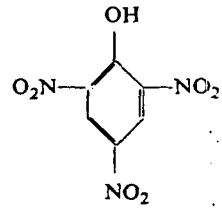
$$C_6H_2(NO_2)_3OH+11HOCl \xrightarrow{85°} 3CCl_3.NO_2+3CO_2+6H_2O+2HCl$$

When reacted with chlorine, aqua regia or K chlorate in the presence of HCl, Picric Acid yields chloranil along with chloropicrin:

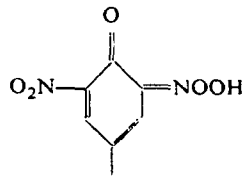
$$C_6H_2(NO_2)_3OH \xrightarrow{Cl_2} CCl_3.NO_2+$$



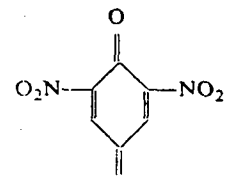
According to Urbański (Ref 35), Hantzsch proposed that PA exists in two forms: a colorless form (I) and two equivalent colored quinoid forms (II):



I



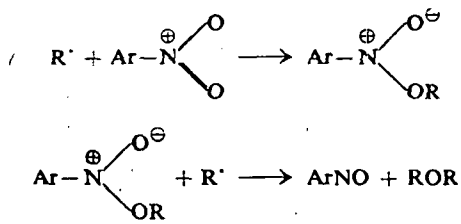
IIa



IIb

Salt formation generally favors the quinoid form and these salt solns are usually brightly colored. Presence of strong acids favors the colorless phenol form. Because of these color changes, nitrophenols have been used as indicators in acid-base titrations

PA exerts an inhibiting action on free radical polymerizations. Bartlett et al (Ref 28) ascribe this to the following reactions:



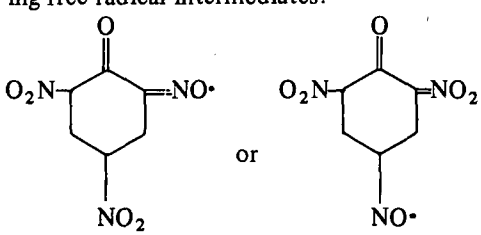
Thermal Decomposition. The definitive study of the thermal decompn of PA was made by Andreev and Liu Pao-Feng (Ref 34). They followed the decompn of liq PA manometrically over the temp

range of 183–270°. They also examined the decompn of PA vapor at 290°. The decompn of the liq is complex and may proceed in as many as five different stages. If the total pressure in the reaction vessel is kept low (low m/V, ie, a small PA mass m in a large vessel of vol V) there is a long induction period at 183°. This induction period can be appreciably shortened by increasing m/V. There is no apparent induction period for decompn at 230° or above. Where induction is observed it is followed by an accelerated decompn stage which goes over into an essentially first order decompn rate. The final stages of decompn may be autocatalytic. At the higher temps most of the decompn is nearly first order

In the vapor state PA decompn is much slower than for the liquid. Above an initial vessel pressure of 110mm Hg the decompn is nearly first order. The decompn rate is strongly enhanced by the presence of added glass surfaces

From the variation of reaction rate with temp in the region where first order kinetics hold, the authors calculate an activation energy of 38.6 kcal/mole and a pre-exponential factor of 4×10^{11} sec^{-1}. These Arrhenius parameters are fairly similar to those of TNT (see article on *Kinetics* in Vol 7, K6-R ff)

Recently Boguslavskaya et al (Ref 49), on the basis of ESR studies, have suggested that thermal decompn of PA proceeds via the following free radical intermediates:



According to Rosen & Dacons (Ref 39) PA dissolved in trinitrobenzene (5 mole % soln) has an initial gas production of 2.8cc at NTP/hour at 210° in a vacuum stability test. For comparison, at nearly identical conditions TNT gives 0.6cc gas/hour at 230°

V. Specifications and Analytical. According to **JAN-A-187** (1945), section E, military PA has to meet the following specifications:
Color – White to yellow
Granulation – Min 99.5 percent thru 1410 micron (No 14) US Standard sieve
Solidification point – Min 120.0°
Moisture–when purchased dry – max 0.20 percent; *when purchased wet* – max 22.0 percent
Ash – Max 0.1 percent
Insoluble matter – Max 0.1 percent
Acidity – total sulfuric acid – max 0.1 percent; *nitric acid* – none
Lead – max 0.004 percent
Analytical. A qualitative test for PA depends on its reaction with aq KCN to form a red colored salt, the so-called "isopurpuric acid". The reactions involved in this test are still in doubt (see Ref 35, p 492). PA is one of the few trinitroaromatics that does not produce a reddish coloration with strong alkalis (Ref 46). It has an IR band characteristic of sym trinitroaromatics, but because of its acidic nature the band is shifted from 9.25 μm to about 9.35 μm (Ref 46). The general method of determining N content of nitroaromatics by titanous chloride reduction and titration of the added excess by ferric chloride is presumably applicable to PA (Ref 46). Hansson (Ref 33) developed a thin-layer chromatographic method for PA and other expls. The expls, as 1% solns in acetone, are put on silica gel layers using benzene or petr ether carriers

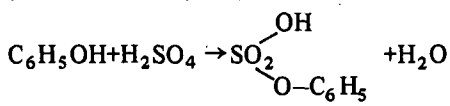
VI. Uses. During the latter part of the nineteenth century and the early part of the present century, PA was widely used as the main expl charge of projectiles and bombs. This is no longer true. Indeed PA per se is hardly used as an expl. Its current limited expl-related use is primarily in the preparation of Explosive D (Ammonium Picrate) and Lead Picrate. It also finds some use as an intermediate in the manuf of dyes. There is some patent literature on the use of PA as a catalyst for polymerizations. For example, PA is claimed as catalyst in polybutadiene polymerizations (Ref 40), and for the prepn of an isobutylene-5-methyl-1,3,6 heptatriene copolymer (Ref 38)

VII. Preparation. There are two industrial methods of manufg PA: 1) nitration of Phenol; 2) nitration of dinitrophenol prepd by hydrolysis of chlorodinitrobenzene

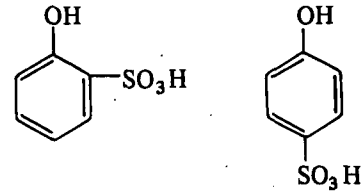
Nitration of phenol. This is a two stage process. First, phenol is sulfonated and the sul-

fonates are then nitrated with nitric acid. The intermediate sulfonation step is necessary because direct nitration of phenol yields undesirable oxidation and condensation side products. Furthermore the two stage process permits the nitration step to be carried out without use of excess acid. Thus the small amount of spent acid need not be recovered, and can be discharged into the drainage system. This is an advantage since the spent acid does contain PA. Production of appreciable amounts of spent acid would entail some rather formidable PA recovery problems. Moreover, PA is fairly volatile in sulfuric acid solns and this presents the risk of escaping and possibly forming dangerous metal salts upon condensing on metal parts or equipment

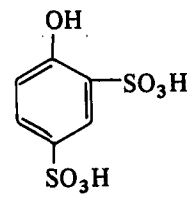
The sulfonation steps are carried out at around 100°, using 4 to 4.5 moles of sulfuric acid per mole of phenol. The reaction proceeds thru an intermediate sulfuric acid ester:



which is then converted to the ortho & para phenolsulfonic acids:

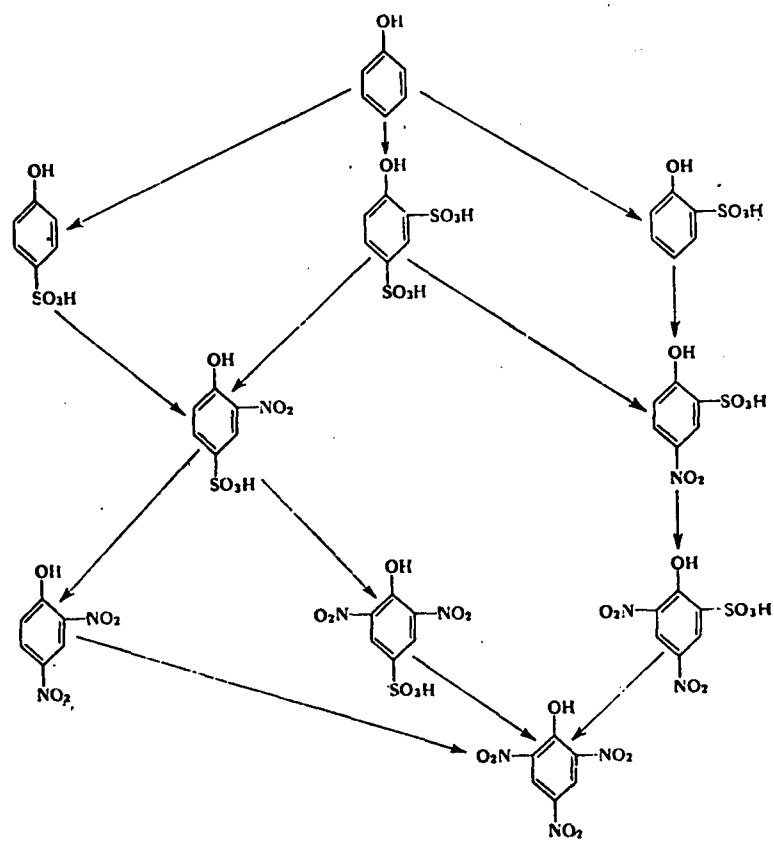


According to Urbański (Ref 35): "At room temperature the conversion proceeds slowly, whereas it occurs rapidly on heating. The higher the temperature, the more p-isomers are formed. At 90–100°C phenoldisulphonic acid is also formed:



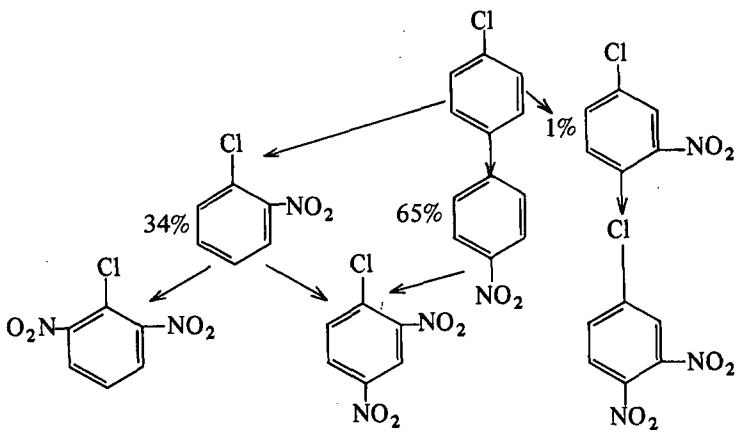
Its presence is advisable, as later it will facilitate the nitration process"

The second stage of this process consists of nitration of the phenol sulfonic acids with concd nitric acid. The overall process is represented diagramatically as:



If sulfonation is carried out at a low temp, nitric acid of higher concn should be used or a higher temp should be maintained during the nitration. The latter must, of course, be kept within safety limits. Apart from this, higher temps naturally favor undesirable side reactions (eg, oxidation)

Nitration of dinitrophenol. This is a multi-stage process. First chlorobenzene is nitrated to chlorodinitrobenzene as shown schematically below:



The dinitrobenzenes are then hydrolyzed at about 100° in a 7% Na hydroxide soln. The Na-dinitrophenate thus formed is acidified with 30% sulfuric acid to produce dinitrophenol which is nitrated with mixed acid (0–5% water content) to form PA

Recently it has been claimed (Ref 42) that PA may be prepd by nitrosating phenol with Na nitrate and oxidizing the resulting nitrosophenols with nitric acid.

VIII. Explosive Characteristics. Picric Acid is generally considered to be a relatively "insensitive" but brisant expl. On a qualitative sensitivity scale of comparing common expls, PA would be judged to be more sensitive than TNT but appreciably less sensitive than Tetryl. Its power and brisance are also similar to those of TNT (112% TNT in the Ballistic Mortar; 101% of TNT in the Trauzl Block and 107% in the plate dent test (Ref 48). In this section we will consider the *steady detonation parameters, initiation characteristics* and *potential hazards* of PA

A. *Steady Detonation Parameters.* As already mentioned, PA is an expl that is currently out of favor. Consequently there are relatively few modern data on its detonation characteristics

Detonation Velocity: Baum et al (Ref 31b, p 352) gives the following tabulation of packing density ρ vs deton vel D:

ρ (g/cc)	D (m/sec)
0.97	4965
1.32	6190
1.41	6510
1.62	7200
1.70	7480

These values agree reasonably well with those obtained from the following formula of Cook (Ref 31a, p 45):

$D = 5255 + 3045\ (\rho - 1.00)$ m/sec

Baum (Ref 31b, p 349) also gives the following tube diameters, d_m, at which D approaches its max (hydrodynamic) value:

PA grain size (mm)	ρ (g/cc)	d_m (mm)
0.1–0.75	0.95	17
"small" (sic)	0.95	11

Johansson & Persson (Ref 45, p 41) show the results of Parisot & Lafitte (1938) in the D vs diameter curves in Fig 1 (expls other than PA also shown). There appears to be some dis-

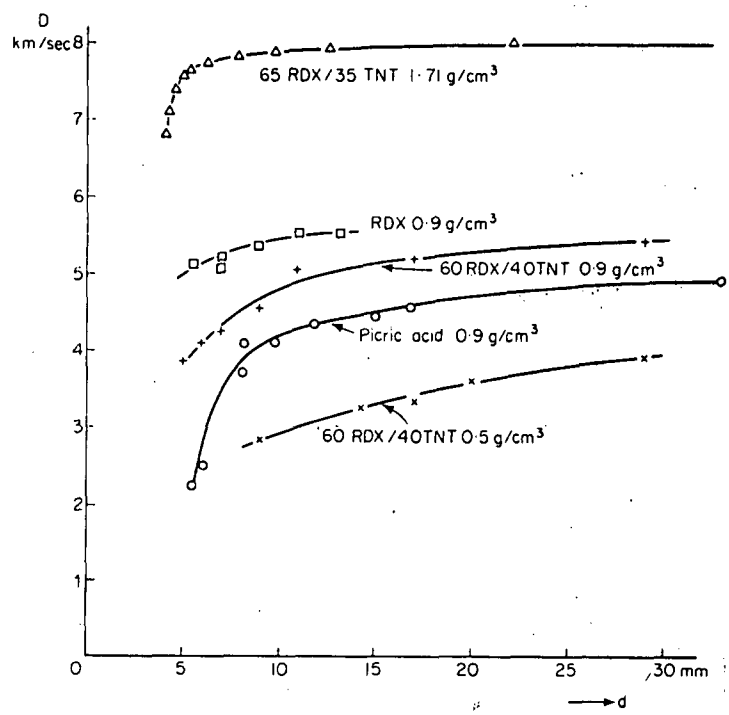


Fig 1
Detonation Velocity vs Charge Diameter

agreement between these data and those of Baum in that Parisot & Lafitte's d_m is rather higher than that of Baum

Critical diameter, d_c, is the diameter below which steady detonation is impossible. For PA, Baum (Ref 31b, p 349) and Andreev & Belyaev (Ref 32, p 289) give:

grain size (mm)	ρ (g/cc)	d_c (mm)	Ref
0.1–0.75	0.95	9.0	31b
"small"	0.95	5.5	31b
0.01–0.05	0.8	2.1–2.3	32
0.05–0.07	0.7	3.6–3.7	32

Detonation Products & CJ Parameters. Mader (Ref 33a) *computed* the following detonation product compns for 1.76g/cc and 1.00g/cc densities:

	1.76g/cc	1.00g/cc
CO_2	2.661	1.310
CO	0.179	2.970
H_2O (g)	1.499	1.409
N_2	1.500	1.496
C_{solid}	3.160	1.713
H_2	–	0.065
NH_3	–	0.008
CH_4	–	0.006

These calcns also provide the following steady detonation (CJ) parameters (Q is the heat of detonation)

	1.76g/cc	1.00g/cc
D(m/sec)	7680	5545
Press (kbar)	265	88
Q (kcal/g)	1.27	1.02
Spec Vol (cc/g)	0.423	0.714

Aside from the expected agreement between computed and exptl D, there is only one other check on the validity of these calcns. In Ref 30, Q for PA at 1 g/cc is given as 1.0kcal/g, which is in excellent accord with the Q value in the above tabulation

Combustion. Like many other granular expls, PA will burn quite stably with an increase in burning rate as the ambient pressure is increased. Andreev (Ref 34, p 377) gives the following expression for the mass burning rate of PA:

$u_m = 0.14 + 0.00805P$

where u_m is in g/cm^2 and P is in kg/cm^2. This expression is claimed to hold for ambient pressures of 25 to 950 atm

The same author (Ref 32) nevertheless states that PA packed at about 60% of its theoretical max density into sealed bombs (equipped with variable rupture disks) detonates partially at 500–700 atm ambient pressure and detonates fully at 1200 atm. Possibly the mass burning rate experiments were made at a much lower loading fraction (vol of PA/vol of container) than the bomb experiments. However Afonina et al (Ref 43) claim that PA at 1 g/cc shows little tendency toward DDT (deflagration-to-detonation transition) in steel tubes that can withstand 5–12kb of pressure

B. *Initiation Characteristics*

Minimum priming charge is the weight of a standard initiating expl required to produce stable detonation in the test expl. For PA the min priming charge is 0.24g of Lead Azide according to Ref 48, but according to Andreev & Belyaev (Ref 32, p 447) it is only 0.08 or 0.03g for pressed charges passing thru 2500 holes/cm^2 or 10,000 holes/cm^2 sieves

Heat Sensitivity. Henkin & McGill (Ref 29) report the following explosion temperatures for PA:

Temp °C	Time to explosion (sec)
350	1.5
315	5.5
277	26.3
267	50.3
260	failed

These data were obtained for 25mg PA samples contained in small-diameter, thin-wall copper tubes which were partially submerged into a heat bath

Andreev & Belyaev (Ref 32, p 476) state that PA ignites in 5 secs at 322°, which is in reasonable accord with the above. They also report that for "slow" heating (20°/min) PA ignites at 300–310° (Ref 32, p 475)

Impact Sensitivity. In the Bureau of Mines impact test (see Vol **7**, I36–40) PA shows a 50% height of 65–93cm (Refs 30 & 48). In the Picatinny impact test it has a 13-inch height (Ref 48). On a relative scale (which is the only really significant scale) PA is thus somewhat less impact sensitive than TNT. This is also borne out by the results of Afanasev & Bobolev (see Vol **7**, I51) who obtain the following critical stresses for impact initiation of PA & TNT respectively: 9.5×10^3kg/cm^2 & 11×10^3kg/cm^2

According to Andreev & Belyaev (Ref 32, p 471) PA shows some slight sensitivity to friction in that it produces a weak burning odor under con-

ditions where Tetryl crackles and Lead Picrate explds

Projectile Sensitivity. Andreev & Belyaev (Ref 32, p 473) showed that PA packed in wooden crates detonates if impacted by a 4g projectile moving at greater than 400m/sec. In the rifle bullet sensitivity test 0% explosions, 60% partials and 40% combustions were observed for PA (Ref 48)

Vasil'ev (Ref 36) impacted various explosives with steel plates and followed events with a framing camera. PA at 1.59g/cc impacted with a 3-mm thick steel plate at 430m/sec showed only deflagration and no explns. Initially the burning rate was low but reached 600m/sec in about 65 microseconds after impact

C. *Potential Hazards.* The main danger of accidental expln of PA appears to be in fires. There appears to be uncertainty if explns result if PA burns out of contact with metals. On p 494, Urbański (Ref 35) states:

"Picric acid melts prior to burning giving a sooty flame. The heat of fusion lowers the temperature of the layer adjacent to the burning one, so the substance may either stop burning or continue to burn only gently. In large quantities, burning of Picric Acid may proceed slowly, especially when it is spread over a larger area. If, however, the material is concentrated in a small area or when it is in a confined space, explosion may occur. Burning Picric Acid containing metal picrates may result in explosion. Similarly a potential danger exists when burning Picric Acid is in contact with metals, since in the molten state it forms picrates which may initiate explosion. This depends largely on the metal: lead, iron, copper should be considered particularly dangerous"

However, on p 530 Urbański says:

"If Picric Acid is free from picrates, its burning, even in large quantities, does not present any risk of explosion. A case is known (in the USA) when 100 tons of Picric Acid caught fire. It burned relatively smoothly although the flame attained a height of 10–15m and a characteristic loud whistling noise was heard. Slight explosions were observed only when roof fragments fell into the burning mass, causing blasts from a violent eruption of confined gases"

Several violent explosions have occurred when PA burned in contact with metals. Urbański (Ref 35, p 530) refers to three such explns:

"A violent explosion of Picric Acid in a Manchester factory in 1887 was ascribed to the formation of picrates. Burning, molten Picric Acid flowed down onto lithopone, forming lead picrate which in consequence caught fire. The latter, being an initiator, detonated and caused the Picric Acid to detonate

A fire, followed by an explosion at Huddersfield in 1900 was also caused by detonation of iron picrate (presumably Fe^{++}). The iron picrate had been formed on the surface of steam pipes located in the Picric Acid drier shop. It ignited when a plumber, unaware of the fact, struck one of the pipes with a hammer. The flame spread along the pipe and set the drying Picric Acid on fire

In a French factory streaks of Picric Acid had been formed alongside a narrow gauge railway. As the soil beneath was calcareous, calcium picrate formed which, having dried up in the summer, was ignited by friction or a blow, spreading flames all over those parts of the factory marked with calcium picrate streaks"

Written by **J.ROTH**

IX. *Refs:* 1) P. Woulfe, PhilTransRoySoc **61**, 129 (1771) 2) Haussmann, JPhys **32**, 162 (1788) 3) Welter, AnnChim (1) **29**, 301 (1799) 4) H. Braconnot, AnnChim (1808) 5) M.E. Chevreul, AnnChim (1), **72**, 113 (1809) 6) Marchand, JPraktChem (1) **23**, 363 (1841) 7) A. Laurent, AnnChim (3) **3**, 195 (1842); Ann **41**, 98 (1842); **43**, 200 (1842) 8) R. Schmidt & L. Glutz, Ber **2**, 52 (1869) 9) M. Brugère, CR **69**, 716 (1869); MP **2**, 15 (1884–9) 10) F. Abel, ChemNews **24**, 127 (1871) 11) H. Sprengel, JCS **26**, 803 (1873) 12) E. Turpin, FrP 167512 (1885); BrP 15089 (1885); GerP 38734 (1886) 13) J.H. Dolinski, Ber **38**, 1836 (1905) 14) H. Dautriche, MP **16**, 28 (1911) 15) Anon, TechnRecordsOf-ExplosSupply (1914–18), quoted by Urbański (Ref 35) 15a) R. Saladini, ArchdiFarm **24**, 97 (1917) 16) F. Koelsch, SS **14**, 143 (1919) 17) Designolle, see H. Kast, "Spreng- und Zündstoffe", Vieweg & Sohn (1921), 8 18) C.A. Taylor & W. Rinkenbach, JACS **46**, 1504 (1924) 19) J. Matussevitch, SS **22**, 258 (1927) 20) C. Drucker, Monatsh **53**, 64 (1929) 21) J.C. Duff & E.J. Bills, JCS **1930**, 1331 22) I.V.

Lebedev, "Spravochnik po proizvodstvu vzryvchatykh veshchestv", (Edited by Ushakov-Lebedev), Goskhimtekhizdat, Moskva-Leningrad (1934) 23) Nawrocki et al, Trudy i materialy Ukrain Tsentral Inst Gigieny i Profzabolevanii **16**, 53, Kharkov (1938) 24) A.F. Belyaev & N. Matyushko, CompRendURSS **30**, 629 (1941) & CA **37**, 531 (1943) 25) A.F. Belyaev, ZhFizKhim **22**, 91 (1948) 26) S.V. Panpushko, according to H. Gorst, "Porokha i vzryvchatyye veshchestva", Oborongiz, Moskva (1949) 27) N.V. Lazarev, "Khimicheskiye vrednyye veshchestva", Goskhimizdat, Moskva-Leningrad (1951) 28) P.D. Bartlett & H. Kwart, JACS **72**, 1051 (1950) & JACS **74**, 3969 (1952) 29) H. Henkin & R. McGill, IEC **44**, 1391 (1952) 30) Anon, NAVORD **2986** (1955) 31) Handbook of Chem & Phys, 13th Edit, 1645 (1957) 31a) Cook (1958) 31b) Baum, Stanyukovich & Shekhter (1959) 32) Andreev & Belyaev (1960) 33) J. Hannson, Explosivst **11**, 73 (1963) & CA **63**, 11237 (1965) 33a) C.L. Mader, **LA-2900** (1963) 34) Andreev & Belyaev (1963), 577 35) Urbański **1** (1964) 36) Ya. Vasil'ev, FizGoreniyaVzryva **1**, 43 (1965) & CA **64**, 12453 (1966) 37) H. Levitsky et al, ApplSpectrosc **22**, 493 (1968) & CA **69**, 111661 (1969) 38) Japan Synth Rubber Co, BritP 1139167 (1968) & CA **70**, 58752 (1969) 39) J.M. Rosen & J.C. Dacons, Explosivst **16**, 250 (1968) & CA **71**, 31921 (1969) 40) S.V. Lebedev, FrP 1550097 (1968) & CA **71**, 40048 (1969) 41) J.D. Cox & G. Pilcher, "Thermochemistry of Organometallic Compounds", Academic Press, NY (1970) 42) D.A. Salter & R.J. Simkins, GerOffen **1**, 959930 (1970) & CA **73**, 76860 (1970) 43) L. Afonina et al, VzryvnoeDelo **68/25**, 149 (1970) & CA **73**, 89713 (1970) 44) H.H. Licht, Symp on Chem Problems connected with Stability of Explosives, Tyringe, Sweden (1970), p 177 45) C.H. Johansonn & P.A. Persson, "Detonics of High Explosives", Academic Press, NY (1970), 41 46) F. Pristera, Encycl of Indust Chem Analysis **12**, 405–471 (1971) 47) P.G. Hall, TransFaradSoc **67**, 556 (1971) & CA **74**, 103825 (1971) 48) Anon, EngrgDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 288–93 49) N.I. Boguslavskaya et al, DAN **220**, 617 (1975) & CA **82**, 111364 (1975)

Picric Acid Explosives and Picrate Explosives.

As was mentioned in the Picric Acid (PA) article, straight PA was used extensively for cast and press loading of various projectiles. Fr, Engl and Japan appear to have used PA more than any other HE almost to the beginning of WWII. However, the use of straight PA is not always advisable because of the following disadvantages: 1) a high mp, 120–22°, which makes cast loading a fairly dangerous operation, 2) corrosive action on metals, except for Al and Sn; and 3) instability in storage at tropical temps

The first of these disadvantages can be overcome by adding selected nitrocompds to PA which have the property of lowering its mp. The following table, taken from p 14 of Ref 2, shows the mp's of a few characteristic mixts of this nature, the proportions being molecular

One of the most common addition compds to PA to lower its mp was trinitro-m-cresol, eg, in the Fr expl Cresylite. Other compds used were DNPh, DNT, DNM, MNM, MNPh, TNT, TN-m-X, DNB, TNB, etc

An ingenious method for the prepn of cast expls contg 90–95% PA and 5–10% nitrocompds, such as TNT, TNCr, TNB, TNN, TNX, DNB, DNT, DNPh, etc, was patented in Ger in 1892 [GerP 69897 (1892)]. It consisted of placing a mixt of PA with 5–10% of the nitrocompd in mounds of the desired shape, and heated for a short time to a temp slightly above the mp of the nitrocompd, with or without the employment of pressure. The nitrocompd melts and cements the PA crystals together so that when cooled the mixt forms a hard mass. It was claimed that the manuf of such charges was absolutely safe, and that they possessed no dangerous properties in use or transport (Ref 2, p 697)

In addition to adding nitrocompds to PA to lower its mp, other substances could be added, such as oxidizers (K nitrate, Na nitrate, AN, Ba nitrate, Pb dioxide, Amm dichromate, K chlorate, K perchlorate, etc), fuels (such as sawdust, S, starch, lignite, charcoal, tar, naphthalene, etc), picrates, NG, NC resins, etc. Some expls even contained fuming acid, eg, Emmens Acid and Emmensite

The following is a selected list of expls, covered in this Encycl in detail under their alphabetical listing, contg PA or picrates as the

Table 1
Nitrocompound Addition to Picric Acid for Melting Point Lowering

Proportion	Nitrocompounds and their Melting Points in °C	Melting Point of the Mixture in °C
1:1	PA (122°) + Nitronaphthalene (61°)	49°
1:1	PA (122°) + TNT (80.2°)	47°
1:1	PA (122°) + Trinitrocresol (107°)	70°
2:1	PA (122°) + Trinitrocresol (107°)	78°

main ingredient: Abel's (or Picric) Powder, Anderson's Explosives, Borlinetto Powder, Brugere Powder, Buck's Explosive, Cresylites, DD 60/40 Explosive, Designolles Powder, Designolles and Casthelaz Powder, Dienite, Emmens Acid, Emmensite, Explosive D, Green French Powder, Heracline, Jalias Explosives, Kolowratnik's Explosives, Lederite, Maicite, Maximite, Maxim's Explosives, MAP Explosives, MDN Explosive, MDPC Explosive, Melinite O, Melinite P, MMN Explosive, MTTC Explosive, MTX Explosive, Oxonite, Picratol, Shellite, Tridite, Trimonite, Tschirner Explosive, Victorite, and Xylite P (See also under British, French, German, Italian and Russian Explosives)
Refs: 1) Marshall **2**, 553 & 557 (1917) & **3**, 170–74 (1932) 2) Colver (1919), 318–25 3) Vennin, Burlot & Lécorché (1932), 457 4) Pepin Lehalleur (1935), 441 5) Davis (1943), 72, 166 & 358 6) Pérez Ara (1945), 220–24, 525 & 528

Picric Nitrogelatine (Nitrogelatine Picrique in Fr). A gelatinous expl compd patented in Ger in 1887, prepd by mixing 10p of NG with 1 p of PA and gelatinizing the resulting soln with a small amt of collodion cotton. Such materials as flour, starch, nitrates, chlorates, perchlorates, etc, could be added to this jelly
Ref: Cundill (1889) [A Fr translation can be found in MP **6**, 47–48 (1893)]

Picric Powder. See under Abel Powder in Vol **1**, A1-R

Picrinita. A Spanish name for Picric Acid

Picrit (Pikrit). A Ger industrial expl, prepd from surplus stocks left after WWI. It consisted of PA in which up to 10% could be substituted by any aromatic nitrocompd which would not make the expl more dangerous to handle than straight PA
Ref: Pepin Lehalleur (1935), 457

Picrite. Brit name for Nitroguanidine (NGu), also known as Guanyl Nitramine. See in Vol **6**, G154-R ff

Picrolonic Acid [1-(4-Nitro-phenyl)-4-nitro-3-methyl-Pyrazolone-(5)].

$O_2N.HC$——————$C.CH_3$
$OC.N(C_6H_4.NO_2).N$

mw 264.245; N 21.21%, OB to CO_2 −115.04%; yel ndls; mp 118–19°. Sol in ethanol, w, methanol, eth and Na alcoholate. Prepn is by reacting 1-phenyl-3-methyl-pyrazolone-(5) with nitric acid (d 1.49g/cc) at 10–15°. Co-reaction prods are dissoc at 60° with 33% acetic acid. The compd deton when heated quickly to 124°
Ref: Beil **24**, 51 & (218)

Picronitronaphthalene. See under Trinitronaphthalene in Vol **8**, N12-R to N14-R

Picryl Compounds

The *picryls* are usually prepd by reacting a picryl such as picryl chloride with an organic compd. Picryl peroxides and salts also exist. The entries below are picryl compds which can be considered expls, some of these such as Picryl Fluoride and Picrylpicryl Chloride have been used as expls

Picrylacetate. $(O_2N)_3C_6H_2.O.C(O).CH_3$; mw 271.20; N 15.50%; colorl cryst, mp 75–76°. Prepn is by heating PA with acetic anhyd
Ref: Beil **6**, 291 & (141)
There are several expl derivs of this compd; viz,
Pyrazolidimethylenepicrylacetate.
$C_{11}H_{11}H_3O_8$; mw 313.29; N 13.42%; OB to CO_2 −99.59%; pale yel cryst; mp 144° (decompn). Puffs off on heating or on contact with concd sulfuric acid
Ref: Beil **6**, (141)
Trimethylenepicrylacetate. $C_{11}H_{11}N_3O_8$; ndls; mp 140–41°. Puffs off on heating or on contact with concd sulfuric acid
Ref: Beil **6**, (141)

Picryl Allyl Ether. See Allyl Picrate in Vol **1**, A139-R

Picrylaniline. See 2,4,6-Trinitrodiphenylamine in Vol **5**, D1433-L. This compd forms salts, some of which are expl, viz,
Potassiumethylate Salt.
$C_{12}H_8O_6N_4{+}C_2H_5.OK$; mw 388.435; N 14.43%; OB to CO_2 −117.39%; brn-blk cryst; mp 115° (decompn). Prepn is by reacting K hydroxide in ethanol with picrylaniline (Ref 4). The compd explds on heating above its mp
Potassiummethylate Salt.
$C_{12}H_8O_6N_4{+}CH_3.OK$; mw 374.405; N 14.97%; OB to CO_2 −104.70%; brn-blk cryst. Sol in warm acet, ethanol and methanol. Prepn is by reacting a methanol soln of K hydroxide with a benz soln of picrylaniline (Refs 3 & 4). The compd is stable in dry storage. It explds when heated
The nitrated compds of picrylaniline are listed in Vol **5**, D1434
Refs: 1) Beil **12**, 765, (368) & [421] 2) C. Clemm, JPraktChem **1** (2), 145 (1870) 3) J.J. Sudborough & N. Picton, JCS **89**, 593 (1906) 4) M. Busch & W. Kögel, Ber **43**, 1550 (1910) & CA **4**, 2641 (1910)

Picryl Azide. See 2,4,6-Trinitrophenyl Azide in Vol **1**, A643-L and Vol **2**, B43-L
Addnl Refs: 1) Urbański **1** (1964), 602 2) Ibid **3** (1967), 192

Picryl Chloride. See 2,4,6-Trinitrochlorobenzene in Vol **3**, C250-L to C251-R
Addnl Refs: 1) Blatt, OSRD **2014** (1944), 186 2) Urbański **1** (1964), 178, 400, 459, 460 & 461

Picryldiazide. See 1,3-Diazido-2,4,6-trinitrobenzene in Vol **2**, B43-L

Picryl Fluoride. See Fluoro-2,4,6-Trinitrobenzene in Vol **6**, F137-L. This compd has been evaluated at PicArsn as an expl. The parameters are presented in the following limited distribution *Refs:* 1) H.J. Jackson et al, "A Comparative Evaluation of Selected Fluoroexplosives", PATR **3941** (1970) 2) L. Avrami et al, "Effects of Gamma Radiation on Selected Fluoroexplosives", PATR **3942** (1970) also, *Addnl Refs:* 1) Blatt, OSRD **1085** (1942), 77 2) Ibid, OSRD **2014** (1944)

Picryl Hydrazine. See under 2,4,6-Trinitrophenylhydrazine in Vol **7**, H207-R

Picryl Hydroxylamine Toluene. See under 2,4,6-Trinitro-3-hydroxylaminotoluene in Vol **7**, H247-R

Picrylhydroperoxide; Sodium Salt.
$(O_2N)_3C_6H_2.O.O.Na$; mw 267.14; N 15.73%; OB to CO_2 −29.95%; red-brn cryst; mp 154°. Sol in ethanol and w. Prepn is by reacting equimolar amts of picryl chloride and Na peroxide in w and allowing the mixt to stand. The compd decomps on standing and puffs off on heating. Ref 2 claimed it to be a powerful expl
Refs: 1) Beil **6**, 291 2) H. Voswinkel, GerP 96855 (1898)

Picrylnitramine (2,4,6-Trinitrophenylnitramine). $(O_2N)_3C_6H_2.N(H).NO_2$; mw 273.18; N 25.64%; OB to CO_2 −32.21%; yel ndls or crysts; mp 75–90° (deflgr). Sol in eth. Prepn is by reacting either a soln of 2-nitroaniline or 4-nitroaniline in sulfuric acid with a soln of K nitrate

in sulfuric acid at 5°. The compd is v expl and sens. Lead block expansion is 140% of PA
Refs: 1) Beil **16**, 668 2) Blatt, OSRD **2014** (1944)

Picryloxamide (Oxalic acid amide-[2,4,6-Trinitroanilide]). $(O_2N)_3C_6H_2.N(H).CO.CO.NH_2$; mw 299.22; N 23.41%; OB to CO_2 −56.15%; ndles; mp 255–60° (decompn). Sol in ethanol and hot acet ac. Prepn is by heating 1 part of 2,4,6,-2′,4′,6′-hexanitrooxanilide with 1p of K acid carbonate and 30p of w
Ref: Beil **12**, 767

Picrylphenylenediamines. See under Trinitroaminodiphenylamines in Vol **1**, A197-L & R.

Picrylpicryl Compounds. These are listed as dipicryls in Vol **5**, D1488-R to D1490-L. This listing includes: **Dipicrylamine, Di(picrylamino)-anthraquinone, Dipicrylaminoethyl Nitrate, Dipicrylarginine, Dipicrylcarboxamideacetylene, Dipicryldianthranilide, Dipicryldisulfide, Dipicrylethane, Dipicrylethanol, Dipicrylether, N,N′-Dipicrylethylenediamine, N,N′-Dipicryl-ethylenedinitramine, Dipicrylglycerylether Nitrate, Dipicrylguanidine, Dipicrylmethane, Dipicrylmethylamine, Dipicrylmethylenedihydroxyphenylpropane, Dipicryloxamide, Dipicrylphenylenediamine, Dipicrylpiperazine, Dipicrylpropylenediamine, Dipicrylselenide, Dipicrylsulfide, Dipicrylsulfone, Di(picrylthiol)-ethylbenzene, Di-(picrylthiol)-xylene, Dipicryltolylpropane** and **Dipicrylurea.** In addition, there are several other dipicryl compds of interest. They are entered next under the picrylpicryl nomenclature

m-Picrylpicryl Chloride (3-Chloro-2,2′,4,4′,6,6′-Hexanitrobiphenyl, PIPICl).
$(O_2N)_3(Cl)C_6H.C_6H_2(NO_2)_3$; mw 458.72; N 18.32%; OB to CO_2 −47.09%; pale yel cryst; mp 186–88°. Sol in acet. Prepn is by a two step proc with the first step being the addn of pyridine to 3-methoxy-2,2′,4,4′,6,6′-hexanitrobiphenyl. This is accomplished by refluxing 75ml of pyridine with 0.33 mole of the biphenyl suspended in 1.2ℓ of benz for 1 hr at 100°. The second step is accomplished by dissolving the prod of step one into 400ml of P oxychloride and warming for one hr at 100°. Ice w pptn of the second step prod is followed by filtrn, w washing, drying, purification and recrystn from n-hexane. A yield of 89% is obtd. Currently, the compd is used as an expl
Ref: J.C. Dacons & M.J. Kamlet, "A New Synthesis For 3-Chloro-2,2′,4,4′,6,6′-Hexanitrobiphenyl, PIPICl", NOLTR **65-215** (1966)

N,N′-Dinitro-N,N′-Picrylpicryl-Propyl-1,3-Diamine. $(O_2N)N.(CH_2)_3.N(NO_2)$;
$(O_2N)_3C_6H_2 \quad C_6H_2(NO_2)_3$
mw 587.33; N 24.01%; OB to CO_2 −51.76%; yel cryst; mp 202°. Prepn is by reacting nitric acid with N,N′-diphenylpropane-1,3-diamine. The compd is expl
Ref: Beil **12**, {1741}

1-Picryl-Semicarbazide (1-[2,4,6,Trinitrophenyl]-Semicarbazide).
$(O_2N)_3C_6H_2.NH.NH.CO.NH_2$; mw 286.23; N 29.37%; OB to CO_2 −55.90%; yel ndles; mp 218–19° (decompn). Sol in alk aq solns; sl sol in solvents such as acet and acet ac. Prepn is by reacting picryl chloride and semicarbazide in aq ethanol
Ref: Beil **15**, [222]

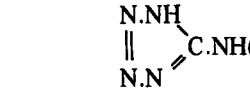
1-Picryl Semioxamazide (1-[2,4,6-Trinitrophenyl]-semioxamazide).
$(O_2N)_3C_6H_2.NH.NH.CO.CO.NH_2$; mw 313.25; N 26.84%; OB to CO_2 −56.19%; mp 249–50° (decompn). Sol in alc alkalies; sl sol in organic solvents. Prepn is by reacting picryl chloride with semioxamazide in boiling ethanol
Ref: Beil **15**, [222]

1-Picryl-Thiosemicarboazide (1-[2,4,6-Trinitrophenyl]-thiosemicarbazide).
$(O_2N)_3C_6H_2.NH.NH.CS.NH_2$ (becomes the desmotropic form); mw 302.28; N 27.81%; OB to CO_2 −58.22%; bright yel ndles; mp 183–84° (decompn). V sol in ethanol, acet and acet ac; sl sol in benz, chlf and petr eth. Prepn is by re-

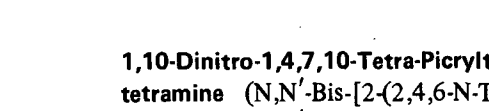
acting picryl chloride with thiosemicarbazide in ethanol at 100°
Ref: Beil **15**, [222]

Picryl Sulfide. See Hexanitrodiphenylsulfide in Vol **5**, D1477-R

Picryl Sulfone. See Hexanitrodiphenylsulfone in Vol **5**, D1480-L

Picryltetrazolylamine.

mw 293.22; N 38.22%; OB to CO_2 −54.57%; prepn is by reacting picryl chloride with tetrazolylamine. The compd explds on impact
Ref: Blatt, OSRD **2014** (1944)

Picryltetrazylazide. A compd patented by W. Friederich for use as a primary filler in detonators and detonating fuzes. No method of prepn or structure is revealed in the patent
Ref: W. Friederich, USP 2170943 (1939) & CA, not found

1,10-Dinitro-1,4,7,10-Tetra-Picryltriethylenetetramine (N,N′-Bis-[2-(2,4,6-N-Tetranitro-anilino)-ethyl]-N,N′-dipicryl-ethylenediamine).

mw 1080.82; N 23.33%; OB to CO_2 −62.18%; bright yel cryst; mp 165° (decompn). Prepn is by reacting nitric acid with 1,4,7,10-tetrakis-(2,4-dinitro-phenyl)-triethylenetetramine at −15°. When quickly heated the compd explds
Ref: Beil **12**, {1740}

Picrylurea (2,4,6-Trinitrophenylurea).
$(O_2N)_3C_6H_2.N(H).CO.NH_2$; mw 271.21; N 25.83%; OB to CO_2 −56.05%; yel cryst; mp 201–03° (decompn). V sol in ethanol, eth, acet and acet ac; sl sol in chlf and petr eth. Prepn is by reacting an alc soln of ammonia with N-nitro-N-ethyl-N′-[2,4,6-trinitro-phenyl]-urea
Refs: 1) Beil **12**, [423] 2) M. Giua, Gazz **55**, 665 (1925) & CA **20**, 1061 (1926) 3) L.C.A. Kniphorst, Rec **44**, 701 (1925) & CA **20**, 589 (1926)

Pieper Explosives. Safety expls patented in 1893–94 in Fr. A blend of aromatic nitrocompds with AN, using a solvent common to both ingredients. The incorporation of a small amt of alc in some expls was recommended. One of these expls was "Ronsalite" (qv)
Ref: Daniel (1902), 631

Pierre and Pottgiesser Explosive. A safety expl patented in 1896 contg AN 93, Nitroaniline 5, and Mn dioxide, Pb dioxide or Cr trioxide 2%
Ref: Daniel (1902), 631

Pierrit. See Vol **3**, C443-R

Piezoelectric Gages. See under Closed Bomb (or Vessel) Techniques in Vol **3**, C339-L to C345

P.I.G. and P.S.G. Brit designations for Percentage Initiation by Grit and Percentage Sensitization by Grit

Particles of grit such as carborundum, when added to an expl, can artifically create "hot spots" (see Vol **7** H170-L to H175-R) when the expl is suddenly compressed by impact as in an impact sensy device. Only grit particles of mp higher than that of the expl can initiate higher temp hot spots and thus increase the sensitivity of the expl

The values for both P.I.G. and P.S.G. are computed from the areas under curves generated, using impact sensy devices, by plotting the number of impacts leading to expl detonation vs impact height. The two terms differ only in the manner of defining *detonation.* For P.I.G., the area under the curve is based on *complete* detonation or failure, a partial expln being called

Table 1
Relative Sensitivity Based on Figure of Insensitiveness (F.I.) (from Ref 3)

Explosive	F.I. of Pure Explosive	Number of Grit Particles/Cap	P.I.G. or % Initiation Sensitization	P.S.G. or % Gas Sensitization
TNT	120	60	69	–
RDX/Wax	100	60	57	–
PA	100	60	67	-
RDX	64	60	61	60
PETN	38	60	68	68
Tetryl	72	12	48	23
RDX	64	12	52	49
PETN	38	12	66	64

a failure. For P.S.G., the area under the curve is based on *gas evolution,* each sample cap giving a quantity of gas greater than exptl error being called an ignition whether detonation occurred or not. Thus to express either term mathematically:
P.I.G. or P.S.G. =

$$100 \times \left(1 - \frac{\text{Area under expl with grit curve}}{\text{Area under pure expl curve}}\right)$$

Table 1 illustrates the difference in values obtained using three impact sensy techniques, F.I. (see Vol **6**, F39-R to F40-R), P.I.G. and P.S.G. The expls used contain known percentages of −100 to +200 mesh carborundum of 1.2×10^{-2} mm^2 avg particle cross section
Refs: 1) Cook (1948), 178–83 2) F.P. Bowden & O.A.J. Gurton, ProcRoySoc **A198**, 350 (1949) 3) J.L. Copp et al, TrRoySoc **A241**, 197 (1949)

Pigou Propellants. Smokeless proplnts, patented in 1896, manufd by blending nitrated hydrocellulose with Ba nitrate and starch
Ref: Daniel (1902), 632

Pike and Thew Explosives. Patented in Engl in 1897; prepd by mixing nitrated potato wastes with other ingredients
Ref: Daniel (1902), 632

Pikratol. Ger for Ag Picrate. See in this Vol under Picrates, Inorganic

Pikrinsäure. Ger for Picric Acid

Pikrit. See under Picrit in this Vol

Pile Driving Device. Said to have originated in America, this device uses a cartridge of expl placed between the head of a wooden pile and a driving ram. The expln of the charge drives the pile into the ground and simultaneously raises the ram which, upon falling, drives the pile further. This idea was utilized in "drop hammers" which were explosively, not steam, operated
Ref: Daniel (1902), 631

Pile Test for Dynamites (Épreuve de Pieux ou de Pilotis). In order to determine the impulsive energy or work (in kg/m) performed by various Dynamites, Col Prodonovic (Hungary) proposed the following test in 1881:

A charge (one or several) of the expl to be tested is attached to an iron disk 38cm in diam and 11cm thick, and covered either with sand or clay. The disk is placed on the top (head) of a wooden pile inserted in the ground. Alongside of this pile is placed a similar pile with a charge of a "standard" expl. After exploding both charges simultaneously, the depth of penetration of the piles into the ground is measured and compared
Ref: Daniel (1902), 633

Piling and Stacking of Ammunition. Techniques using geometry and/or physical protection have been evolved for ammo which reduces its vulnerability during temporary combat area storage (Ref 3), increases its safety in transport, and increases its shelf life while in permanent storage. Descriptions and drawings of the arrays of all types of end-items on individual pallets, in individual packages, as well as the quantity-distance relationships for safety in piling and stacking these items are shown in Refs 1 and 2. See also under Packaging and Packing of Ammunition in this Vol

Refs: 1) Anon, "Storage and Outloading Primary Index", **TM 743-200-1** (July 1970) 2) Anon, "Ammunition and Explosives Standards", **TM 9-1300-206** (August 30, 1973) 3) H.J. Reeves, "General Principles of Vulnerability Reduction of Stacked Ammunition", **BRL MR No 2376** (1974)

Pimelic Acid and Derivatives.

Pimelic Acid (Heptanedioic Acid or 1,5-Pentanedicarboxylic Acid). $HOOC.(CH_2)_5.COOH$; mw 160.17; white prisms; mp 106°; bp 272° at 100mm (subl), and 212° at 10mm; d 1.329 g/cc at 15°. Sol in w, ethanol, eth and hot benz. Prepn is by oxidn of cycloheptanone, capric acid or oleic acid; treatment of salicylic acid with Na in amyl alc, or by decarboxylating 1,1,5,5-pentanetetracarboxylic acid with heat

Pimelic acid has been combined with *cis* and *trans*-1,4-cyclohexanediol to give polyesters, and with m-xylene-α,α'-diamine or polymethylenediamines to form polyamides. With diperoxides, the acid forms resins. It is also used as the parent compd to form the expls presented below

Refs: 1) Beil **2**, [586] 2) Kirk & Othmer **1** (1963), 248–49 3) ChemRubHdb (1975), C-322

4,4-Dinitroheptanedioyl Azide.

$N_3OC.CH_2.CH_2.C(NO_2)_2.CH_2.CH_2.CON_3$; mw 300.26; N 37.33%; OB to CO_2 −63.94%; colorl crysts, mp 68–69° (decompn). Sol in chlf. Prepn is by dropwise addn at 5–10° of a 0.035 mole soln of 4,4-dinitroheptanedioyl chloride in acet to a 0.14 mole soln of Na azide in w. W pptn and washing gives a 90–95% yield

Refs: 1) Beil, not found 2) L. Herzog et al, JACS **73**, 749–51 (1951) & CA **45**, 5609 (1951)

4,4-Dinitropimelic Acid (DNPA,4,4-Dinitro-1,7-Heptanedioic Acid).

$HOOC.(CH_2)_2.C(NO_2)_2.(CH_2)_2.COOH$; mw 250.23; N 11.19%; OB to CO_2 −70.34%; white cryst plates; mp 137°; d 1.52g/cc. V sol in acet; sol in w and v sl sol in toluene. Prepn is in two steps; the first being the synthesis of the dimethyl ester of 4,4-dinitropimelic acid followed by acid hydrolysis to yield the acid. In the first step 13.5 moles of methyl acrylate is added dropwise with stirring at RT to an aq soln of 2.5 moles of K dinitroethanol. The addn is completed in three hrs with eight more hrs of stirring reqd to complete the reaction. After completion of the stirring, the ester is extrd with eth decolorized with charcoal, and the eth removed under vac. The impure ester is then recryst from methanol. The mp of the 58% yield is 45° (Ref 4). The second step hydrolyzes 0.14 mole of the ester by refluxing it with 350ml of 18% hydrochloric acid for several hrs. After cooling, the 4,4-dinitropimelic acid is crystd from w. This step has a yield of 95–97%. The total yield based on K dinitroethanol is 55 to 56% (Refs 3 & 5). Several pilot plant and comml processes are given in Refs 6 & 7

4,4-Dinitropimelic acid is compatible with NC in a 20% mixt of the acid; Q_c at 25° of 3010cal/g (liq w ref); Q_f of −235kg cal at 25° and 1 atm press; has an impact sensy of > 100cm using a BM app with a 2kg wt; a thermal stability at 65.5° of over 5 hrs; a thermal stability at 134.5° of over 40 mins (unchanged after 5 hrs); and is stable in storage at RT (Ref 3)

The acid is used as an intermediate in the synthesis of polynitroaliphatic expls and proplnts, and as a monomer in a proplnt polymer developed by the Aerojet Engrg Corp which is presented next

Refs: 1) Beil, not found 2) L.H. Brown & R.D. Geckler, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", Aerojet Engrg Corp, Calif, **QSR No 371**, ONR Contract N7 onr-462 (1949), 62 3) R.D. Geckler et al, Ibid, **QSR No 386** (1949), appendix A1–4 4) R.D. Geckler & M.H. Gold, Ibid, **QSR No 404** (1949), 42 5) L. Herzog et al, "The Chemistry of Aliphatic

Dinitro Compounds. I. The Michael Reaction", JACS **73**, 749–51 (1951) & CA **45**, 5609 (1951) 6) J.C. Dacons & M.J. Kamlet, "Improved 'One-Pot' Process for the Preparation of 4,4-Dinitropimelic Acid and 4,4,4-Trinitrobutyric Acid", **NAVORD Rept 4437** (1956) 7) J.R. McCandless, "DNPA Summary Report", American Cyanamid Co, Penn, Contract NOw-60-0745-C (1965)

The Polyester Polymer 4,4-Dinitropimelyl Chloride and 2,2-Dinitro-1,3-Propanediol.

$$\text{-}\{\text{C}.(\text{CH}_2)_2.\text{C}(\text{NO}_2)_2.(\text{CH}_2)_2.\overset{\text{O}}{\overset{\|}{\text{C}}}.\text{O}.\text{CH}_2.\text{C}(\text{NO}_2)_2.\text{CH}_2.\text{O}\text{-}\}_n$$

mw $(380.32)_n$, approx 4000–9000; N 14.73%; OB to CO_2 −58.90%; amber molded pellet or cream colored powder; softening pt 180–85°. Sl sol in acet, dioxane and tetrahydrofuran; v sol in dimethylformamide. Prepn is a two-step process which first involves the synthesis of the chloride, and then the polyester. The chloride is prepd by *cautiously* heating a mixt of 0.2 mole of 4,4-dinitropimelic acid with 90cc of thionyl chloride at reflux for 2 hrs. Hot filtrn is followed by rapid cooling to −15°. Recrystn from thionyl chloride gives a 95% yield of the chloride with a mp of 57° (Ref 4). The polymer is then prepd using equiv amts (0.1 mole) of the monomers which are mixed with 50ml of dioxane under dry nitrogen at 100° for 173 hrs. The w washed polymer is then vac steam distd at 25°, and dried over phosphorous pentoxide at 2mm (Ref 3)

The polyester has a Q_c of 3020kcal/g; a 50% pt impact sensy of 85–95cm using a BM app with a 2kg wt; a specific impulse of 204lb-sec/lb; a thermal stability of 215 mins at 65.5° and 15 mins (unchanged appearance of the sample after 5 hrs) at 134.5° (Refs 2 & 3)

Refs: 1) Beil, not found 2) R.D. Geckler et al, "Research in Nitropolymers and Their Application To Solid Smokeless Propellants", Aerojet Engrg Corp, Calif, **QSR No 386** (1949), Table VIII 3) M.H. Gold et al, Ibid, **QSR No 468** (1950), 45, 46, 51, 53 & 54 4) L. Herzog et al, JACS **73**, 749–51 (1951) & CA **45**, 5609 (1951) 5) K.G. Shipp et al, "Synthesis of New High Explosives. IV.", **NOLTR 64-211** (1965)

Addnl Refs: The following refs are under *limited distribution;* A) P. Szecsi, "Intermediates for High Temperature Stable Polymers", **AFML-TR-65-46**, Wyandotte Chem Corp, Mich, Contract AF 33657/0819 (1965) B) M.B. Frankel & F.C. Gunderloy, "Development of High-Energy Polymer Systems", **AFATL-TR-70-17**, Rocketdyne, Canoga Park, Calif, Contract F 08635-69-C-0121 (1970)

Pin-Fire Cartridge System. A cartridge ignition system invented in 1836 by LeFaucheux of Paris. It was the first practical cartridge system which contained in one unit the cartridge case, the proplnt, the bullet and the primer cap. A version of this invention is still used today in blank pistols designed in Europe. The cap was placed inside the cartridge near the base in such a manner that the priming compd, usually Fulminate of Mercury, faced the pin which was parallel to the base and protruded thru the side of the cartridge. When the protruded end of the pin was struck by the gun's hammer coming down vertically on the side of the cartridge (instead of penetrating horizontally from the rear, as is done in modern cartridges), the other sharpened end of the pin struck the primer and caused the ignition of the primary compn and of the proplnt

Refs: 1) M.M. Johnson, "Ammunition, Its History, Development and Use", Morrow, NY (1943), 37 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 350

Pinite and Derivatives. See Inositol and Derivatives in Vol **7**, I109-L to I110-R

Pin Method or Pin-Oscillograph Method For Detonation Rate Measurement. See Vol **3**, C315-R

Pin Switch Technique for Measuring Detonation Velocity. See Vol **3**, C313-R to C319-L

"Pinwheel". A rocket helicopter developed in 1951 by Rotor-Craft Corp of Glendale, Calif.

It weighs 100 lbs and is designed to carry one person. Thrust is generated by self-starting, throttle controlled liq fuel rockets mounted in the tips of the two small rotor blades. The rotor is attached to a steel tube which curves downward to support the fuel tanks, a pilot seat and a cargo hook. A tube extending backward from the rotor hub carries a small rudder, and another extending forward and down is the pilot's control column

Ref: Anon, Ordn **36**, No 190, 618 (1952)

Piobert's Law of Combustion. When a solid grain of a proplnt (such as smokeless powder) is ignited in air, each surface burns independently and progressively in parallel layers and at the same rate. Indeed, the process of burning is so regular that if it is stopped before completion, the unconsumed portion of the grain will have the same shape as the original grain, but it will be smaller in size

The same regularity of burning is observed in grains with perforations, except that the shape of the partially burned grains is not exactly the same as the original grains because the diameter of the outer layer diminishes and the diameter of the inner layer increases during burning

That the burning proceeds uniformly by layers may be shown by firing a gelatinized NC powder from a gun too short to allow total consumption of the proplnt. The grains ejected from the nozzle will be identical in geometry but differ in size from the original grains

It should be noted that Piobert's Law is valid only for non-porous powders which deflagrate but do not expld. Hence, it is inapplicable to powders which are porous such as BlkPdr, non-gelatinized, compressed NC, etc. See "Burning and Burning Characteristics of Propellants for Artillery Weapons and Small Arms" in Vol **2**, B346-L to B347-L

Refs: 1) Marshall **1** (1917), 310–11 2) Pérez Ara (1945), 417–18 3) S. Fordham, "High Explosives and Propellants", Pergamon Press, NY (1966), 194

PIPE. A plastic expl developed by the US Ordn Corps during WWII. It is a mechanical mixt of PETN (81%) and Gulf Crown E Oil (19%); mw 300; N 18.08%; OB to CO_2 –74%; d 1.35 g/cc (hand tamped). PIPE has a detonation rate in a hand tamped 1.0-inch diam charge (1.37 g/cc d) of 7075m/sec; a fragmentation test using a 3-inch HE, M42A1 proj of 428 frags (514 for TNT); a friction pendulum test of "unaffected" with both steel and fiber shoes; a heat test at 100° of 0.17% loss in 48 hrs, an addnl 48 hrs showed no loss and no expl in 100 hrs; a hygroscopic gain of 0.02% at 90% RH and 30°; an impact sensy of 11 inches (8 inches for RDX) using a 27mg sample in a PicArsn app with a 2kg wt; a rifle bullet impact test of "100% unaffected"; a sensy to initiation of 0.20g with either Mercury Fulminate or Pb Azide; and a vac stab test at 100°, using 5g sample, of 0.48cc in 40 hrs, and over 11cc in 16 hrs at 120°. It is considered a Class 9 expl of Group I compatibility and is stored dry. PIPE is used as a demolition expl

Ref: Anon, EngrgDesHdbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 294–95

Pipeline Digester for Nitrocellulose. Known as the Milliken continuous digester. It consists of approx 0.8 mile of 4-inch diam chrome steel tubing in numerous sections connected by numerous return bends. According to Yeager:

"The first sections are steam jacketed, the intermediate sections simply insulated to hold the temperatures reached by the mass in the heated part, and the final section is provided with a cold water jacket to stop the digestion and cool the mass below the atmospheric boiling point of water. Since the digestion must be conducted under pressure to permit the necessary temperature, the required hydrostatic head on the entire system is provided by piping the mass from the discharge of the digester up over a 200-ft tower, then down again to a final treatment and sampling tub. The tower was chosen as the best method of supplying back pressure, since other methods such as valves and pumps would be unreliable due to fouling

Nitrocellulose is always in motion in the digester and well suspended in water, so that each fiber receives uniform treatment, producing a uniform viscosity much superior to the batch product. The continuous product has no oppor-

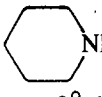
tunity to pick up contamination from brick and cement and the process eliminates gas pockets where overheating and possible explosion could occur. Labor required is less and much disagreeable work is eliminated. Furthermore, control is superior . . ."
Ref: J.R. Yeager, "Pipeline Digester For Nitrocellulose", ChemMetEngrg **52**, No 5, 113–14 (1945) & CA **39**, 2911 (1945)

Piperazine and Derivatives. See Diethylenediamine and Derivatives in Vol **5**, D1230-R to D1231-R. An addnl ref is: A.T. Blomquist, OSRD **4134** (1944), 7 & 68

Other refs which, although unclassified, are of *limited distribution:* 1) Anon, "Research on Ultra-High Impulse Propellant Systems", Imperial Chem Ind Ltd, Stevenson (Scotland), Contract N625584076, Prog Rept **No 16**, 1 Apr–30 June 64 (1964) 2) Ibid, Annual Prog Rept **No 18**, 1 Jan–31Dec 64 (1964) 3) Ibid, Prog Rept **No 19**, 1 Jan–31 Mar 65 (1965) 4) Ibid, Prog Rept **No 20**, 1 Apr–30 Jun 65 (1965) 5) Ibid, Prog Rept **No 21**, 1 Jul–30 Sep 65 (1965) 6) Ibid, Prog Rept **No 22**, 1 Oct–31 Dec 65 (1965) 7) Ibid, Prog Rept **No 24**, 1 Jan 65–30 Jun 66 (1966) 8) Ibid, "Research on Ultra-High Impulse Propellant Systems. Data Sheets for Compounds Prepared under US Navy Contracts", Imperial Chem Ind Ltd, Stevenson (Scotland), Rept for 1 Jul 60–30 June 66, contracts N62558-2576 & N62558-3318 (1966) 9) F.C. Shulman, "New Gun Propellant", **AFATL-TR-70-45**, Hercules Inc (Cumberland, Md) Contract FO8635-69-C-0164 (1970)

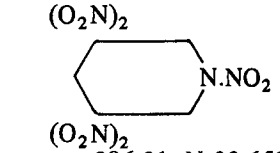
Piperidine and Derivatives

Piperidine (Hexahydropyridine or Pentamethyleneimine).



NH; mw 85.15; N 16.45%; colorl liq; mp –9°; bp 106°; d 0.8606g/cc at 20/4°; RI 1.4530. V sol in ethanol and w; sol in eth, acet, benz and chlf. Prepn is by reducing py with Zn and HCl or by heating ε-iodo-n-amylamine with w. Piperidine has a fl pt in air of 3°. It is the parent compd for organometallic azides used in heat resistant plastics; compds used as anti-materials, insect repellants, anti-radioactivity agents, psychotropic drugs and chemical warfare agents; also to the expls presented below
Refs: 1) Beil **20**, [6] 2) Sax (1968), 1029–30

1,3,3,5,5-Pentanitropiperidine.

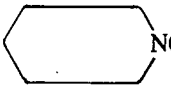


mw 296.21; N 23.65%; OB to CO_2 –70.22%; cryst; mp 120–25°; d 1.82g/cc. Sol in chlf. Prepn is by treating 0.4g of 3,3,5,5-Tetranitropiperidine with a mixt of 8ml of 100% nitric acid and 8ml of acetic anhydride at 5°. Yield is 78%. Pentanitropiperidine is a brisant expl with a Q_c of 2056cal/g
Refs: 1) Beil, not found 2) M.B. Frankel, USP 2978452 (1961) & CA **55**, 17657 (1961); Ibid, Explosivst **1**, 243 (1964)

There are four piperidine expl addn compds extant, viz,

Piperidine-Chromic Acid.
$(C_5H_{11}N)[HCrO_5]$; mw 218.20; N 6.42%; OB to CO_2 –80.66%; cryst; mp, explds when heated; v sol in w.
Ref: Beil **20**, 12

N-Perchlorylpiperidine.



$NClO_3$; mw 167.6; N 8.40%; OB to CO_2 –114.56%; mp, explds *violently* on heating; RI 1.4646. Sol in w and eth. Prepn is by reacting an aq soln of piperidine (8.0g/250ml w) with perchloryl fluoride gas at RT. The gas is bubbled thru the soln for 20 mins at a rate of 170cc/min. The soln is then nitrogen purged for 10 mins, extrd with eth, dil HCl washed, and dried at RT under vac. Yield is 66%. The perchlorate is a *dangerously sensitive* mat. It explds on heating, exposure to sunlight or on contact with anhyd piperidine. It is desensitized by adsorption on powd alumina and

can be stored indefinitely at –80°
Ref: D.M. Gardner et al, JOC **29**, 3738–39 (1964) & CA **62**, 9099 (1966)

Piperidine Triazido Cuprate. $[Cu(N_3)_3](C_5H_{11}N)$; mw 274.81; N 50.98%; OB to CO_2 –90.25%; dark red-brn crysts; mp 178–80° (explds). Sol in w. Prepn is by dissolving Cu azide in piperidine. A brisant expl, but rather insensitive to shock, having an impact sensy of 100cm using a 2kg drop hammer
Refs: 1) Beil, not found 2) A. Cirulis & M. Straumanis, Ber **76B**, 825–30 (1943) & CA **38**, 1970–71 (1944)

Diperidino-Tetrazido Cuprate. See Vol **5**, D1490-L

Pipitz Propellant. Patented in 1899, consisting of grains prepd by coating a core of NC with collodion. An overcoat of paraffin was applied after solvent evapn
Ref: Daniel (1902), 633

Piquet and Pochez Explosives. Expls prod in a patented procedure by nitration of manure
Ref: Daniel (1902), 633

Pirodialiti. See Pyrodialites in Vol **6**, E366-R to E367-R

Pirokollodion (Pyrocollodion). A single-base proplnt contg NC of 12.45% N invented by D.I. Mendeléev in 1891. This proplnt served as a prototype for the Pyrocellulose single-base proplnt introduced in the US in 1895 by Bernadou and adopted by the Navy. Pyrocellulose, or simply "Pyro" is based on NC of about 12.6% N. See "Collodion Cotton or Pyroxylin" and "Pyrocellulose, Pyro or Pyrocotton" in Vol **2**, C103-R to C106-L
Ref: J.B. Bernadou, "Smokeless Powder, Nitrocellulose, a Theory of the Cellulose Molecule", 1st Edn, J. Wiley & Sons, NY (1901)

Pironome. See "Pyronome (1881)" in Vol **2**, C206-L

Pirsch Propellant. Patented in 1897; prepd by mixing an acetonic soln of NC with 10–15% Dinitrobenzene, graining and evapg the solvent
Ref: Daniel (1902), 633

Pitite. An expl manufd in Engl in 1898 by the New Explosives Co, Ltd. It contained NG 25–27, K nitrate 30–35, Ba nitrate 30–35, woodflour (contg 5–15% moisture) 40–43, sulfated benz 0.5, Na carbonate 0.5, and Ca carbonate 0.5 parts
Ref: Daniel (1902), 634

Pitite No 2. A British "permitted" expl consisting of NG 24, woodmeal 34.5, K nitrate 29.5, amm oxalate 8, and w 3.5%
Refs: 1) Daniel (1902), 633 2) Barnett (1919), 135

Pittius Explosives. C. vanPittius of Holland obtd a BritP in 1910 on expls consisting of combustible mats and oxidizers. The combustible constituent is prepd by mixing resin (10p) and stearin (5p) together at 150°, and incorporating paraffin (10p) and a blend consisting of TNT (25p) and NG (5p) or NC (3p). Molten TNT (50p) is then added and blended while maint the mixt at 85°. The reddish-brnmixt is termed "TNT paste". To use this expl the TNT paste is mixed with oxidizers, viz,
a) TNT paste 20, K nitrate 30, amm perchlorate 30 and K perchlorate 20%; b) TNT paste 8 and amm nitrate 92%
Ref: Colver (1918), 679–80

"Plancastita". Expls having a greater energy, velocity of deton and brisance compared to that of Dynamites; viz,
a) TNT 10 and liq nitrogen peroxide 12p;
b) MNT 30.3 and liq nitrogen peroxide 69.7%.
These mixts are less dangerous to handle than "Panclastites" (qv)
Refs: 1) Sancho (1941), 213 2) Pérez Ara (1945), 229 3) M.Y. Manheimer, MAF **28**, 505–21 (1954) & CA **49**, 2733 (1955)

Plane Combustion Wave. See "Combustion Wave Propagation" in Vol **3**, C433-R
Ref: J.H. Burgoyne & F. Weinberg, "A Method of Analysis of a Plane Combustion Wave", **4th SympCombstn**, Williams & Wilkins, Baltimore (1953), 294–302

Plane Detonation Waves with Finite Reactions. See "Detonation Waves: Steady-state, One-Dimensional Reaction Waves with Finite Reaction Rate" in Vol **4**, D703-R to D704-R
Ref: S. Brinkley, Jr & J.M. Richardson, **4th SympCombstn**, Williams & Wilkins, Baltimore (1952), 450–57 & CA **49**, 6608 (1955)

Plant Layout, Location, Design and Construction. For information on the special techniques required in the loading and fabrication of expls pertinent to ammo plant layout and design, see the entry under that title in Vol **7**, L46-L to L57-L. For what has been done to accomplish modernization of munitions plants now extant, see "Modernization Engineering Project for US Army Ammunition Plants" in this Vol, M147-L to M148-R. The problem of pollution created by ammo plants is examined in an article under this topic in this Vol

The following ref is of general interest to this topic: Kirk & Othmer, 2nd Ed, **15** (1968), 689–99: M.M. Goetz, "Plant Layout", 700–20: L.V. Kaltenecker, "Plant Location"

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Plasma; Its Definition, Generation and Ordnance Applications. The term *plasma* is defined by Funk & Wagnall (Ref 44a) as ". . . any gas composed of . . . equal numbers of positive ions and electrons . . .". This definition has been expanded enormously in terms of concept, theory

and mathematical presentation, as can be seen by the extensive list of refs on these subjects; viz, refs 2 thru 16, 26 thru 28, 30, 33, 34, 36 thru 39, 42, 45, 46 & 48

Plasma can be *generated* in many ways; viz, by detonation (see "Detonation Plasma" in Vol **4**, D258-L to D264-L, D348 & D471-R to D474-R); by controlled nuclear fusion, the abundant energy source of the future (Refs 3, 9 & 12); by uncontrolled nuclear fission and fusion as in atomic and fusion explns (see "Atomic (or Nuclear) Bomb" and "Atomic (or Nuclear) Energy; Atomic (or Nuclear) Reactions; Atomic (or Nuclear) Explosions" in Vol **1**, A499-L to A504-L); by the combustion of a proplnt, liq or solid, as in a gun, internal combustion motor or rocket engine (see under the appropriate titles in the Encycl); or by the combustion of any fuel leading to an ionized gaseous state

The ordnance applications of plasma are numerous; including not only the above referenced means of generation for constructive purposes, destructive purposes, motive power, etc; but, also for such purposes as studying the effect of expl detonation on plasmas and vise versa (Refs 17, 18, 35, 44, A Q and W*); the use of plasma jets as research, manufg and testing tools (Refs 2, I, L, P & S); the use of plasmas as light sources (Ref R); studying the effect of interstellar plasma on RF signals (Refs O and V); studying the energy source plasma obtained using nuclear fuel (Ref X); studying the parameters of plasma physics (Refs 19, B, C, E, G, J and K); plasma pulse power electricity generation (Ref F); the measurement of plasma flow (Ref 20); the use of plasmas for rocket propulsion (Refs 22, 23, 25, 40, 47, T and V); the generation of electricity from plasma using pyrots (Ref D); the simulation of rocket plumes using pyrot generated plasma (Ref M); the study of shock generated plasma on re-entry vehicles (Refs 41 and H); and the study of techniques such as spectroscopy to measure parameters such as plasma temp (Refs 29, 32 and N)

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Technical Report 2595, March 1959", PLASTEC Note **22** (1970) 33) N.E. Beach & V.K. Canfield, "Compatibility of Explosives with Polymers (III), An Addendum to Picatinny Arsenal Technical Report 2595 and PLASTEC Rept 33", PLASTEC Rept **40** (1971) 34) A.F. Readdy, "Applications of Ionizing Radiations in Plastics and Polymer Technology", PLASTEC Rept **41** (1971) 35) J.B. Titus, "Solid-Phase Forming (Cold Forming) of Plastics", PLASTEC Rept **R42** (1972) 36) A.F. Readdy, "Plastics Fabrication by Ultraviolet, Infrared, Induction, Dielectric and Microwave Radiation Methods", PLASTEC Rept **R43** (1972) 37) E.C. Schramm & D.W. Levi, "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers, IV", PLASTEC Note **N23** (1972) 38) A.H. Landrock, "Ecological Disposal of Plastics with Emphasis on Foam-in-Place Polyurethane Foam", PLASTEC Rept **R37A** (1973) 39) J.B. Titus, "Environmentally Degradable Plastics, A Review", PLASTEC Note **N24** (1973) 40) J.A. Maciejczyk, "Low Energy Impact Strength of Graphite/Epoxy Composites: An Initial Exploration", PLASTEC Note **N25** (1973) 41) N.E. Beach, "Government Specifications and Standards for Plastics. Covering Defense Engineering Materials and Applications (Revised, Final)", PLASTEC Note **6C** (1973) 42) J.B. Titus, "Reverse Osmosis Bibliography: Abstracted and Indexed", PLASTEC Rept **R45** (1973) 43) Anon, "Plastics for Aerospace Vehicles–Part I. Reinforced Plastics", **MIL-Hndbk 17A** (1973) 44) R. Winans, A.M. Shibley & J.R. Hall, "Weldbonding in the United States: An Annotated Bibliography and History", PLASTEC Note **N26** (1974) 45) J.B. Titus, "Trade Designations of Plastics and Related Materials (Revised)", PLASTEC Note **N9B** (1974) 46) R.J. Valles & J. Nardone, "Directory in Plastics–Knowledgeable Government Personnel (Revised)", PLASTEC Rept **R5D** (1975) 47) Anon, EngrDesHndbk, "Rotational Molding of Plastic Powders", **AMCP 706-312** (1975) 48) Anon, EngrDesHndbk, "Short Fiber Plastic Base Composites", **AMCP 706-313** (1975) 49) A.H. Landrock, "Specifications and Other Standardization Documents Involving Cellular Plastics (Plastic Foams), Cushioning and Related Materials", PLASTEC Note **N30** (1976) 50) J. Nardone, "Computerized Material Property Data Information System", PLASTEC Note **N31** (1976) 51) A. Csete & D.W. Levi, "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers, V", PLASTEC Note **N29**, Parts 1 & 2 (1976)

Plaster Shooting. See *mudcapping* or *Adobe shooting* under Agriculture and Forestry Uses of Explosives in Vol **1**, A113-R; also, under Mudcapping in Vol **8**, M160-R

Plastex Eversoft. A pre-WWII Brit Dynamite contg NG + Nitroglycol 25.5, collodion cotton 0.5, DNT+TNT 2.5, AN 35, woodmeal 2.5, and NaCl 34%. BalPend swing 2.45″ vs 3.27″ for Brit Standard Gelignite contg 60% NG
Ref: Marshall **3** (1932), 120

Plastic Bonded Explosives. See under PBX in this Vol

Plastics and Polymers, Compatibility with Explosives. See refs 10, 25, 32 & 33 under PLASTEC in this Vol

Plastics and Polymers, Military Applications. See refs 19 & 41 under PLASTEC in this Vol

Plastit. A WWII plastic expl contg RDX 64, collodion cotton 3.5, and liq or semi-liq nitrohydrocarbons 32.5% (Refs 1 & 2). Ref 3 states that it is a Swiss trade name for a plastic mil expl based on PETN, manufd by Schweiz, Sprengstoffe-Fabrik A-G
Refs: 1) All&EnExpls (1946), 127 2) PATR **2510** (1946), Ger 134-R 3) Private communication from Dr.A. Stettbacher (Dec 14, 1953)

Plastolit (Swiss). See Vol **3**, C444-L

Plastomenites. Proplnts, patented in Ger by Güttler in 1889–90, consisting of NC, Nitrolignine, Nitrosugar, Nitrostarch, etc, gelatinized by the addition of nitrated aromatic compds such as benz, toluene, phenol, naphthalene, etc. Inorganic nitrates, chlorates, chromates, picrates, etc, could be added to the mixt

One of the varieties of Plastomenites used in Ger as sporting powder was prepd by melting 5p of DNB on a w bath, and adding 1p of NC

In Engl, Plastomenites consisted of NC, DNB and Ba nitrate, and three varieties were known; JCP (for sporting use), BP (for carbines), and KMP (for mil use)

Their compn was modified by Güttler in 1897 by incorporating 0.5 to 10% of powdered rosin (colophany). According to Colver (Ref 2), some Plastomenites consisted of DNT 80 and Nitrolignine 20% (blended in a hot condition), and occasionally, some Ba nitrate. After the incorporation, the fused mass was granulated

Refs: 1) Daniel (1902), 634 2) Colver (1918), 169 3) Marshall **3**, 98 (1932)

Plastrit or Plastrotyl. Plastic expls patented in 1906 by C.E. Bichel. They were prepd by mixing 85–87p of TNT with liq and/or solid resins (such as copaiba, balsam, benzoin gum, styrax, turpentine, etc), and collodion cotton, with or without liq DNT

Refs: 1) Colver (1918), 249 2) PATR **2510** (1958), Ger 134–35

Plastrita (Span). A soft, doughy exptl plastic expl prepd by La Fabrica de Polvoras of Granada, Spain, by mixing pulverized TNT with collodion. It expl power was less than that of TNT

Refs: 1) Sancho (1941), 152 2) Pérez Ara (1945), 505 3) Vivas, Feigenspan & Ladreda **2** (1946), 380

Plate Denting Tests or Plate Tests. See Vol **1**, Introduction XIX to XX

Platinum. Pt; aw 195.09; silver-gray, lustrous, malleable and ductile metal; face-centered cubic structure; also prepd in the form of a black powder (Pt black) and as spongy masses (Pt sponge); mp 1773.5°; bp about 4530°; d 21.447g/cc

Pt is attacked by bromine trifluoride at 280° in the presence of K fluoride (Ref 5). Finely divided Pt and some other metals will cause a mixt of H_2 and O_2 to expld at ordinary temps (Ref 1). A little Pt black dropped into a hydrogen peroxide soln can cause an expln (Ref 2). Pt and molten Li react violently at 540° ± 20° (Ref 7), and an incandescent reaction occurs when it is warmed gently in gaseous oxygen difluoride (Ref 6). The decompn of 92% permonosulfuric acid is expl in the presence of smooth or finely divided Pt (Ref 3). The reacting mass formed by the mixt of P and Pt can become incandescent when heated (Ref 8). Dry, used Pt catalyst has expld while being screened (Ref 4)

Refs: 1) Mellor **1**, 325 & **16**, 146 (1946–47) 2) Ibid **1**, 936 3) Ibid **10**, 483 4) M. VanCampen, C&EN **32**, 4698 (1954) 5) Mellor **2**, Suppl **1**, 164 (1956) 6) Ibid, 192 7) Anon, C&EN **39** (5), 42 (1961) 8) Mellor **8**, Suppl **3**, 228 (1971)

Platinum Compounds. Several Pt compds, including trimethylplatinum derivatives are explosively unstable (Ref 9). Ammipentahydroxoplatinum, H_8NO_5Pt, explds fairly violently above 250°, as does the pyridine analogue (Ref 3). Ammonium Hexachloroplatinate(2-), $Cl_6H_8N_2Pt$, when boiled with alkali gives a product which, after drying, will expld violently on heating alone to 205° or with combustible materials (Ref 5). Ammonium Tetranitroplatinate(II), $H_8N_6O_8Pt$, decomps explosively on heating (Ref 1). *Cis*-Diamminedinitroplatinum(II), $H_6N_4O_4Pt$, decomps explosively at 200° (Ref 11). Hexamethyldiplatinum, $C_6H_{18}Pt_2$, explds sharply in a shower of sparks on heating (Ref 8). Platinum(IV) Oxide, PtO_2, when added as a catalyst to a hydrogenation reaction in acet ac caused an immediate expln (Ref 4). Both Platinic Bromide ($PtBr_4$) and Platinic Chloride ($PtCl_4$) are vigorously attacked by bromine trifluoride (Ref 10). Platinous Hypophosphite, $Pt(PH_2O_2)_2$, liberates spontaneously flammable phosphine above 130°

(Ref 6). Platinumammine nitrates and perchlorates may be impact sensitive. $Pt(NH_3)_2NO_3$ and $Pt(NH_3)_4(OH)_2(NO_3)_2$ detonate when heated (Ref 7). Potassium Dinitrooxalatoplatinate(2-), $C_2K_2N_2O_8Pt$, decomps violently at 240° (Ref 2). Tetramethylplatinum, $C_4H_{12}Pt$, explds weakly on heating (Ref 8), while Trimethylplatinum Hydroxide, $C_3H_{10}OPt$, detonates (Ref 12)

Refs: 1) L.F. Nilson, JPraktChem **16** (2), 249 (1877) 2) M. Vèzes, CR **125**, 525 (1897) 3) I. Jacobsen, CR **149**, 575 (1909) 4) R. Adams et al, OrgSynth, Coll Vol **1**, 66 (1941) 5) Mellor **16**, 336 (1942) 6) Ibid **8**, 890 (1946–47) 7) Ibid **16**, 412 (1946–47) 8) H. Gilman et al, JACS **75**, 2065 (1953) 9) F.A. Cotton, ChemRev **55**, 577 (1955) 10) Mellor **2**, Suppl **1**, 165 (1956) 11) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol **2**, 1560, Academic Press, London (1965) 12) M.N. Hoechstetter et al, InorgChem **8**, 400 (1969)

Pleopentaerythritol. A mixt of polypentaerythritols consisting of di- and tri-pentaerythritols with some tetra- and other compds, which remain after the separation of PE from mother liquor in the prepn of PE by the condensation of formaldehyde and acetaldehyde in the presence of alkali

Pleopentaerythritol can be nitrated, and the resulting mixt is an expl which can be utilized in the prepn of commercial expls. Nitropleopentaerythritol is not as powerful as PETN or DPEHN

Refs: 1) H. Burrell, IEC **37**, 86 (1945) 2) H. Burrell & P.I. Bowman, USP 2390202 (1945) & CA **40**, 1049 (1946) 3) S.F. Marrian, ChemRevs **42**, 198 (1948)

Plessit. A Ger blasting expl introduced during WWI contg K chlorate with not more than 9.5% kerosene and 0.5% albumen. One variety, Wetter-Plessit III, used in coal mines, contained NaCl as well

Ref: Marshall, Dict (1920), 76

Plodex Explosives. Patented in 1898; contained as a base products prepd by the nitration of potato and beet-root wastes.

Ref: Daniel (1902), 635

Plomoplastrita (Span). An expl obtained by mixing Plastrita (qv) with Pb nitrate. It is as powerful as TNT, possesses a higher d, is less sensitive to mechanical action, and does not evolve poisonous gases on expln

Ref: Sancho (1941), 153

Plosophore or Explosophore. See under Auxoexplose or Auxoplosophore in Vol **1**, A513-R to A514-R

Plugs, Closing (Closing Plugs). These are threaded cylindrical blocks made of steel, Al or plastic material, and are provided with a head to fit a wrench. The plugs are intended to close the fuze hole of those fixed or semi-fixed shells which are shipped or stored unfuzed, although loaded with HE. Plugging of the fuze hole is necessary in order to prevent the entrance of foreign material as well as to protect the treaded portion of the hole from damage during handling of the shell

In so-called *deep-cavity shells,* a short length of cardboard tubing, called a *spacer,* is provided and placed between the supplementary charge and the closing plug in order to keep the former from movement

Ref: Anon, OrdTechTerm (1962), 227-L

Plumbatols. Buff colored expls consisting of Pb nitrate 60 or 70 and TNT 40 or 30%, which were used exptly during WWII. They could be cast loaded, and not being hygroscopic, could be stored dry. They were manufd by simple mechanical mixing of Pb nitrate in molten TNT

The 70/30 variety had the following properties: OB to CO_2 −5.4%; OB to CO +9.3%; 5 sec expln temp, 238°; impact sensitivity, 13″ vs 14″ for TNT (using PicArsn app with a 2kg wt); brisance by 200g bomb sand test, 32.4g vs 48.0g for TNT; deton velocity at d 2.89g/cc, 4850m/sec; sensitivity to initiation,

min deton charge in g, Pb Azide 0.20g, Tetryl 0.10g. Its shaped charge effectiveness, using a glass cone, was: hole depth, 103% of TNT; hole volume, 114% TNT

Note: In 1891, a Belg engineer, J. deMacar, proposed an expl mixt of PA and Pb nitrate, but it was too sensitive. Later, the same investigator proposed replacing the PA with TNT, and the new expl became known as **Macarite** (see in this Vol, M1-L to M1-R). Another expl contg Pb nitrate and TNT was developed in 1906 by J. Rudeloff, and was called **Triplastite** (qv)

Refs: 1) Colver (1918), 247 2) Anon, All&EnExpls (1946) 3) Anon, EngrDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 296–97

PLX. A liq expl developed at PicArsn (**P**icatinny **L**iquid **Ex**plosive) during WWII for use in minefield clearing devices, to be loaded by pumping. It consisted of Nitromethane 95 and ethylenediamine 5%, which were stored and transported separately, and mixed just prior to use

PLX is a light yel liq; OB to CO_2 –48.0% (vs –39.3% for straight Nitromethane); OB to CO –21.0% (vs –13.1% for straight Nitromethane); d 1.12g/cc at 20°. Its expl props, as detd at PicArsn, were as follows:

Ballistic Mortar. 134% TNT

Brisance (by Sand Test). 50.6g crushed vs 8.1g for straight Nitromethane and 48.0 for TNT

Explosion Temperature (5 sec). 430°

Friction Sensitivity. With BuMines Friction Pend app, unaffected

Impact Sensitivity. 100+cm with BuMines app using a 2kg wt; 20" with PicArsn app using a 2kg wt

Rifle Bullet Sensitivity. Unaffected from the action of .30 cal bullets fired from a distance of 90 ft

Trauzl Test. 127% of PA

Velocity of Detonation. 6165m/sec as detd in a glass tube 15/16" diam and 1/32" wall thickness; vs 6210m/sec for straight Nitromethane

PLX corroded brass, but did not affect stainless steel, mild steel, or duriron

Ref: Anon, EngrDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 298

PNL. See under D-1in Vol **3**, D1-L

Pohl's Powder (Polvora blanca de Pohl). A Span expl resembling Augendre Powder (see Vol **1**, A507-L) in compn. It contained K chlorate 49, K ferrocyanide 28, and sugar 23%

Ref: Pérez Ara (1945), 23

Pobedity. See under Coal Mining Explosives, Russian Permissible Explosives, in Vol **3**, C454-R

Poisoning by Explosives. See under Toxicity

P.O.L. Ger acronym for Pulverohne Lösung, which means Solventless Powder

Polar Ajax. A Brit Permitted Expl contg NG (+ Nitroglycol) 25.5–27.5, NC 0.25–1.25, AN 39.0–42.0, Na chloride 23.0–25.0, carbonaceous material 2.5–4.5, china clay 2.0–3.0, and other ingredients 1.0–2.5%. D 1.55g/cc; power (% Brit Gelignite, as detd by BalMort) 56. It is a plastic expl, and has been used in drifting, ripping and blasting hard coal. See also Vol **3**, C452 & C453

Ref: J. Taylor, "Detonation in Condensed Explosives", Clarendon Press, Oxford (1952), 20

Polar Dynabel No 2. A Brit Permitted Expl contg NG (+ Nitroglycol) 13.0–15.0, NC 0.25–0.75, AN 60.0–63.0, Na chloride 15.0–17.0, carbonaceous material 3.5–5.5, china clay 0.1–1.1, and other ingredients 0.5–2.0%. D 1.12g/cc; power (% Brit Gelignite, as detd by BalMort) 62. It is a cohesive powder, and has been used in drifting, ripping and blasting hard coal

Cartridges of this expl are usually sheathed in the following manner: each waxed cartridge of Polar Dynabel No 2 is placed in a larger paper cylinder, and the annulus between the cartridge and the outer cylinder is filled with a sheathing compd contg a dry, finely divided mixt of 1 p Na bicarbonate and 0.33–2.0p of a material composed of 61% commercial Al oxide and 39% chalk, both ground to pass 150 mesh

(Brit Standard Sieve). See also Vol **3**, C452 & C453
Refs: 1) J. Taylor & A.H. Phillips, USP 2513531 (1950) & CA **44**, 9150 (1950) 2) J. Taylor, "Detonation in Condensed Explosives", Clarendon Press, Oxford (1952), 20

Polarite. A Brit expl introduced prior to WWI as a substitute for Gelignite. It consisted of non-freezing Gelignite contg TNT, in which K perchlorate replaced K nitrate
Refs: 1) Marshall **1** (1917), 384 2) Barnett (1919), 111

Polar Thames Powder. A Brit Permitted Expl contg NG (+ Nitroglycol) 9.0–11.0, AN 59.5–62.5, Na chloride 18.0–20.0, carbonaceous material 7.5–9.5, china clay 0.1–1.1, and other ingredients 0.1–1.1%. D 0.98g/cc; power (% Brit Gelignite, as detd by BalMort) 56. It is a granular material and has been used in moderately hard ripping and blasting operations of hard coal. See also Vol **3**, C452 & C453
Ref: J. Taylor, "Detonation in Condensed Explosives", Clarendon Press, Oxford (1952), 20

Polar Viking. A Brit Permitted Expl contg NG (+ Nitroglycol) 9.0–11.0, AN 68.5–71.5, Na chloride 9.0–11.0, carbonaceous material 7.5–9.5, and china clay 0.1–1.1%. D 0.98g/cc; power (% Brit Gelignite, as detd by BalMort) 66. It is a granular material and has been used in moderately hard ripping and blasting of hard coal. See also Vol **3**, C452 & C453
Ref: J. Taylor, "Detonation in Condensed Explosives", Clarendon Press, Oxford (1952), 20

Polaris Missiles. US nuclear delivery system (UGM-27 series). A solid proplnt two-stage missile developed by Lockheed for the US Navy, designed to be fired from a submerged submarine, and first fired in 1958. Forty-one nuclear-powered submarines are currently in service (Ref 1), each carrying 16 ballistic missiles of the Polaris series. The initial Polaris **A1** (UGM-27A), which became operational in 1960, has been phased out. The **A2** (UGM-27B) equips about 10 submarines, while the remainder have the improved **A3** (UGM-27C). A comparison of specifications for the latest 2 versions are shown in Table 1
The new *Poseidon* (qv) missile with MIRV multiple warheads will eventually equip 31 of the 41 submarines
Refs: 1) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 153-R
2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 352

Polis Explosive. A mixt contg Nitrotoluene and Pb nitrate as basic ingredients, which could be expld by heating
Refs: 1) Daniel (1902), 635 2) Gody (1907), 576

Pollard Explosive. A mixt of S, paraffin, and either a nitrate or chlorate
Ref: Daniel (1902), 635

Pollard's Test for Stability of Propellants. This test, proposed in 1924–25, is based upon the action of nitric peroxide on colloidal Ag oxide
Procedure. A current of air is passed over a sample of proplnt in storage into a colloidal soln of Ag oxide. If free nitrogen peroxide is present, it reacts with the colloid and decreases the amt of light diffused by it. The larger the decrease, the higher the amt of NO_2 present, and the more decompd is the proplnt
Ref: Reilly (1938), 80

Table 1
Polaris Missile Specifications

	Length	Diameter	Weight	Range (miles)	Speed	Warhead (megatons)
UGM-27B (A2)	31′	4′6″	30,000 lbs	1700	Mach 10	0.7
UGM-27C (A3)	31′	4′6″	30,000 lbs	2875	Mach 10+	0.7

POLLUTION ABATEMENT IN THE US MILITARY EXPLOSIVES AND PROPELLANTS MANUFACTURING INDUSTRY

Virtually all of the HEs and most of the proplnts for all three Services are manufd in a network of Army Ammo Plants (AAPs) scattered mainly over the eastern and southern portions of the country. They are loaded in other facilities of the same AAPs, in other AAPs which do not themselves manuf chemicals, and in a series of Naval Ammo facilities (NADs). Two Navy facilities manuf some supplementary ingredients, notably NG and casting powder; but mostly they load expls obtained from the AAPs

The map in Fig 1 shows the distribution of the AAPs and NADs which do the bulk of the high expl and proplnt manufg and loading. There are approx as many more which deal in small arms or metal parts or serve as storage depots, but they are outside the scope of this article. There are also several AAPs which load warheads but do not manuf the fills; they are not discussed in any detail in this article because their relatively minor wastewater problems are well typified by those facilities which are discussed

Major Steps in the Manufacture of Munitions. The manuf of end item munitions can be divided into four major steps: a) manufacture or purchase of ingredients such as NC, NG, TNT, HMX, binders, etc; b) combination of ingredients into blends, grains or formulations, such as cannon powder, Comp B, extruded double-base proplnt grains, etc; c) loading of warheads, bombs, rocket motors, etc, with the blends or formulations; and d) final assembly and pack-out of complete munitions, including metal parts

Manufacture of Ingredients. The manuf of chem expls and proplnts such as TNT or NC is completely similar to any other chem manufg operation; and the plants are much like any other chem plant except that they tend to be more isolated from their neighbors, more spread out within their own fences, and rather less modern than average. They are isolated and spread out for safety, since their products are hazardous materials; and they are less modern than most chem plants because they tend to be rather old. That last factor is changing rapidly at this writing. A massive modernization program is underway, spurred by the need to reduce air and w pollution but also taking full advantage of opportunities to improve production rates and efficiency by the installation of new and modern equipment

A typical chem manufg operation is the production of trinitrotoluene – TNT, the dominant mil expl. It involves the manuf of huge quantities of nitric and sulfuric acids, from sulfur and ammonia, in chem plants exactly similar to those which make nitric and sulfuric acids in the civilian economy. Mixed nitric and sulfuric acid is then combined with liq toluene in a series of reaction kettles to produce mononitrotoluene, dinitrotoluene, and finally trinitrotoluene which is a solid. The trinitrotoluene is separated from the mother liquor, washed with w, and then treated with a sulfite soln called "Sellite" which extracts undesirable isomers and impurities, leaving purified α-TNT. The TNT is washed, solidified, flaked, and finally shipped out in boxes

The operation is a thoroughly typical chem manufg operation not unlike those found in the plastics, petroleum, food, paint or solvents industries. It involves pumping of liqs, stirring of slurries, heating and cooling of streams, filtra-f tions, evaporations, dryings, bagging and boxing, and all the other usual chem manufg operations. It also involves wastewater streams containing unreacted material and by-products, waste acids, decompn products and extracted impurities, and exhausted reagents. These wastewater streams, if untreated, constitute major pollution problems

The manuf of NC is similar in that it involves the same nitrating acids as used for TNT, but used to treat cotton linters or wood pulp (raw cellulose) in a series of vats and reactors similar to the ones used for TNT. The crude NC is similarly subjected to a series of w and aq soln washes until it is finally delivered as a purified, fibrous mat – ordinarily wet with w or alc for safety. Again, there are major wastewater streams laden with spent reagents and extracted impurities

Tetryl, HMX, RDX, NG, and a whole host of minor ingredients are all made similarly – in typical chem process plants with typical equip-

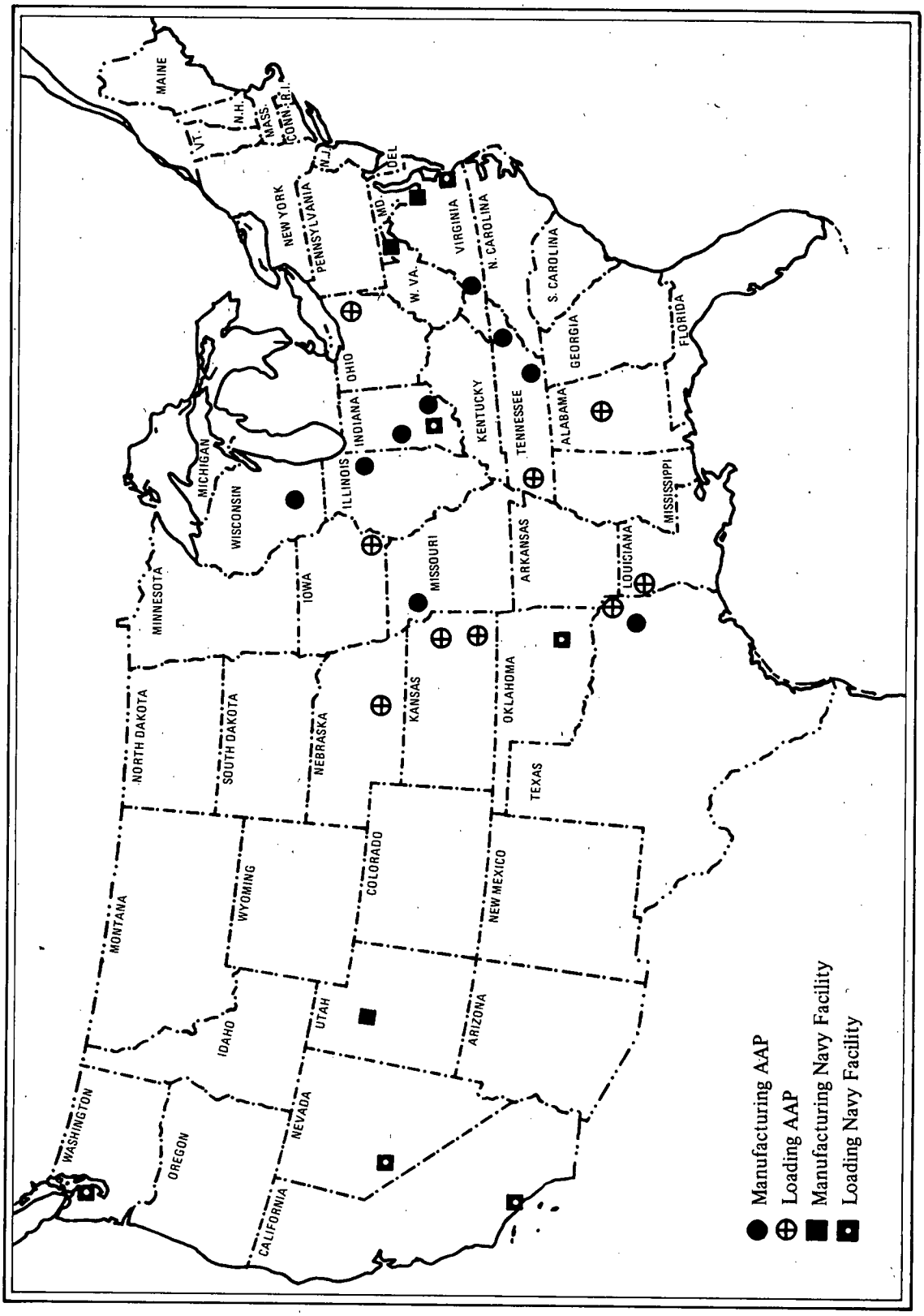


Fig 1 Major Explosives and Propellant Facilities in the USA

ment and controls and typical wastewater streams

Production of Grains or Blends. Most expls and all proplnts are blends of ingredients rather than single substances. Comp B, for example, is an intimate mixt of 60% RDX and 40% TNT, with a little wax added for stability. It is normally made in the RDX plant by blending in TNT and wax right on the production line without ever storing the RDX. There are four different Cyclotols, which are blends of RDX/TNT without wax: 75/25, 70/30, 65/35, and 60/40; and there are two Octols, blends of HMX/TNT: 70/30 and 75/25. They are also made on the RDX/HMX line. There are dozens of other formulations incorporating other ingredients such as Tetryl, Al powder, PETN, etc. Most of them are made in the chem manufg plant and shipped to the loading plant as flakes or chunks, but some of them can also be made up in the melt-mix kettles in the loading plant

NC and NG are rarely used singly, but are usually incorporated into double-base or multi-base proplnts which may have up to a dozen other ingredients including metal powders, oxidizers and various stabilizers and burning rate catalysts. The proplnts are processed into shapes which range from pinhead size pellets to cylinders two or three feet in diameter and six feet or so long. The pellets may be used as-is as gun proplnts, or they may be incorporated into still more complex formulations in the casting of large rocket motors, The larger cylinders are usually complete rocket motor grains themselves, ready to be inserted into finished rocket motor hardware

A small but important class of formulations comprises the Composite Solid Rocket Propellants. Composites typically contain a major amount of an oxidizer such as AP or HMX, a metal powder such as Al, a binder which is one or another type of rubber (or double-base), and up to a dozen trace ingredients such as catalysts, stabilizers, etc. There are literally hundreds of formulations, all to a degree similar; and the choice comes down to specific missions, economics, and special requirements

Loading of End Items. The blends and formulations described above may be loaded into their hardware in the plant where they are made, or they may be shipped to another plant for Load/Assemble/Pack (LAP). There are a number of AAPs which are solely LAP plants, and four of the six Navy plants engage only in LAP

Most current expl fills are blends of TNT with other ingredients, and are melt-cast loaded into bombs and warheads. Typically, several thousand pounds of the flaked blend are charged to a stirred melt kettle and heated to just above the melting point of TNT. It forms a mobile slurry when molten, and is poured into the empty bomb or shell cases, where it solidifies. Additional ingredients such as Al may be added in the melt kettle, depending on the particular formulation being poured and the particular munition product

Small rocket motors are usually, but not always, loaded with pre-shaped double-base grains which are simply slipped into the motor case like a battery into a flashlight. Large motors are usually, but not always, loaded with a cast-in-place, composite grain which is mixed in special kettles and poured into the motor case to harden. An alternate loading method is to fill the motor case with tiny, loose, double-base pellets and then infuse the bed with a Casting Solvent consisting of NG and/or similar other energetic solvents for double-base. The solvent semi-dissolves the pellets and blends the whole into a tough, rubbery mass of adequate mechanical strength. Both the pellets and the casting solvent can, of course, have numerous other, minor ingredients. There are enough exceptions and overlapping cases to disprove any manufg classification; for example, pre-formed, slip-in grains are also used for certain rocket motors up to a couple of feet in diameter, which is quite large by most standards

There is also an as-yet small but growing class of formulations known as "PBX", Plastic Bonded Explosive. PBXs are similar to rubber-base, composite rocket proplnts in that they consist of 85% or so of powdered high-energy explosive incorporated into a "plastic" matrix (which can be a conventional plastic or a double-base) and cast into place.

Final Assembly and Pack-Out. The loaded warheads, rocket motors, etc, are finally assembled with their cases, electronics, etc, into finished munitions. This "dry" assembly involves no wastewater effluents

Wastewater Streams – Sources and Types. The greatest number of AAP w pollutants (or potential pollutants) are similar to those from any chem manufg operation, eg, acid drippings, solvent spills, rust, stack scrubber drainings, floor washdown, and the like; but an important few are military-unique, eg, "Red Water" from TNT purification and w solns of various expls themselves. They are discussed briefly here under four headings,

(1) *Acid Manufacture.* Relatively small; mostly leakage plus drainings from air pollution abatement scrubbers. Also included are: a) acid waters, neutralized with lime or soda ash; b) sometimes azeotroping agents such as n-propyl acetate; c) sometimes heavy metals from equipment corrosion; and d) nitrobodies from acid recovery

(2) *Basic Explosives Manufacture.* The major quantities and the toughest problems are here. They include: a) acid waters, treated with lime or soda ash, chemical washes, spills, washdowns; b) "Red Water" from TNT purification. A complex, brick-red soln of Na nitrate, Na sulfate, Na sulfite, Na nitrite, and about 17% organics which include sulfonated nitrotoluene isomers and complex, unidentified dye-bodies; c) dissolved expls, eg, "Pink Water" which is approx 100ppm TNT in w; d) suspended expl particles – dust and chips; and e) sometimes solvents such as acet, benz, and dimethyl aniline

(3) *Compounding of Explosives and Propellants.* Small. Generally similar to streams from manufg, except that the chem purification wastes are absent. They include: a) dust and chips; b) dissolved expls, generally a few to 100ppm; c) solvents; d) organic materials such as collagen; and e) AN or AP

(4) *Load/Assemble/Pack Operations (LAP).* Small. Mostly floor washdowns and generally similar to Pink Water. They include: a) dissolved expls; b) dust and chips; and c) heavy metals from paints and corrosion and metal cleaning. The washout of reject munitions at some LAP plants can contribute substantial additional effluents when washout operations are running

Table 1 summarizes – and oversimplifies for clarity and emphasis – the most characteristic wastewater problems of each of the products or operations highlighted in Table 2. Every operation has some aspects of every problem, but these are the outstanding ones. The major problems are the large volume, high concn, chem wastes from the manufg operations; the streams from acid manuf and loading operations are much smaller and much simpler. The most noticeable waste streams are the Red Water and Pink Water from TNT manuf and loading, respectively

Pink Water is simply a soln of TNT in w. α-TNT is sol in w to the extent of approx 100 ppm at ambient conditions, the exact value depending strongly upon temp and the presence or absence of other solutes. Freshly-made-solns of TNT in w are virtually colorless; but exposure to ultraviolet light, including sunlight, causes the formation of highly-colored, complex, incompletely identified substances similar to dyes. They impart a characteristic pink color which persists even after dilution down to a few ppm with clean w. The release of Pink Water to receiving streams is thus objectionable. Pink Water is ubiquitous where TNT is made or handled, because of the need to wash down equipment and working areas from time to time. The largest volumes and the highest concns are found in plants which manuf TNT or unload it from obsolete warheads, but it is also the major component in the (relatively small) wastewater streams from loading plants. There are a number of technically feasible approaches to removing dissolved TNT and the derived dyebodies from wastewaters, and one or another is planned for each installation with the problem

Red Water – which can be almost black at times – also contains dissolved TNT; however, it is not an incidental stream like Pink Water; it is a major by-product stream from TNT manuf. The mixed-acid nitration of toluene yields not only 2,4,6-trinitrotoluene, the desired product, but also a host of other isomers and by-products amounting to approx 4.5% of the total yield; and it is necessary to remove them from the product. They are removed by extraction with a Na sulfite–Na carbonate soln which sulfonates and dissolves them; the extract is called Red Water. Red Water is a very complex and somewhat variable mixt containing 15% or so of sulfonated or sellited nitrobodies and a number of inorganic salts. Typical components are: w, Na_2SO_3–$NaSO_4$, $NaNO_2$–$NaNO_3$, sulfonated or

Table 1
Major Wastewater Problems

Wastes	Manufacture of Chemicals										Loading		
	Trinitrotoluene & DNT	Tetryl	Primer materials	RDX/HMX	Nitrocellulose	Nitroglycerin	NC-based propellants	Ball Powder	Black Powder	Acid manufacture	Filling of warheads	Mfg of extruded rocket grains	Mfg of cast rocket grains
Acid waters, nitrate & sulfate salts, etc.	+	+		+	+	+				+			
Red Water	+												
Pink Water	+										+		
Other dissolved explosives and/or dust and chips	+	+	+	+	+	+	+	+	+		+	+	+
Organic solvents and resins		+		+			+	+					+
Chromium and other metals from corrosion										+	+		
Perchlorate and other oxidizers													+

sellited nitro compds, solids, and ash. Red Water is not released into receiving waters. Some of it is sold to paper manufacturers who can use it as a process feedstream, and the rest is evaporated to dryness and the residue incinerated. Extensive research and development is in progress on better processes, and eventually its components will probably all be reclaimed for recycle

The above discussion has purposely been presented from a chem viewpoint in order to give a feel for the origin and nature of the wastewater streams. It has been usual to describe them in the conventional terms of BOD, pH, suspended solids, etc, and most of the surveys and permits are couched in these terms, although specific, military-unique parameters would be preferable

Table 2
The US Military Explosives and Propellants Industry

	Activity				Product Capabilities																		Dry Assembly	Ingredients Used in Formulations														
	MFRE*			LAP**	Acids						Explosives							Propellants																					
	Acid	Expls	Proplnts	Expls	Proplnts	Acet Anhyd	Glac Acet Ac	Conc HNO_3	Weak HNO_3	Conc H_2SO_4	Oleum	DNT	TNT	NG	Tetryl	RDX	HMX	NGu	Primers	NC	Single Base	Multi-Base	Solventless	Composite		Al	AP	$CaCl_2$	DNT	HMX	NC	NG	NGu	NH_4NO_3	Amm Picrate	Polybutadiene	Polyurethane	RDX	Solvents	TNT	Wax	$NaNO_3$
Army Ammunition Plants																																							
Badger	+	+	+					+	+	+	+			+						+	+	+	+					+											
Cornhusker				+																																			
Holston	+	+				+	+	+	+								+	+										+				+			+		+	+	
Iowa				+															+						+			+							+		+	+	
Indiana	+		+					+	+	+										+	+																		
Joliet	+	+		+				+	+	+	+	+	+		+				+						+											+				
Kansas				+																					+											+		+		
Louisiana				+																																+		+	+	
Lake City		+		+															+																				
Longhorn					+																				+	+								+						+
Lone Star				+																					+											+		+		
Milan				+																					+											+		+		
Newport	+	+						+	+	+			+																										
Radford	+	+	+					+	+	+	+		+	+						+	+	+	+	+						+									
Redstone					+																			+	+								+			+				
Sunflower								+	+	+										+	+	+	+																
Volunteer	+	+						+	+	+	+		+																										
Navy Ammunition Plants																																							
NAD Crane				+																					+				+				+	+		+		+	+	+
NAD Hawthorne				+																					+											+		+	+	
NOS Indianhead		+	+		+									+								+	+		+	+							+	+	+	+	+		
NAD McAlester				+																					+											+		+	+	
NIROP Magna		+		+	+									+											+	+								+						
NWS Yorktown				+																					+		+									+		+	+	
Air Force Ammunition Plants																								+																
Plant 44																								+																
Plant 77																																								
Plant 78					+																				+	+			+	+	+									+

* Manufacture
** Load/Assemble/Pack

Munition Plant Modernization Program. Both the US Army and the Navy have extensive plant modernization and pollution abatement programs planned and underway, and the wastewater picture is changing rapidly. So rapidly, in fact, that field data are out of date by the time they can be put into a report. Perhaps the best way to present the story is to force-fit all information into one of three time eras:

Before Modernization. Manufg processes from the early 40's to the late 60's. In general, this meant little or no pollution awareness or abatement, with things like Red Water being discharged directly into rivers; and effluent characterization was essentially a description of the raw process discharges

Transition Period. The past few years, today, and the next few years, while new treatment processes are being developed and installed. Presentday plants exhibit a mixed picture of modern abatement facilities alongside antique process units, and effluent streams range from

raw discharge to zero discharge. New construction is everywhere, and even more construction is in the planning stage. Research and development is in progress on even better abatement processes. Consequently, even current wastewater data have only the most limited significance except as trend indicators

After Modernization. That day in the future (1980's) when all the planned installations are complete and on stream. There will still be a few problem areas then, but by and large, the military munitions plants are planned to be models of clean outfalls. Those effluent data will be the first to be truly indicative of state-of-the-art or best-available

Note: This article is abstracted from a comprehensive state-of-the-art study of the military expls and proplnts production industry and its w pollution abatement problems and programs, carried out by an ad hoc committee of the American Defense Preparedness Association for the Environmental Protection Agency. A comprehensive report authored by Col. Norman I. Shapira (USA, Ret), Drs James Patterson and John Brown, and Messrs William Duckert and Jack Polson is available from the National Technical Information Service, Springfield, Virginia 22161, in two volumes: EPA-600/2-76-213a and EPA-600/2-76-213c. (EPA-600/2-76-213b is a third volume which has not been published)

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The Inorganic Chemicals Industry: Commercial Explosives", US EPA Rept **EPA-600/2-74-009b** (1975)

Pólvoras Negras (Span for BlkPdrs). Fairly detailed description of Span method of manuf is given by Sancho (Ref, p 264). The sources of the charcoal used were stems of hemp (tallos de cáñamo), of flax (lino), of oleander (adelpha), of yew-tree (tejo), etc. Following, in Table 1, are given typical compns of some Span BlkPdrs

Table 1
Composition of Typical Spanish Black Powders

	Potassium Nitrate	Sulfur	Charcoal
Powder of the Fábrica de Murcia	80.0	15.0	5.0
Infantry powder	75.0	12.5	12.5
Artillery powder (fine grains)	78.0	10.0	12.0
Artillery powder (6 to 10mm grains)	74.0	10.0	16.0
Prismatic powder (with 1 or 7 perforations)	74.0	10.0	16.0
Prismatic powder (brown)	80.0	3.0	17.0

See also under Black Powder or Gunpowder in Vol **2**, B165-R ff
Ref: Sancho (1941), 253–85

Pólvora Progressiva de Fusil Tipo "G". A Span proplnt contg NC 97.75, DPhA 0.75, Na oxalate 1 (the latter two serving as stabilizers), graphite 0.1 (surface), and volatile matter 0.4%. Its manuf and properties are described in the Ref
Ref: Vivas, Feigenspan & Ladreda **3** (1948), 225–393

Polyacetylenes (or Polyynes). See under "Acetylenic Condensation and Polymerization Products" in Vol **1**, A62-L to A63-L. Selected polyacetylene expl compds as an adjunct to this article are presented below, as well as addnl refs
Addnl Refs: 1) A.L. Henne & K.W. Greenlee, "Preparation and Physical Constants of Acetylenic Compounds", JACS **67**, 484–85 (1945) & CA **39**, 1839 (1945) 2) E.R.H. Jones, "Acetylene and Acetylenic Compounds in Organic Synthesis", JCS **1950**, 754–61 & CA **44**, 6805 (1950) 3) E.R.H. Jones, et al, "Synthesis of Polyacetylenic Compounds", Nature **168**, 900–03 (1951) & CA **46**, 6076 (1952) 4) E. Delaney, "Acetylenic Polymers For Solid Propellants", Report **RMI-157-L2**, Reaction Motors Inc, Denville, Contract No NORD-17851 (1957) 5) Anon, "Polyynes for Solid Propellants", C&EN, 41–42 (Sept 28, 1959) 5a) W.W. Graessley & J.H. Zufall, "Fifth Quarterly Progress Report On Fission Product Applications Using Gaseous Beta Sources", USAEC Contract AT(30-1)-2343, Task II, Air Redn Co, Murray Hill, NJ (1960) 6)J.H. Wotiz, et al, "A Novel Synthesis of Polyacetylenes", JACS **83**, 373–76 (1961) & CA **55**, 11281 (1961) 7) J.H. Wotiz & C.G. Parsons, "Rearrangement of Terminal Polyacetylenes", USP 3166605 (1965) & CA **62**, 9005 (1965) 8) R.F. Gould, Ed, "Advances in Chemistry Series", ACS (1966), 118–31, D.D. Perry et al, "Acetylenic Propellant Binders", Chapter 12 9) J. Schalberger, "Composite Propergol Charges Using Liquid Combustion Supporters Stable at Normal Temperatures", FrP 1605107 (1973) & CA **81**, 108109 (1974)

Diacetylene or Butadiyne and Its Silver Salts. See Vol **5**, D1120-L

Diacetylenic Dihydroperoxides. See Vol **5**, D1120-R

Dichloroacetylene or Dichloroethyne. See Vol **5**, D1203

1,6-Dichloro-Hexa-2,4-diyne.
$CH_2Cl.C{\equiv}C.C{\equiv}C.CH_2Cl$; mw 147.00; liq; bp 61° at 0.5mm; d 1.219g/cc; RI 1.5750. Prepn is by reacting hexa-2,4-diyne-1,6-diol with thionyl chloride in py. Explds on distn
Ref: Beil **1**, ⟨1119⟩

Diiododiacetylene or Diiodobutadiyne. See Vol **5**, D1298-L

1,8-Dimethyloctaacetylene.
$CH_3(C{:}C)_4CH_2(C{:}C)_3(C{:}CH)$; mw 222.24; OB to CO_2 −280.78%; white ndls turning brn at RT; mp, explds below mp. Prepn is by reacting methyldiacetyleneMgBr in eth under N_2 with dry Cu chloride. The mixt is extd with aq ammonium chloride, concd to 100ml and cooled to −78°. The crude yield is purified by chromaty on Al oxide using 1:2 eth-petr eth as the eluting agent
Refs: 1) Beil–not found 2) H.H. Schlubach & V. Franzen, Ann **572**, 116–21 (1951) & CA **45**, 10206 (1951)

1,8-Diphenylbutylacetylene.
$C_6H_5.C{:}C.C{:}C.C{:}C.C{:}C.C_6H_5$; mw 250.30; OB to CO_2 −287.65%; fine yel ndls; mp 113°. Prepn is by reacting phenyldiacetyleneMgBr in eth under red light with Cu chloride. Purification of the crude ppt involves filtration, washing with aq ammonium chloride, evapn to 100ml of soln, soln in 4:1 ligr-benz, followed by chromaty on Al oxide. The polyacetylene compd is stable in the dark at RT. It explds on rapid heating
Refs: 1) Beil–not found 2) H.H. Schlubach & V. Franzen, Ann **572**, 116–21 (1951) & CA **45**, 10206 (1951)

1,16-Diphenyloctaacetylene.
$C_6H_5.(C{:}C)_8.C_6H_5$; mw 346.38; OB to CO_2 −281.77%; red ndls; decomps in the dark at 20° within a few hrs after prepn. Prepn is by condensing α-bromocinnamaldehyde with penta-2-4-diyne-1-ol. The cryst glycol formed is first converted to the dichloride (using thionyl chloride), then to the monophenylbutylacetylene using Na amide and finally to the diphenyloctaacetylene by treatment of the monophenyl compd with Cu chloride and oxygen. The prod explds on touch or on attempts to heat it
Refs: 1) Beil–not found 2) E.R.H. Jones, et al, Nature **168**, 900–03 (1951) & CA **46**, 6076 (1952) 2) Ibid, RecordChemProgr **14**, No 1, 1–5 (1953) & CA **48**, 9896 (1954)

1,10-Diphenylpentaacetylene.
$C_6H_5.(C{:}C)_5.C_6H_5$; mw 274.32; OB to CO_2 −285.80%; yel cryst; mp, stable at 0°, brn at 60°, then blk and explds at about 160°. Sol in benz and petr eth. Prepn is by reacting under red light diethynylMgBr with phenylacetylene-aldehyde at −15° in eth. The mixt is allowed to reach RT and stand for 12 hrs. The cryst prod of this step is further treated with ammonium chloride, then thionyl chloride at −10°. The next step involves pptn of the crude yield of diphenylpentaacetylene with K ethanolate under nitrogen. The crude yield is purified by repeated chromaty using petr eth-benz elutant. The final yield is 6.1%
Refs: 1) Beil–not found 2) H.H. Schluback & V. Franzen, Ann **573**, 105–09 & CA **46**, 1955 (1952)

Iodbutadiyne (Iodinediacetylene).
$CH{:}C.C{:}CI$; mw 175.95; OB to CO_2 −40.92%; cryst; mp ca −40°; bp 71°; d 1.824g/cc at 15/4°; RI 1.5058. Prepn is by reacting one mole of iodine with acetylene-bis-Mg bromide in eth. The compd is sens and will expld at temps over 30°
Ref: Beil **1**, [246] & ⟨1117⟩

Hexa-1,5-diyne (Bipropargyl or Dipropargyl).
$HC{:}C.CH_2.CH_2.C{:}CH$; mw 78.12; OB to CO_2 −307.22%; mp −4.27°; bp 87.86°; d 0.788 g/cc; RI 1.43934. Sol in eth; insol in w. Prepn is by reacting monosodiumacetylenide with 1,2-dibromoethane in a mixt of dimethylformamide and tetrahydrofuran at 30°. Bipropargyl explds *violently* when heated to 110–20°
Ref: Beil **1**, 266, (128), [247], {1057}& ⟨1118⟩

Hexatriyne (Triacetylene).
$HC{:}C.C{:}C.C{:}CH$; mw 74.08; OB to CO_2 −280.78%; liq; mp −20°. Sol in acet. Prepn is by reacting 1,6-dichloro-hexa-2,4-diyne with Na hydroxide in eth. Hexatriyne explds in air at 0°. It is stable under nitrogen and in air at −20°, but its polymer, which exists below its mp, can be expld by touching it with a glass rod. Its silver salt, **Di silver hexatriyne**, Ag_2C_6, can also be expld by touch
Ref: Beil **1**, {1070} & ⟨1141⟩

Penta-1,3-diyne (Methyldiacetylene). $CH_3.C{:}C.C{:}CH$; mw 65.10; OB to CO_2 −294.93%; liq; mp −4.5 to −38.5°; bp 76–77° (explds at atm press), 45° at 140mm; d 0.7909 g/cc at 20/4°; RI 1.4762 (Ref 3) and 1.4817 (Ref 1). Sol in ethanol and petr with a bp > 180°. Prepn is by reacting monosodium-acetylenide with dichloromethane in liq ammonia at 20 to 40°, followed by treatment with ammonium chloride. The product is stable in the dark at −35° but polymerizes readily at above −20° in the light. Penta-1,3-diyne forms two expl salts: **Copper penta-1,3-diyne**, CuC_5H_3, dark yel ndls, by reaction with CuCl, explds on shock or by rubbing; and **Silver penta-1,3-diyne**, yel-brn ndls, by reaction with aq silver nitrate in ammonium hydroxide, a v expl compd

Refs: 1) Beil **1**, [247], {1057} & ⟨1117⟩ 2) H.H. Schlubach, et al, Ann **568**, 141–59 (1950) & CA **44**, 8313 (1950) 3) L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, NY (1971), 35–6

2,2,23,23-Tetramethyl-tetracosa-7ξ,9ξ,15ξ,17ξ-tetraene-3,5,11,13,19,21-hexayne. $(CH_3)_3C.C{:}C.C{:}C.CH{:}CH.CH{:}CH.C{:}C.C{:}C.CH{:}CH.CH{:}CH.C{:}C.C{:}C.C(CH_3)_3$; mw 362.54; OB to CO_2 −304.52%; yel cryst; mp, explds at about 250°. Sol in eth and methanol. Prepn is by reacting [8,8-dimethyl-non-2ξ-ene-4,6-diyne] triphenyl phosphonium bromide with butyl-lithium in eth followed by propiolaldehyde. The product of these reactions is then treated with a mixt comprised of a soln of 11,11-dimethyldodeca-3ξ,5ξ-diene-1,7,9-triyne in methanol and copper acetate in aq pyr

Ref: Beil **1**, ⟨1170⟩

Polyacrylates. See Vol **1**, A96-R to A97-R and the following limited and unlimited distribution

Addnl Refs: 1) E.T. Niles, et al, "LMH-1/Hydrazine Heterogeneous Propellant Development", **AFRPL-TR-68-216**, Contract AF-04-(611)-11606, Dow Chem, Midland (1968) (limited) 2) J. Simicek, et al, "Explosive Acrylic Polymers", Rept No **FSTC-HT-23-1046-73**, AFS TC, Charlottesville (1973) 3) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants", JSciIndRes **32** (6), 282–99 (1973) & CA **80**, 121565 (1973) (unlimited) 3a) L. Leneveu & F. Villey-Desmeserets, FrP 2182663 (1974) & CA **81**, 51891 (1974) 4) L.B. Childs Jr & J.D. Martin, "Rocket Propellant with Acrylate Binder and Difluoroamino Plasticizer", USP 3933542 (1976) & CA **84**, 138050 (1976) (unlimited)

Polyalkylbenzenes, nitration of. See in Vol **1**, A129-R to A130-R and

Addnl Refs: 1) Urbański **1** (1964), 74–5 2) D.V. Nightingale, ChemRevs **40**, 117–40 (1947) & CA **41**, 2687 (1947)

Polyamide Gels. Several matls of this type have been invented for use in demolition charges for concrete structures (Ref 1), or for incendiary bombs and flame throwers (Ref 2). The former consists of a slurry type expl contg a clay that swells when wet which consists of one or two resinous plastics such as polyamides. The latter consists of a suitable solvent such as petr eth, octyl alc or acetophenone and a polyamide prepd by reacting, typically, a mole of cetyl-malonic ester with a mole of 1,3-diaminopropane. These reactants give a waxy matl with an avg mw of 2400 and a mp of 165°. The gel is prepd by mixing the polyamide with one of the solvents, heating the mixt to its bp and cooling to 25–30°

Refs: 1) D.E. Floyd, USP 2662068 (1953) & CA **48**, 4222 (1954) 2) T. Takayama, JapP 75-18052 (1975) & CA **83**, 195956 (1975)

Polyamides. A plastic matl prod by condensation processes resulting in a chain polymer consisting of repetitive amide groups. The best known amide polymer is called generically, Nylon. The mil uses for polyamides such as Nylon are numerous and include adhesives, airframes, armor, bearings, cements, foams, greases, primer coatings for metals, projectile coatings, ration packaging, rocket motor linings and tires. A general use mil spec exists for Nylon (Ref 1). For further information on polyamides, see "PLASTEC" (a source of appropriate publications) in this Vol, as well as

"Amides and Imides, Organic" in Vol **1**, A170-R and the following
Refs: 1) Anon, "Nylon Plastic, Flexible, Molded Or Extruded", **MIL-N-18352** (1955) 2) Kirk & Othmer **16** (1968), 1–105 3) Anon, FrP 2079054 (1971) & CA **77**, 64221 (1972)

Polyamines. See under the various topics in Vol **1**; viz, "Aminoethylcellulose (AEC) (Polyaminoethylated Cellulose)", A203-R to A204-L; "Aminoethylcellulose Perchlorate (AECP) or Polyaminoethylcellulose Perchlorate", A204-R; "Aminoethylnylon (AEN) and its Perchlorate (AENP)", A205-L; "Aminoethylpolyurethane (AEPU)", A205-R; "Aminoethylpolyvinyl Alcohol (AEPVA) and Its Perchlorate (AEPVAP)", A205-R; "Aminoethylpolyvinyl Chloride (AEPVC)", A205-R to A206-L; "Aminoethylprotein (AEP)", A206-L and "Aminoethylstarch (AES) and Its Perchlorate", A206-L and R. Also, the following limited distribution *Addnl Ref:* B.D. Strauss, "Development of Polyamine Nitrate Propellants", PATM **2086** (1973)

Polyamylose, Nitrated. See under "Amylose" in Vol **1**, A398-R to A399-R

Polybenzyl, Nitrated. See Vol **2**, B95-R under "Benzyl Chloride and Derivatives" and *Addnl Ref:* C.S. Marvel, OSRD **875** (1942)

Polybutadiene and its use as a Binder with Energetic Materials. For "Butadiene and Derivatives", see Vol **2**, B365-R to B366-R. For "Composite Propellants", including a general discussion of butadiene polymers, see Vol **3**, C464-L to C474-L. A more specific and updated discussion of Polybutadiene follows

There are two types of Polybutadiene polymers used in ordn; viz, carboxyl terminated (CTPB) and hydroxy terminated (HTPB). The preferred polymer for energetic material binder purposes is the hydroxy terminated variety because of its low viscosity, hence ease of prod prepn, and better ageing and burning characteristics than the carboxyl terminated variety (Refs 7, 8, 9, 10, 12, 13 & 15). Hence, information on HTPB is presented in some depth

Hydroxy-Terminated Polybutadiene (1,2-Polybutadiene or HTPB).

$$\left[\begin{array}{l} -\text{C.CH} - \\ \quad\dot{\text{C}}\text{H} \\ \quad\ddot{\text{C}}\text{H}_2 \end{array}\right]_n$$

; mw 11,600; the compd exists in several cryst structures whose properties are tabulated below (Ref 7a)

	Isotactic (99%)	Syndiotactic (98%)
Lattice	rhombohedral	helical
Monomers/Unit Cell	2	3
MP, °	126	156
Crystal density, g/cc	0.96	0.96
RI	1.5154	1.5156
Solvents	benz, chlf, pyr, toluene & xylene	

Hydroxyl terminated polybutadiene can be prepd by an anionic polymerization technique (Ref 4) resulting in hydroxyl groups terminating each end of the polymer chain. The process uses an isopropanol-solid carbon dioxide bath (−78°) contg a reaction vessel into which above stoichiometric amounts of tetrahydrofuran (900ml), lithium metal (0.217g), and naphthalene (4.204g) are introduced under argon, and then magnetically stirred for two days or until the lithium dissolves in the naphthalene. Gaseous butadiene (177g) is then slowly bled into the reaction vessel over a period of eight hours. Five ml of ethylene oxide is then quickly added to the mixt, prod a colorl gel. The reaction mixt is then warmed to RT and stirred for several days until the ethylene oxide penetrates the initial gel and the entire system is colorl and solid

Polybutadiene is used extensively in many expl and proplnt compns. One such expl usage was patd by dePrisque et al (Ref 11). Here, HMX, PETN or RDX is used to comprise 40–80% of the compn which is formulated, for example, to include powd Al (43 parts) and graphite (0.2 part), along with one of the above expls (50 parts). This mixt is combined at 80° with 6.8p of a binder contg polybutadiene, dioctylazelate, nonylphenyl phosphite, Fe naph-

thalate, plus an epoxy resin. After mixing to a uniform particle suspension, the mass is allowed to solidify

According to Krowicki et al (Refs 1a & 5), a typical composite proplnt compn consists of: a combustible component amounting to (on a wt basis) 10.5%, contg (by wt)

Butadiene/2-methyl-5-vinyl py (90/10)	100p
Flexamine	3p
Liq polybutadiene-plasticizer	25p
Light petroleum oil-plasticizer	25p
P-quinone dioxime	2p

plus Amm perchlorate as an oxidizer (on a wt basis) 84.5%, and boron (on a wt basis) 5.0%

Manuf of these proplnts, according to Urbański (Ref 2), is accomplished in steps:

a) *Milling.* The oxidizer is milled into granules with a particle size ranging from 5 to 500 microns. Fineness of the particles controls the rate of burning of the mixt

b) *Mixing.* The polybutadiene is mixed with such ingredients as carbon black, plasticizer, accelerator and inhibitor on rollers usually employed in the rubber industry. In the final mixing the oxidizer and combustion catalyst are added to the binder-fuel. This stage of mixing is usually accomplished within 2 hrs between rollers heated to 50–60°

c) *Pressing.* The hot, homogeneous mass is shaped in a hydraulically-operated extrusion press of the type used for smokeless powdr. It is usually cruciform. A guillotine cuts the extruded matl to the reqd length. The outer surfaces of the limbs of the cross are covered with a substance which does not burn readily (ie, strips of plasticized cellulose acetate or polystyrene, 1.5–5mm thick), and cemented in place to prevent uneven burning at the surface

d) *Curing.* The final operation in polybutadiene proplnt manuf is the curing of the binder. The shaped matl is put into a curing oven for 16–48 hrs at 70–110°. The temp and duration of this operation depend on the compn of the mixt, charge dimensions and the physical properties desired

The parameters of a typical polybutadiene–Amm Perchlorate proplnt are presented next (Ref 2):

Burning under press (kg/cm^2)	1–140
Specific impulse I_s at P=70 kg/cm^2	250
Rate of burning (mm/sec) under press P=70kg/cm^2	11.9
Exponent n in the eq $V = kp^n$	0.236
Density, g/cc	1.74

The most significant use for HTPB proplnts is in ballistic missiles (Refs 12 & 13). The most unique usage is in the functioning of a laser by means of the chemical exhaust species generated by a HTPB–Amm Perchlorate fuel matrix (Ref 9)

Some ordn uses have been found for carboxyl terminated polybutadiene; viz, as rocket motor liners for proplnt mixts contg HTPB (Ref 17) and as part of a terpolymer binder for proplnts (Ref 16)

The US military specification for polybutadiene is for the *carboxyl* terminated variety (Ref 1b). The requirements of this spec are listed below for Type I (low acid), Type II (high acid)

Table 1
Chemical and Physical Requirements for CTPB

	Type I		Type II	
	Min	Max	Min	Max
Viscosity, Poise at 77°F [a]	230	350	230	350
Viscosity Ratio, 77°F/100°F [b]	1.5	3.0	1.5	3.0
Specific Gravity, 60°F/60°F [c]	0.890	0.925	0.890	0.925
IR, 25/D [d]	1.514	1.519	1.514	1.519
Carboxyl Content, Wt % [e]	1.10	1.40	1.60	1.90
Unsaturation Type [f]				
Cis (% of Total)	25	45	25	45
Trans (% of Total)	35	55	35	55
Vinyl (% of Total)	15	25	20	30
Volatiles, Wt % [g]		1.0		1.0
Moisture, Wt % [h]		0.05		0.05
Antioxidant, Wt % [i]	1.0	1.5	1.0	1.5
Insol in Trichlorethylene, Wt % [j]		0.2		0.2
Ash, Ignited, Wt % [k]		0.05		0.05
Q_c, BTU/lb net [l]	17,900	18,400	17,900	18,400

Footnotes to Table 1:
a – Detd by the use of a Model RUF Brookfield Viscometer, Brookfield Engrg Labs, Stoughton, Mass
b – Detd by calcg the ratio
c – Detd using a pycnometer gravimetrically
d – Detd by using a refractometer
e – Detd by titration using Na methylate and a thymol blue indicator under nitrogen
f – Detd spectrophotometrically using a Model 21PE infrared spectrophotometer
g – Detd gravimetrically using a Rinco rotating vac evap
h – Detd by Karl Fischer titration
i – Detd by differential UV spectrophotometry of alcoholic KOH saponified trichlorethylene sol CTPB using a Beckman DV instrument
j – Detd gravimetrically by loss-in-wt after drying at 220°F for 30 minutes min
k – Detd gravimetrically by loss-in-wt after ignition at about 1000°F for one hour
l – Detd calorimetrically

Refs: 1) Beil **1**, {937–948} 1a) K. Krowicki et al, "Solid Rocket Propellants", StalePaluva-Rakietowe(Pol), **Trnsln No HT6600730, TM 7000397**, FTD, Wright Patterson AFB (1964) 1b) Anon, "Polybutadiene, Linear, Carboxyl Terminated", **MIL-P-23942** (1) (1966) 2) Urbański **3** (1967), 392 3) J.T. Cheng et al, "Thermal Effects of Composite-Propellant Reactions", Report No **AFOSR 68-0243**, Contract AF-AFOSR-40-66 & 67, Utah Univ, Salt Lake City (1967) 4) D.H. Richards et al, "Synthesis and Characterisation of Hydroxy-Terminated Polybutadienes", Report No **6/R/66**, ERDE, Waltham Abbey, Essex (Engl) (1967) 5) Anon, "Polymer Binder for Explosives", FrP 1495086 (1967) & CA **69**, 11879 (1968) 6) R.W. Bryant & W.A. Dukes, "Measurement of Embrittlement Temperatures (Brittle Points) of Composite Propellants By The Bending Beam Method", Report No **ERDE-15/M/68**, Waltham Abbey (Engl) (1968) 7) A. Tice et al, "A Low-Temperature Differential Thermal Analysis of Hydroxy-Terminated and Carboxy-Terminated Polybutadiene", Rept No **CRREL-SR-149** (1970) 7a) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vol **2**, J. Wiley & Sons, NY (1970), 726–47 8) A.J. Dimilo et al, "Evaluation of The Mechanical and

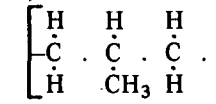
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Addnl Refs: (limited distribution refs indicated by asterisk): 1) Anon, "... Rocket Propellants ...", Report No **11504***, SPIA/A11 (1952), 199 2) Ibid, Report No **12419***, SPIA/A12 (1953), 181 3) A. Leech & R. MacDonald, "Control Analysis In the Manufacture of Polybutadiene Propellant", Rept No **CARDE-TR-578/67***, Valcartier(Can) (1967) 4) B. Brown, "Explosive Hazards of Composite Solid Propellants", Report No **IDA/HQ-67-6659***, Contract DAHC15-67-C-0011, Arlington (1968) 5) C.O. Parker & E.T. Stevens, "Bonding Agents and Processing Aids for HTPB Propellants", Rept No **S-205***, Contract DAAH01-68-C-0632, Rohm & Haas Co, Huntsville (1969) 6) A.M. Bedard, "Evaluation of Liner Formulations For Polybutadiene Propellants Used In Small Rocket Applications", Report No **DREU T.N. 1825/69***, (Can) (1969) 7) A.K. Roberts, "Preliminary Data On Unstable Combustion In Aluminized Polybutadiene Rocket Motors", Rept No **DREU T.N. 1824/69*** (Can) (1969) 8) M.K. King & E.T. McHale, "An Optical Bomb Study of the Combustion of Solid Propellants in High Acceleration Fields", **Final Tech Rept***, Contract N00014-67-C-0455, Atlantic Research Corp, Alexandria (1969) 9) R.W. Bryant & R. Gledhill, "Effect of Variations in Composition on Physical Properties of Polybutadiene Propellants at Low Temperatures", Report No **TRC BR-25796***, Waltham Abbey (Engl) (1971) 10) A.H. Lepie & A. Adicoff, "Dynamic Mechanical Behavior of Highly Filled Polymers: Dewetting Effect", Rept No **NWC-TP-5486** (1971) 11) H. Yasutake et al, "Thermal Reactivity of Polybutadiene", Rept No **FTD-HC-23-662-73***, (1973) 12) R. McGuchan & G.J. Spickernell, "CTPB Cure Studies, Part 2. Effect of Experimental Variables on Epoxides Cure and Properties of Gumstocks", Rept No **ERDE-TR-151**, DRIC BR-42458, Waltham Abbey (Engl) (1973) 12a) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants", JSciIndRes, 283–99 (1973) & CA **71**, 121565 (1973) 13) J.S. Noel et al, "Air Launch Instrumented Vehicles Evaluation (Alive) Program. Technical Report. Phase I. Program 1.", Report No **AFRPL TR-74-40***, Contract F04611-74-C-0009, Rockwell Intl Corp, McGregor (1974) 14) E.J. Mastrolia & H.J. Michigian, "Selection and Evaluation of Bonding Agents for HTPB Propellants", Rept No **ASPC-1085-26F***, RKCR-75-18, Aerojet Solid Proplsn Co, Sacramento (1974) 15) G. Thompson & E.E. Day, "Development of HTPB Propellant for Ballistic Missiles", Rept No **AFRPL TR-74-68***, Contract F04611-72-C-0048, Thiokol Corp, Brigham City (1974) 16) F.R. Mayo, "The Chemistry of Aging of Hydrocarbon Binders in Solid Propellants", **CPIA Publ 262***, Johns Hopkins Univ, Silver Spring (1975)

17) Anon, "Material Specification, Propellant, PBAN General Specification For", Rept No **SPEC-XWS-16716***, Contract N00030-74-C-0100, Lockheed Missiles & Space Co, Inc, Sunnyvale (1975) 18) J.Q. Schmidt, "Attenuation and Phase Velocity Measurements of Polybutadiene Composites Using Ultrasonic Pulses", Rept No **BRL-1908*** (1976)

Polybutene, Polybutylene, Polyisobutene, Polyisobutylene, Poly 2-Methylpropene, Poly γ-Butylene, Poly unsym Dimethylethylene or PIB. For "Butene and Derivatives", see Vol **2**, B375-R to B376-L. For "Butene Polymer Dynamite", see Vol **2**, B376-R. For the use of polyisobutylene in "Composition C Type Explosives", see Vol **3**, C484-L to C488-R

PIB exists either as a low mw (about 12,000) viscous or atactic liq or as a cryst matl of about 100,000 mw. In this latter form the *isotactic* (chain) type configuration predominates over the atactic and amorph forms (Ref 8). Since the isotactic form is the form designated by mil spec (Ref 2), its parameters are presented below; viz,



Cell or unit quantity =18(n); mw 99,000 to 120,000; colorl rhombohedral cryst; mp 135.5 to 141°; d 0.95g/cc; the RI increment in n-heptane at 60° and 546mμ [Δn/c(m/g)] is 0.115. Sol in most inert hydrocarbons such as benz, ethylcyclohexane, n-nonane, n-heptane and decalin. Prepn is by reacting 1-butene in an inert hydrocarbon solvent such as benz with a polymerization catalyst such as Ti chloride or V chloride under an inert gas and at temps of from 20 to 100°. The reaction is deactivated at completion by w addn and the polymer is then thoroughly dried (Refs 3 & 8)

The prepn of PIB binder for inclusion with energetic materials to form expls or proplnts is as follows (Ref 1a): Using a hot w-heated 100 gal Baker-Perkins mixer equipped with two sigma-shaped blades rotating to give a kneading action (the front blade is rotated at 15rpm and the rear blade at 30rpm) to perform the actual mixing, mix 354 lbs of di(2-ethylhexyl) sebacate with 96 lbs of SAE No 10 engine oil at 82–90° Next, add 75 lbs of sheet PIB in 4" x 4" x 1/16" pieces while continuing the agitation. Then cool to 25°, and add 12 lbs of n-hexane to decrease visc. Still agitating, incorporate an addnl 150 lbs of PIB. Reheat the mixt to 82–90° for an addnl 10½ hrs. Cool to 30°. Yield is 600 lbs

Aside from the aforementioned uses of PIB in expls and composite proplnts, other uses have been found in proplnt igniters (Addnl Ref 1) and expl ignition trains (Addnl Ref 4)

A typical compn of plastic proplnt in which PIB is used is shown below (Ref 3); viz,

Constituent	%
Ammonium Perchlorate	78
Aluminum	10
Burning rate catalyst	1
Surface-active agent	1
PIB binder	10

"This compn has more than 79% by volume of solid constituents. Plastic propellant is thus a very highly filled suspension and it is only possible for it to contain such a high proportion of solids if there is a wide, specially graded range of particle sizes. This grading is achieved partly by careful choice of starting material, and partly by breakdown of the solid particles during the manufacturing process"

". . . In some compositions the PIB is plasticized with ethyl oleate to improve low temp properties . . . Since the proplnt is a stiff paste it can be inserted into a rocket motor by a type of injection moulding process" (Refs 3 & 5)

In a recent patent of Bartley's (Ref 11), a PIB proplnt is described which has the following compn and properties:

Composition	
Rubber binder, %	11.13
consisting of:	
Isobutylene (10–20%)	
Nitrate oxidizers (80–90%)	
Amm Nitrate, %	79.03
Ferrous Oxide, %	1.09
Additives, %	8.74
Burning Rate at 80°F, inches/sec	0.14
Specific Impulse at 1000psi, lb sec/lb	200

Several disadvantages to plastic proplnts contg PIB have been noted. One is the existence with certain formulations of combustion in-

stability at 1000psi (Ref 4). The other disadvantage is dimensional instability, ie, grains made using PIB binder do not retain their original form, and sag or dimensionally deform on storage. Also, in some instances, there is a noticeable tendency to harden and fissure upon ageing (Ref 9)

The US military specification (Ref 2) lists the following requirements for PIB: (1) stability against depolymerization at 125°F; (2) color – shall not be darker than a soln of 0.008g/ℓ of $K_2Cr_2O_7$/w by visual comparison; and (3) chemical properties as shown in Table 1

Table 1
PIB Chemical Properties

Properties	Min	Max
Intrinsic Viscosity, centistokes [a]	3.15	3.72
Iodine No [b]	–	1.32
Chlorine, % [c]	–	0.10
Acidity (as HCl), % [d]	–	0.01
Insol Matter, % [e]	–	0.20

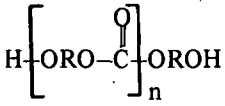
Footnotes to Table 1:
a – Obtd using a No 1 Ubbeholde viscosimeter
b – Obtd by Wijs procedure using KI and Na thiosulfate titrant solns
c – Obtd colorimetrically using Ag nitrate soln with Nessler tubes
d – Detd by titration with std NaOH soln
e – Detd gravimetrically in a Gooch crucible after washing with xylene

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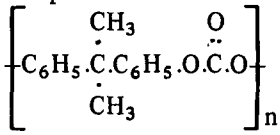
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Buswell, "Solid Propellent Rheology: The Effect of Confining Pressure on the Mechanical Properties of Plastic Propellant", Rept No **RPE-TM-519**, TRC BR-18655, Westcott (Engl) (1970) 12) C.J. Brett & A.T. Roff-Jarrett, "The Analysis of Ethyl Oleate and Its Determination in Plastic Propellant and Propellant Premixes by Gas Chromatography", Rept No **QAD (MATS)-166** (Engl) (1970)

Polycarbonates. Linear thermoplastic polyesters of carbonic acid with aliphatic or aromatic dihydroxy compds. A general structure presentation is as follows (Ref 4):



The most widely used *monomer* compd is 2,2-Bis (4-hydroxyphenyl)-propane or bisphenol-A. For a description of this monomer see Vol **2**, B147-R. The properties of the *polymer* or resin comprised of this monomer are presented next:



transparent amorph solid; mp 268°; d 1.20g/cc; RI 1.586. Sol in sym-tetrachloroethane, methylene chloride, Cis-1,2-dichloroethylene, chlf and 1,1,2-trichloroethane; insol in acet, eth and carbon tetrachloride. Prepn is by reacting bisphenol-A dissolved in py with phosgene in the following manner (Ref 1a):

"Twenty-three grams (0.1 mole) of bisphenol-A are dissolved in 200ml of pyridine in a vigorously stirred flask provided with a cooling bath to maintain the temperature at 25–35°. Phosgene is introduced into the reaction mixture thru a wide-bore tube at a rate of 1.0g/min. After 7 to 8 minutes the reaction mixt is saturated with pyridine hydrochloride and pptn may start. About ten minutes after the start of the reaction the mixt is too thick for convenient stirring. The polymer may be recovered by the addition of methanol or other solvents which will dissolve the pyridine hydrochloride and ppt the polymer." The yield is essentially quantitative and the polymer will have an intrinsic viscosity of (about) 79,000 to 674,500 poise measured in dioxane at 30° (Refs 1a & 4)

Polycarbonate resins can be cast or injection molded. They possess a high degree of thermal stability and undergo little decompn below 250°. They can be mixed with fiberglas for addnl strength. Techniques of fabrication and copolymerization are presented in refs 1 thru 8, as well as prolonged weathering effects (Ref 6a). See also under "Epoxy Resins or Epoxies" in Vol **5**, E106-R to E107-L

Polycarbonates have wide applications in ordn. However, the applications which are of special interest here are used as various types of armor (Refs 3, 5 & 8) and as pyrot binders (Refs 6 & 7)

The need for transparent airframe areas such as radardomes, ballistic surfaces or impact shields has resulted in a thorough investigation of the utility of polycarbonates in this area. The work of Ball et al (Ref 3) shows that a high-clarity polycarbonate can be fabricated by injection molding and that ballistic properties are not related to low rate (Izod) impact but to homogeneity, ie, a single homogeneous plate of polycarbonate is superior in ballistic performance to multiple plies of the same material. Belkin et al (Ref 5) noted that, ". . . In addition to their high specific impact strength, polycarbonates are characterized by their rigidity, hardness and elasticity. As opposed to many other plastics, polycarbonate laminates do not shatter on impact. This property makes it fit the needs in many cases of the defense industry." Specific usage in critical aircraft transparencies is noted by Voss in Ref 8, ie, windshields and canopies for the F-15 and YF-16 fighters, and bird-proof windshields for T-37 and A-37 aircraft. Extensive service use has revealed only one significant problem area, namely surface scratch and erosion protection. The currently developed soln to this problem involves direct fusion cladding of an erosion and scratch-resistant polyurethane layer onto the surface of the polycarbonate

The work of Hamermesh and Witucki (Refs 6 & 7) on pyrot polycarbonate binders is of interest. As reported in Ref 6, the authors prepd a polyalkyl carbonate by the reaction of a glycol with phosgene:



At 70–80° the yield is 55–75%. The binder is cured at 160°F for 72 hrs. Because the polymer

is a liq of 32,000cps visc before cure, a polyisocyanate cross-linker is used. The binder is incorporated with standard pyrot flare and signal ingredients (Refs 6 & 7)

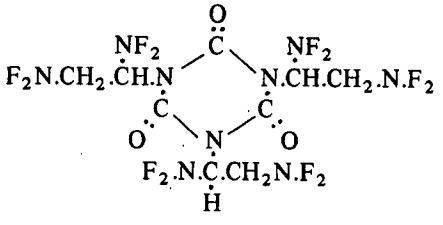
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Polydiamides. See under "Diamides" in Vol **5**, D1125-L and R

Poly (Difluoroamino)-Substituted Cyanuric and Isocyanuric Acid Derivatives. For Cyanuric Acid and Derivatives see Vol **3**, C589-R ff. For "Difluoroamino Compounds" see Vol **5**, D1258-L

Of particular interest is **Tris[1,2-Bis (Difluoramino)-ethyl] Isocyanurate.**



mw 519.261; N 24.28%; OB to CO_2 –60.09%; gummy crystln solid; mp 48–50°. Sol in chlf. Prepn is by reacting tetrafluorhydrazine (F_2NNF_2) under 200psig initially with 3g of trivinyl isocyanurate in 75ml of chlf. The mixt is then heated to 125° and the reaction is continued at this temp for 32 mins at a press of 305psig. At the end of the 32 mins the reaction vessel is cooled, vented, and the chlf is distd off. The expl prod is insens to heat and static. It has an impact sensy of 435cm. It is used as a rocket proplnt and an expl (Ref 1)

Difluoroamino polymers contg $-NF_2$ groups at the carbon atoms have been found to act as oxidizing groups in the binder in the same way as an $-NO_2$ group. However, the introduction of an $-NF_2$ group increases the density of the binder. Some fluorocarbon proplnt motors can be stopped and restarted, placing solid proplnts on somewhat of an equal footing with liq proplnts (Ref 2)

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Polyesters. The polycondensation prods of dicarboxylic acids with dihydroxy alcohols. These compds may be modified by monocarboxylic acids or polyhydroxy alcohols. This definition includes the polycarbonates (qv), which are a well-defined segment of the general class of polyesters. Unsaturated polyesters, which are produced when any of the reactants contain non-aromatic unsaturation, can be cross-linked or copolymerized with an unsaturated copolymerizable monomer. The formulas and properties of the class "polyester" are as varied and extensive as the reactants themselves. For specific information on the various sub-classes and sub-sub classes, the following refs should be consulted: 9, 10, 11, 16a, 17, 18, 20, 23, 26, 29 & 38

The ordn uses of polyesters are varied. They range from adhesives (Ref 4), ammo boxes (Ref 5), grenade deactivator (Ref 7), component sealers (Refs 4 & 8), rocket launchers (Ref 1a), minesweeper hulls (Ref 14), to binders in expls (Refs 3, 6, 19, 21, 32, 33, 34, 35, 37 & 40), proplnts (Refs 12, 15, 16, 22, 24, 25, 27, 28, 30, 31, 32a, 32b & 39), and pyrots (Refs 2 & 13)

To illustrate the properties of expls with polyester binders, see the data in Table 1 from Refs 3, 6 and 37

Bissel (Ref 19) developed a binder for extrusion-cast expls with the compn 70.0/19.0/7.3/3.7 bis(fluorodinitroethyl)-formal/epoxide B/maleic anhydride/diethylene glycol, using 0.5 wt % of ferric acetylacetonate as the catalyst. The binder is cured for 48 hrs at 60°. The cured binder has the following properties: d 1.487g/cc; DTA exotherms at 200° (minor) and 240° (major); a glass transition temp of –18°; thermal stability at 120°/22 hrs/0.25g sample evolved 0.76cc of gas (STP)

Also in an invention of Frankel et al (Ref 40), a castable expl has been developed which, typically, consists of a polyester binder (20%) such as 3-(2′,2′-dinitro-2′-fluoroethyl)-1,2-propanediol reacted with an isocyanate curing agent plus HMX (80%)

For other compns with polyester binders see the article on "Plastic-Bonded Explosives" in this Vol

A current example of the use of a polyester resin as a proplnt binder is the patd compn of Cohen and Scotoni (Ref 32b). In this formulation conventional polyester-olefinic copolymers are used (50.1) together with NG (42.5), triacetin (2.7), adiponitrile (2.7), PbO (0.5) and acetylsalicylic acid (1.5%) to obtain 27 and 152mm caseless ammo

Exploratory work in the use of polyesters as pyrot binders was initiated at PA by Eppig in 1950 (Ref 2). He found that the Laminac series of resins, especially formulation 4116, which is an unsaturated polyester manufd by the American Cyanamid Corp (Ref 9), could be successfully used in a non-hygroscopic yellow flame ignition compn specifically developed for use with illuminant and signal compns contg Na nitrate. However, in a flare type compn contg Mg and Na nitrate together with Laminac 4116 polyester as the binder, Eppig found a marked decrease in burning time after one month storage at 65° (from 178 to 102 secs in one case). Because of this he recommended the use of a mercaptan resin binder (Thiokol) in flare compns. More recently, work by Haas (Ref 13) has shown that burning time is controlled by the length of the time expended in going from the

Table 1
Explosive Properties of Three Polyester-Bound Explosive Compositions

Properties	Values		
	CB49-3 (Ref 3)	CB53-2 (Ref 6)	Reichel et al (Ref 37)
Composition			
RDX, %	60	80	–
HMX, %	–	–	% unknown
Al, %	23	10	–
Polyester Resin, %	17	10	% unknown
Paraffin wax, %	–	–	% unknown
Cast density, g/cc	1.61	1.60	1.68–1.79
Detonation rate, m/sec	5855	6773	8400–8690
Explosion Temp, °C	265	265	–
Impact Sensitivity:			
a) PA App, 2kg, inches (TNT=14–15)	18	16	0.5 to 1.5kg-m
b) B/M Test, 221 lbs, feet, 50% pt; (TNT=11.2)	no deton at 20ft	10.2	–
Max brisance, gm			
sand crushed	58.7	64.5	–
Min detonation charge:			
a) Tetryl, g	–	0.050	–
b) LA, g	–	0.200	–
Pendulum Friction	–	–	24 to > 36kg
Rifle Bullet Impact:			
a) Unconfined, no trials/unaffected	5/5	5/5	–
b) Confined,			
no trials/unaffected	5/5	–	–
no trials/partial deton	–	5/5	–
Vacuum Stability, 100°C, ml gas/40 hrs	0.32	0.31	–

mixing to the pressing of a flare compn in which a polyester binder (the same Laminac 4116) is used. The shorter this manipulation time, the less the effect on burning time and other performance parameters. For addnl information and refs on Laminac 4116 see under this title in Vol **7**, L3-L

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Polyether. A polymer in which the repeating unit includes a carbon-oxygen bond derived from aldehydes, epoxides, polyalcohols or similar materials (Refs 1 & 4a).

Specific ordn using polyethers, such as *Polysaccharides* and *Polyurethanes*, are entered separately below. Polyethers already entered include Polyformaldehyde in Vol **6**, F164-L to F167-L; and Epoxy Resins in Vol **5**, E106-R to E107-L

Some physical properties of model polyethers are presented in tabular form below (Ref 2)

Among the more than several uses for polyethers in ordn application is as a binder for extrusion-cast expls (Ref 3), and in a caseless proplnt charge where the charge is used as an ammo element (Ref 5). Also, some development work on the use of *Polyacetal* resins (polyformaldehyde) as a fuel has been done by Singhal & T'ien (Ref 7)

Refs: 1) Beil – not found 1a) O. Schmidt & E. Meyer, "Ethers of Polyhydric Alcohols", USP 1922459 (1933) & CA **27**, 5082 (1933) 2) T.P. Hobin, "Model Polyethers V – Some Physical Properties", Rept No **ERDE-26/R/67**, Waltham Abbey (Engl) (1968) 3) E.R. Bissell, "New Polyester-Polyether Binder for Extrusion-Cast Explosives", **UCRL-50541**, UAEC, Univ of Calif (1968); Ibid, NuclSciAbst **23** (9), 17314 (1969) & CA **71**, 71343 (1969) 4) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vols **1, 6, 8, 9, 10, 11 & 13**, J Wiley, NY (1970) 4a) CondChemDict (1971), 706 5) T. Netzer & H.J. Block, "Caseless Propellant Charge Containing Nitrocellulose in a Synthetic Resin", USP 3676233 (1972) & CA **77**, 154627 (1972) 6) N.A.J. Platzer, Ed, "Polymerization Reactions and New Polymers", Advances in Chemistry Series 129, ACS, Washington (1973), 42–51 7) S.N. Singhal & J.S. T'ien, "Flammability Study of Polymer Fuels Using Opposed-Jet Diffusion Flame Technique, "Rept No **SQUID-TR-CWRU-3-PU**, Contract N00014-67-A-0226-0005, Purdue Univ, Lafayette (1975)

Addnl Refs: (limited distribution) 1) J.T. Hamrick & L.C. Rose, "Evaluation and Loading of New Explosive Formulations", Rept No **AFATL TR-68-90**, Contract F08635-68-C-0030, Aerospace Research Corp, Roanoke (1968) 2) V. Grakauskas, "Synthesis of Aliphatic Ex-

Table 1
Properties of Model Polyethers
$H[(CH_2)_yO]_x(CH_2)_yH$

y	x	MP, °C	Density g/cc@20°	Refractive Index
4	1	–95	0.982	1.420–1.440
4	2	–38	–	–
4	3	–39	–	–
4	4	–17.4	–	–
5	1	–69.3	0.966	1.445
5	2	–32	–	–
5	3	–12	–	–
5	4	–1.2	–	–
6	1	–41.5	0.939	1.420–1.450
6	2	–5.4	–	–
6	3	6.5	–	–
6	4	20.5	–	–
10	1	15.7	0.892(60°)	1.435–1.447
10	2	40	–	–
10	3	50	–	–
10	4	59	–	–

plosive Compounds", Rept No **AFATL-TR-72-47**, Contract F08635-71-C-0112, Fluorochem Inc, Azusa (1972) 3) A.S. Tompa & D.M. French, "Thermally Unstable Polymers", Rept No **NOS-IHMR-72-176**, Indian Head (1972) 4) Ibid, Rept No **NOLX-86**, White Oak (1974)

Polyethylene Glycols. See in Vol **6**, E252-L to E253-R under "Ethyleneglycol Polymers; Polyethyleneglycols or Polyglycols".
Addnl Refs: 1) J.L. Moilliet, USP 2454643 (1948) & CA **43**, 3619 (1949) 2) H. Sakai & K. Tsutsui, JapP 7101600 (1971) & CA **76**, 5475 (1972)

Polyethyleneglycol ethers. These compds are recommended as addns to gelatin Dynamite in quantities of about 0.4% to improve plasticity. They usually contain at least 8 linear carbon atoms and at least two adjacent ethyleneoxy groups
Ref: S. Fordham & J.L. Moillet, BritP 586224 (1947) & CA **41**, 7120 (1947)

Polyethyleneimine (PEI) and Its Perchlorate (PEIP). See under "Organic Perchlorates" in this Vol. *Addnl Ref:* H.A. Muenker et al, USP 3798086 (1974) & CA **81**, 15273 (1974)

Polyethylidene Peroxide. See under "Ethylideneperoxide, Polymeric" in Vol **6**, E306-R

Polyethyl Methacrylate. See under "Ethyl Methacrylate" in Vol **6**, E308

Polyfunctional Organic Azides

An improvement in M2 proplnt is offered by the work of Kuhn and Duckworth of BRL (Ref 2). By incorporating independently several diazidodinitrates; viz, 2,3-Diazido-1,4-Dinitratobutane and 3,3-Diazido-2,4-Dinitratopentane, they obtd proplnt films that compare favorably with M2 proplnt but have lower flame temps (see tabulated data below). See also "Organic Azides" in Vol **1**, A627-R to A644-L and diazidos in Vol **5**, under various diazido compds, D1154-R to D1155-R

2,3-Diazido-1,4-Dinitratobutane (DADNBU). $(NO_3)CH_2.CHN_3.CHN_3.CH_2(NO_3)$; mw 262.21; N 42.74%; OB to CO_2 −30.51%; cryst (meso), liq (racemic); mp 70–71° (cryst); bp 150° (decompn). Sol in acet and ethanol. Prepn is by nitration of 2,3-diazido-1,4-butanediol with mixed acid. The procedure involves dropwise addn of 2.58g of the diol to a cooled (0–5°) mixt (1/1) of acetic anhydride/100% nitric acid. The reaction is held to 5–15° and stirred for 30 mins. Several recrysts from ethanol give a (approx) 40% yield. The compd is friction sensitive; Q_c 682.8 and 671.8kcal/mole; Q_f 98.8 kcal/mole; impact sensy at 50% pt is 6.3cm using a 2kg wt in an Aberdeen Impact App and No 12 tools (PETN=26.7cm); impact sensy of proplnt films (85.15% NC/14.85% diazido compd) is 29–36cm (M2 film=34–36cm) at the 50% pt

3,3-Diazido-2,4-Dinitratopentane (or DADNPE). $CH_3.C(ONO_2).C(N_3).CH.CH_3$; ONO_2 N_3
mw 276.24; N 40.63%; OB to CO_2 −46.34%; mp 64–66°; bp 135° (decompn); sol in ethanol & hexane. Prepn is by slow dropwise addn of 4.2g of 3,3-diazido-2,4-pentanediol to a cold (0–5°) mixt of (1/1 molar) acetic anhydride/100% nitric acid. The temp is maintd at 5–15° for 30 mins while the mixt is stirred. Several recrystns from hexane give an 85% yield. Compd is friction sensitive, expln temp is 165°; Q_c 828.0, 822.8kcal/mole; Q_f 85.4kcal/mole; impact sensy at the 50% pt is 5.7cm using a 2kg wt in an Aberdeen Impact App with bare No 12 tools (PETN=26.7cm); impact sensy for proplnt film (78% NC/22% diazido compds) is 29–36cm (M2 film=34–36cm) at the 50% pt

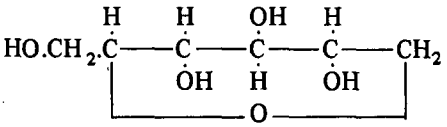
Calcn (using TIGER code) of the parameters of M2 proplnt compn using each of the diazido compds vs NG or HMX is presented in Table 1

Table 1
Calculated Properties of M2 Propellant Substituting the Diazido Compounds for Compound X

Property		Compound X Value		
Composition:		T, °K	Force, in-lbs/lb	Pc, psi
NC (13.15% N),	76.8%			
Ethyl Centralite,	0.59%			
Water,	0.30%			
Graphite,	0.30%			
Ethanol,	2.28%			
Compound X,	19.34%			
NG		3410	4.52×10^6	39600
DADNBU		3270	4.56×10^6	40500
DADNPE		3120	4.46×10^6	39800
HMX		3230	4.48×10^6	39600

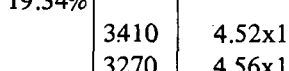
Refs: 1) Beil – DADNBU not found & DADNPE not found 2) L.P. Kuhn & A.C. Duckworth, "The Preparation of Some New Polyfunctional Organic Azides", **BRL Rept No 1607** (1972); also, the following limited distribution *Addnl Ref:* Y.P. Carignan, "Evaluation of Some New Polyfunctional Organic Azides for Propellant Applications", PATR **4592** (1973)

Polygalitol and Polygalitol Tetranitrate. *1,5-Anhydro-d-Sorbitol (3,4,5,1-Tetraoxy-1-methyl-pyrantetrahydride, Polygalitol or Polygalit (Ger).*



Colorl prisms or ndles (from ethanol); mw 164.205; mp 142–43°; bp, decomps on distn. V sol in ethanol; v sl sol in acet acid. Prepn is by prolonged heating of tannin with a 5% aq sulfuric acid soln. It is also a coprod of the hydrogenation of tetraacetyl-2-oxy-glucal (Ger) with a Pd catalyst followed by saponification with Ba hydroxide
Ref: Beil **17**, 191 & [235]
Polygalitol Tetranitrate. $OC_6H_8(O.NO_2)_4$; mw 344.25; N 16.28%; OB to CO_2 −13.94%; ndles (from ethanol), prisms (from chlf); mp 106°. V sol in acet, benz, eth and acet acid; v sl sol in cold ethanol; sl sol in hot ethanol; insol in w. Prepn is by reacting 5g of galitol with 50cc of cold mixed acid (sulfuric and fuming nitric). Polygalitol tetranitrate explds under heavy impact
Ref: Beil **17**, 191

Polyglycidyl-2,2-Dinitro-2-Fluoroethyl Ether Binder for Explosives.
Monomer: Glycidyl-2,2-Dinitro-2-Fluoroethyl Ether (2,3-Propane epoxide-2,2-Dinitro-2-Fluoroethyl Ether).



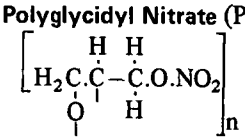
mw 210.15; N 13.33%. Prepn is by oxidn of 2,2-dinitro-2-fluoroethyl alkyl ether with peroxytrifluoroacetic acid, hydrogen peroxide and $(CS_3CO)_2O$. Yield is 58%
Polymer: **Polyglycidyl-2,2-Dinitro-2-Fluoroethyl Ether.**



mw 784–2660; OB to CO_2 −87.56%. Quant polymerization occurs in the presence of BF_3-etherate catalyst. A typical expl compn consists of 80% RDX and 20% polymer. Expl power for compn is 1667 (RDX=1859; RDX/polybutadiene=1017)
Refs: 1) Beil – not found 2) Anon, "Energetic Epoxy-Ether Monomers and Their Polymers", FrP 2196998 (1974) & CA **83**, 60349 (1975)

Polyglycidyl Nitrate (Polyurethane) Propellants (PGN). A series of proplnt compns developed by both JPL of Cal Tech and the Aerojet-General Corp in the late 1950's (Refs 2 & 3), using as the binder fuel a polyurethane resin prepd from PGN. JPL used either Amm Nitrate or Amm Perchlorate as the oxidizer (Ref 2), while Aerojet used Amm Perchlorate with plasticizers such as 4-Nitrazapentanonitrile (NPN) and 2,2-Pentanoate (TNENP) in a plasticizer-to-binder wt ratio of 0.6 (Ref 3).

Since Glycidyl Nitrate is the monomer of PGN, its properties should be noted in Vol **6**, G110-R under Glycide Nitrate
Polyglycidyl Nitrate (PGN)



mw (wash treated) 1094; mp >7330°F (decompn); autoign pt 220°; d 1.473, 1.475g/cc; RI 1.4940, 1.4949. Sl sol in benz; miscible with diethyl phthalate and NG. Prepn is by controlled polym of glycidyl nitrate in the presence of a chain propagating diol (ethylene glycol, etc) with boron trifluoride etherate as catalyst. The polymer is washed with an aq urea soln at 140°F to increase its stability. Gas evoln at STP is 0.12ml/100g/hr during a 24hr test (Warburg app); impact sensy using a JPL app with a 4lb wt is > 30 inches (NG=0.75 inches) (Ref 2). Q_c 3,127, 3,267cal/g; Q_e 730, 735 cal/g (Ref 16)

The proplnts developed by Aerojet (Ref 3) use v small amts of ferric acetylacetonate as the catalyst or polymerization agent. Proplnts developed by JPL (Ref 2) use hexamethylene diisocyanate as the copolymer of PGN, together with a nitric ester plasticizer and ferric acetylacetonate as the curing catalyst.

Refs: 1) Beil **17**, 106, [105] & {1015} 1a) W.J. Murlack et al, "Polyglycidyl Nitrate-Part 1 . . .", **NAVORD Report 2028-Part 1, NOTS 685** (1953) 1b) J.G. Meitner et al, "Polyglycidyl Nitrate-Part 2 . . .", **NAVORD Report 2028-Part 2, NOTS 686** (1953) 2) J.D. Ingham & P.L. Nichols, "High-Performance Polyglycidol Nitrate-Polyurethane Propellants", **Publ No 93**, Contract DA-04-495-Ord 18, JPL, Cal Tech, Pasadena (1957) 3) C.R. Vanneman & M.H. Gold, "Research in Nitropolymers and Their Application to Solid Smokeless Propellants", **Report No 1241**, Contract N70nr-462, Aerojet-General, Azusa (1957) 4) D.B. Bright, "Development of Polyol Prepolymers Containing High Energy Oxidizing Groups", Qrtrly Prog **Rept 1**, Contract AF 04(611)-5690, Shell Development Co, Emeryville (1960)

Polyglycol ethers. See "Glycol, Monophenylether of" and "Glycol, Tertiary ethers of" in Vol **6**, G116

Polyglycols. See "Ethyleneglycol Polymers, Nitrated" in Vol **6**, E279-R

Polyhydric Alcohols. (Polyols). An alcohol with *three* or more hydroxyl groups, each attached to a different carbon atom. They are w-sol and of sweetish taste, which tends to intensify with increasing hydroxyl content. Examples of polyols of ordn interest are listed below. Polyvinyl alcohol is considered in a separate entry as a polymer although it is defined as a polyhydric alcohol. Polyols, when nitrated, make excellent expls, proplnt binders, plasticizers, etc. Prepn can follow the procedure of Lenth & DuPuis (Ref 3) which uses a methanol suspension of either sucrose or dextrose and a special Cu-Al oxide catalyst to yield 60–65% distillable polyols at 240° and 1500psi

Refs: 1) Beil – refs found under individual compds 2) CA, under "Alcohols, Polyhydric" for compds of current ordn interest 3) C.W. Lenth & R.N. DuPuis, "Polyhydric Alcohol Production by Hydrogenolysis of Sugars in the Presence of Copper-Aluminum Oxide", IEC **37**, 152–57 (1945) & CA **39**, 1391 (1945) 4) J. Tranchant, "Poudres à Base de Nitrates de Polyglycols", MP **32**, 287–89 (1950) & CA, not found 5) W. Hensinger, "Procedure for Preparation of Polyalcohols", FrP 1106688 (1955), MP **38**, 467–68 (1956) & CA, not found 6) Kirk & Othmer **1** (1962), 569–98 7) J.A. Monick, "Alcohols – Their Chemistry, Properties and Manufacture", Reinhold, NY (1968), 365–445 8) C.A. Hampel & G.G. Hawley, "Glossary of Chemical Terms", Van-Nostrand-Reinhold, NY (1976), 217

Addnl Refs: 1) K.S. Warren, "Study Nitrates of Polyhydric Alcohols as Explosives", PATR **1103** (1941) 1a) D.B. Bright et al, "Development of Polyol Prepolymers Containing High Energy Oxidizing Groups", Report No **S-13843**, Contract AF 04(611)-5690, Shell Devel Co, Emeryville (1961) (limited distribution) 2) A.D. McElroy, "Basic Approach to Incorporation of NP Propellants", Rept No **RPL TDR 6448**, Contract AF 04(611)-9059, Callery Chem Co, Phila (1964) 3) Urbański **2** (1965), 138–40 4) G.G. Esposito, "Determination of Polyols in Alkyd and Polyester Resins by Gas Liquid Chromatography", Rept No **CCL-214**, APG (1966)

Selected polyhydric alcohols which are valuable in ordn applications, either as parent compds for the manuf of energetic matls, as

proplnt plasticizers, or as utilized in other ancillary functions germane to ammo are presented below:

Butanetriol and Derivatives. See Vol **2**, B370-R to B371-R

iso-Butanetriol and Derivatives. See Vol **2**, B371-R to B372-R

Desoxyinositol and Derivatives. See Vol **3**, D91-R to D92-L

Diglycerol and Derivatives. See Vol **5**, D1261-L to D1262-L

Dipentaerythritol and Derivatives. See Vol **5**, D1407-L to D1413-L

Dulcitol and Derivatives. See Vol **5**, D1567-R to D1568-L

Erythritol (and Derivatives). See Vol **5**, E123-L to E125-L

Glucose and Derivatives. See Vol **6**, G83-R to G84-R

Glycerol or Glycerin and Derivatives. See Vol **6**, G87-R to G93-R

An addnl glycerol compd used as a proplnt binder is presented next

Ethylene glycol-1,6-Dichloro-2,5-Diazahexane-Glycerol-Copolymer. D 0.065lb/inch^3. Prepn is by reacting 0.6 mole of 1,6-dichloro-2,5-dinitro-2,5-diazahexane with 0.56 mole of ethylene glycol and 0.11 mole glycerol by stirring for 24 hrs at 50–60° under partial vac. The copolymer formed (19.2) is combined with Al (12.0), HMX (65) and hexamethylene diisocyanate (3.8%) to form a proplnt with a burning rate of 0.21inch/sec at 1000psi, and a sp impulse of 265

Ref: T.F. Comfort & R.J. Legare, USP 3808276 (1974) & CA **81**, 153482(1974)

Hydrocellulose. See Vol **7**, H213

Mannitol and Derivatives. See Vol **8**, M13-L to M16-R

Methyl Glycoside and Its Tetranitrate. See Vol **8**, M106

Methyl Trimethylolmethane and Derivatives. See Vol **8**, M116-R to M118-L

Metriol and Its Derivatives. See Vol **8**, M120-R to M122-L

Pentaerythritol and Its Derivatives. See Vol **8** (qv)

Phloroglucinol and Its Derivatives. See Vol **8** (qv)

Polyvinyl Alcohol and Its Derivatives. See Vol **8** (qv)

Poly hydrogen Cyanide (Azulmic Acid). Anhydrous HCN is stable at or below RT (See Vol **2**, C167-L under **AC**) if inhibited with 0.1% sulfuric acid. However, in the absence of inhibitor exothermic polymerization occurs. At 175°, *explosively* rapid polymerization occurs after an induction period of 27 mins. If the temp reaches 184°, explosively rapid polymerization occurs *immediately*. A trace of alkali ($2x10^{-5}$ mole NaOH/g HCN) at 100° induces expl polymerization in 304 mins. If a trace of w is present at RT, ammonia is released from the HCN, which polymerizes autocatalytically producing a modified polymer. Polymerization is accelerated by any matl capable of accepting a

proton from HCN, such as metallic hydroxides, cyanides, cyanates, ammonia, tertiary amines and baked Vycor glass. Acceleration also results from any energy input that ionizes the HCN, such as ultra-violet light in aq soln and ionizing radiation in both the liq and gas phases. Indeed, tritium cyanide polymerizes rapidly because of self-radiolysis (Ref 7). The Q_{poly} is 377cal/g(Ref 2)

A lab procedure reported in Ref 7 yields an almost theoretical compn of $(HCN)_x$. Liq HCN dild with an equal wt of chlf is polymerized by reacting with 5 wt % of tributylamine for eight hrs at 25° in the absence of w and air. The polymer produced is comprised of several compns. The simplest is the *tetramer* or *Diaminomalonitrile*, $(HCN)_4$; lab yield is 15%; mp 184° (decompn). Sol in boiling w. A much more complicated, w insol, cryst material is also produced

The polymer, mixed with cyanogen, has been proposed for use as a rocket fuel (Ref 7)

Refs: 1) Beil – not found 2) E.H. Gause et al, JChemEngrgData **5**, 351 (1960) & CA **55**, 18112 (1961) 3) W.L. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, NY (1964), 104 4) F.A. Cotton & G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publ, NY (1966), 312 5) Urbański **3** (1967), 134 6) Sax (1968), 822 7) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vol **7**, J. Wiley, NY (1970), 568–73

Polymeric Peroxides. See under "Peroxides" in this Vol

Polymerization, Violent. Violent monomer polymerization has caused a number of serious explns. Present in Table 1 below is a summary of data pertinent to the causation of these explns, extracted from the ref. The monomers listed may be found under appropriate entry titles thruout the Encycl

Ref: M. Harmon & J. King, "A Review of Violent Monomer Polymerization: A Selected Literature Survey", Report No **USCG-D-159-75**, Contract DOT-CG-51, 765-A, Operations Research, Inc, Silver Spring (1974)

Polymerized Acetaldehyde. See Vol **1**, A14-L to A15-L under *"Paraldehyde . . ."*

Polymerized Alcohols. Polyhydric alcohols (qv) such as pentaerythritol, sorbitol and glycerin can be used as the polyol component of polyethers (qv) which are used as expl and proplnt binders. Polyoxypropylene derivs of sorbitol have been employed extensively as components of polyurethane resins (qv), also employed as a proplnt binder

Ref: J.A. Monick, "Alcohols – Their Chemistry Properties and Manufacture", Reinhold, NY (1968), 414

Polymerized Allyl Type Alcohols. See Vol **1**, A135-R to A136-L. A patented process (Ref) obtains polymers by heating allyl alc, or homologs, at 50–100° in the presence of oxygen and/or an oxygen-yielding catalyst such as a peroxide, perchlorate or persulfate. Nitration of these polymers has yielded some expls

Ref: Anon, DutchP 66784 (1950) & CA **45**, 5451 (1951)

Polymerized Formic Aldehyde. See Vol **6**, F164-L to F165-L under "Formaldehyde Polymers"

Polymerized Glycerin. A prod first obtd by Wohl (Ref 1) by heating glycerin to 130–60° with a small quan of sulfuric acid. The viscous prod contained glycerin (30–40%), diglycerin (54–66%), and polyglycerin (4–6%), becoming an oil on nitration (Ref 3). Will and Störer (Ref 2) improved the process by boiling glycerin at 290–95° for 7–8 hrs with only the addn of about 0.5% soda or alkali sulfides. The yield is 60% diglycerin which can be vac distd from the prod mixt and nitrated to the expl tetranitrate (Ref 4). See also "Diglycerol and Derivatives" in Vol **5**, D1261-L to D1262-L

Refs: 1) A. Wohl, GerP 58957 (1890) 2) Will & D. Störer, SS **1**, 231 (1906) 3) P. Naoúm, "Nitroglycerin", Williams & Wilkins, Baltimore (1928), 199 4) Urbański **2** (1965), 138–40

TABLE 1
A SUMMARY OF DATA PERTINENT TO VIOLENT POLYMERIZATION

Monomer & Formula	Explosion Causing Environment				Explosion Prevention Techniques	Heat of Polymerization in kcal/mole	Ignition Temp, °C	Polymerization Techniques
	Other Mats	Gas (es)	Press, psi	Temp, °C				
Acrylic Acid, $CH_2CHCOOH$	Free Radical Formers such as OH^- Ion	Acrylic Acid Vapor	6000 kg/cm^2	> 75	Inhibitor–Methyl Ether of Hydroquinone-200ppm Storage in a cool, well ventilated area	18.5	429	Heterogeneous Free–Radical with a catalyst such as Azodiisobutyronitrile
Acrylonitrile, CH_2=CHCN	Bromine addn or a trace of alkali	Acrylonitrile Vapor	6000 kg/cm^2	> 200	Ammonia or Aromatic Amine as an inhibitor	17.3	481	Sensitive to light, strong bases or temps > 200°
Butadiene CH_2=CHCH=CH_2	Cu Acetylide, Vinyl Acetylene & Ethylene	Air (Peroxides)	> 300	114	Inhibitor – t-Butyl Catechol – 115ppm	$Q_{Activation}$ 12.0	429	Self-polymerization above RT or press
Ethylene CH_2=CH_2	Acetylene, Cu, Fe, Al, W, Pt, & petr oil	Air (Oxygen) plus Ethylene Vap Limits: Lo-2.75–4.1% Hi-13.7–36.3%	<100mm (vacuum)	500–700	No sparks, Ethylene content over 25%, No Oxygen, and use of inert gas blanket	–	450	Use of Alkylaluminum compds
Ethylene Oxide, H_2COCH_2	Acetylides, Fe, Sn, Organic Acids, Amines, Al oxides & OH^- Ions	Ammonia, H, HCN	> Ambient	> 30	Inhibitor–Phenothiazine, Keep temp below 30° & avoid active catalysts. No sparks	$Q_{Activation}$ > 445°=19.7 < 445°=36.4	429	Use of catalysts–Fe, Sn, Organic Acids and Ammonia
Methyl Acrylate CH_2=CHCOOCH_3	Non-inhibitors such as Biphenyl, Bibenzyl, Triphenyl, etc	Methyl Acrylate Vap plus air	> Ambient	> 120	Inhibitor–Hydroquinone or Methyl Ether of Hydroquinone 10-20ppm. Store Store below 10°; no inert atmosphere. No sparks	18.58–18.8	463	Self polymerizing; above ambient press & temp accelerates polymerization
Methyl Methacrylate CH_2=C(CH_3)COOCH_3	Impure Methyl-Methacrylate	Vap in Air 2.1 to 12.5%	> Ambient	> 110	Inhibitor–Hydroquinone or Methyl Ether of Hydroquinone. Shield from light & avoid sparks. Store in cool place	13.3–13.8	421	Self-polymerizing; initiated by visible light at 20 to 40°

(continued)

TABLE 1 (continuation)
A Summary of Data Pertinent to Violent Polymerization

Monomer & Formula	Explosion Causing Environment				Explosion Prevention Techniques	Heat of Polymerization in kcal/mole	Ignition Temp, °C	Polymerization Techniques
	Other Mats	Gas(es)	Press, psi	Temp, °C				
Styrene $C_6H_5CH=CH_2$	Alkali Peroxy compds	Vap in Air 1.1 to 6.1%	> Ambient	> Ambient	Inhibitor–Methyl Ether of Hydroquinone–10-15ppm, Phenol Subst-Hydroxyl Amine, etc. Store below 70°F. Avoid sparks in vap/air mixt	17.4–17.8	490	Soln polymerization catalyzed with w or Ti tetrachloride. Also self polymerization
Vinyl Acetate $CH_3COOCH=CH_2$	OH compds, HCN, Halides, Halogens, Mercaptans, Amine, Silanes & Oxygen	Vap in Air 2.6 to 13.4%	> Ambient	> Ambient	Inhibitor–Methyl Ether of Hydroquinone or 3-5ppm Diphenylamine. Store in a dry, cool place & shield from light & impurities	20.9–21.5	402; 427	Free-radical polymerization initiated by Benzoyl Peroxide
Vinyl Chloride $CH_2=CHCl$	Acrylates, Styrene, W, or oxidizing agents. Forms the Polyperoxide which decomps exothermally at RT	Air; Vap Monomer. In Air: 4.0 to 22.0% or 3.6 to 33.0%	> Ambient	> Ambient	Inhibitor–Phenol (25-100 ppm). Store under press in a cool place. No sparks	22.9	472	Self-polymerizes, catalyzed by oxygen
Vinylidene Chloride $CH_2=CCl_2$	Monomer forms unstable peroxides by autooxidation; therefore, no oxidg agents or w	Air; Vap Monomer In Air: 7.0 to 16.0%	> Ambient	> Ambient	Inhibitor–Methyl Ether of Hydroquinone (100ppm) Transport & store under inert gas in a cool, dry place. No sparks	–18.0	570	Self-polymerizing, easily copolymerizes with with Acrylates & Styrene. Polymerization catalyzed by light or w

Polymers, Explosive. See under individual names. Generally, explosive polymers are synthetic substances composed mainly of low mw molecules containing explosophores such as peroxide linkages, nitro, nitrate, azo groups, etc (see under "Auxoexplose . . ." in Vol **1**, A513-L to A514-R). The nomenclature used is identical to that used for non-expl polymers; viz, expl polymers are approx multiples of low mw units called *monomers.* An expl compd of higher mw is produced in a process called *polymerization.* The polymer so produced may have combined several varieties of both expl and non-expl monomers such as organic acids and alcohols. When only two monomers of any type are used, the resulting compd is called a *copolymer;* if three varieties, *terpolymer,* etc. Examples of expl polymers can be found under **"Nitropolymers"** in this Vol, N138-R ff, Polyglycidyl Nitrate (qv), and Petrin Acrylate (qv)
Ref: 1) Urbański **1** (1964), 1–5

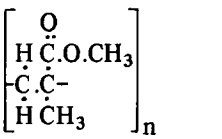
Polymers of Dextrose. See in Vol **5**, D1116

Polymethylmethacrylate (Lucite, Plexiglas, Crystallite or PMMA). A thermoplastic translucent resin of the acrylate resin family. The *monomer,* methyl methacrylate;

$CH_2:C(CH_3).\ddot{C}.O.CH_3$; has the following properties: mw 100.11; colorl mobile liq, mp −50°; bp 101.0°, 54° at 148mm; d 0.9369 g/cc at 25/4°; RI 1.4115 at 25°, 1.4142, 1.4138 and 1.4149 at 20°. Sol in hexane, hydrogen peroxide and a mixt of w and methanol to form a ternary system; sl sol in w and glycerin; insol in formamide. Prepn is by distn of methyl-[α-Chlorisobutyrate] in the presence of Zn

The monomer undergoes *explosively violent* polymerization when uninhibited and catalyzed by heat, radicals and visible light. For information on the conditions conducive to the violent polymerization of methyl methacrylate see "Polymerization, Violent" in this Vol

The acute oral LD_{50} for rats is 7900mg/kg (Ref 6a) and the acceptable air tolerance level is 100 ppm or 410mg per m^3 of air (Ref 5) The properties of the *polymer,* PMMA,



are as follows: mw approx $1x10^6$; OB to CO_2 −191.79%; optically clear atactic or predominantly syndiotactic solid; softening pt 130°; d 1.18g/cc; RI 1.49. Sol in acet, eth acetate, ethylene dichloride, carbon tetrachloride, toluene, acetic acid, and formic acid; insol in w, and many aq inorganic reagents at RT such as hydrochloric acid or amm hydroxide (Refs 2a, 3 & 6a).

Prepn by emulsion polymerization, according to Resnick (Ref 3), is as follows: "A 5-liter 3-neck flask is used. The center neck is fitted with a mercury-sealed stirrer having a sidearm gas inlet. One side neck carries a standard-taper thermometer and the other a "Y" tube, one arm for a condenser and the other for taking samples. Two kg of distilled water is placed in the flask, and the water is brought to a boil by means of a Glas-Col mantle. The mantle is removed and the water allowed to cool to room temperature under an atmosphere of nitrogen. Making certain there is a positive nitrogen pressure in the flask, it is then opened and 10 grams of "Duponol" ME (an emulsifier), 1 gram of $K_2S_2O_8$, and 1 kg of methyl methacrylate containing 1 gram of dodecyl mercaptan is added in that order. With good stirring the flask is then heated at 40–42°. Samples of about 5ml of latex are withdrawn periodically by pipette, and the total solids determined by drying under infra-red. At the end of 2.5 hours the yield should be 88%. At that point the reaction is stopped by shutting off the nitrogen, cooling the flask to ambient temperature, and adding hydroquinone. To precipitate the polymer from the latex, the latex (one volume) is added drop by drop to 3 volumes of ethanol with rapid stirring. About 1/3 volume of water (based on ethanol) is then added and stirring continued for 5 minutes. The mixture is placed on a steam bath, warmed to 45–48°, and then allowed to stand until the polymer is completely coagulated. The polymer is filtered, and washed with a 70/30 mixture of ethanol and water by stirring for 15 minutes. After being filtered again, the polymer is washed 4 times with 1-liter portions of water,

with a filtering after each washing. The polymethyl methacrylate is then placed in glass trays and dried at 58° for 18 hours. The dried polymer is crushed down and re-dried at 53° under vacuum for 7 hours"

Methyl methacrylate can also be polymerized by radiation using either a cobalt-60 source or accelerated electrons at dose rates up to 3 megarads/sec. The activation energy for the electron beam polymerization is about 7.0kcal/mole (Ref 12). Radical polymerization can also occur using diisocyanates or hydroperoxides as the initiating species (Ref 15)

Block copolymers with materials such as a polyester (PE) (qv) can be prepd by the reaction of diisocyanate-terminated polyesters with hydroxyl-terminated PMMA according to Wilkes and Grezlak (Ref 21). The basic structure was found to be PMMA-PE-PMMA, with a mw of from 7500 to 47000. The purpose of the work was to produce a stronger copolymer (in terms of stress-strain) by tailoring the amt of each monomer used to produce the copolymer

Further information on polymerization can be found in Refs 2a & 6a

PMMA finds ordn usage in several areas: in ballistic or impact shields for missiles or airplanes; also as windows, windshields or canopies in aircraft (Refs 7 and 22); as a Laser Q switch host using an organic Ni complex dye (Ref 22); and in proplnts as fuel (with Al and NG as cofuels – Ref 20) and Amm perchlorate or K perchlorate as oxidizers (Refs 2, 4, 8–11, 13,14 & 16–20). Also see under "Aeroplex Propellants" in Vol **1**, A108-R and under "Composite Propellants" in Vol **3**, C464-L to C474-L

Refs: 1) Beil **2**, [398] and {1279 & 1283} 2) P.J. Blatz et al, "Research in Nitro Polymers and Their Application to Solid Smokeless Propellants", Rept No **622**, Contract N7onr-462, Aerojet Engrg Corp, Azusa (1952) 2a) C.E. Schildknecht, "Vinyls and Related Polymers", J. Wiley, NY (1952) 3) A. Resnick, "Preparation of Polymethyl Methacrylate", PATR **2182** (1955) 4) Urbański **3** (1967), 380–81 5) Sax (1968), 929 6) C.L. Segal et al, Eds, "Polymers in Space Research", Marcel Dekker, NY (1970) 6a) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vols **1, 2, 4, 12, 13** & **15**, J. Wiley, NY (1970) 7)J.L. Illinger et al, "Effect of Interlayer on Impact Resistance of Acrylic/Polycarbonate Laminates", AMMRC, Watertown (1972) 8) L.I. Aldabaev et al, "The Effect of Solid Oxidant Additives on Diffusion Burning of Polymers in Air", **FTD-HT-23-642-74** (1972) 9) O.I. Leipunskii & A.A. Zenin, "The Effect of a Catalytic Agent on the Characteristics of the Combustion Zone of a Condensed Substance", Rept No **FTD-HT-23-628-74** (1973) 10) V.S. Hikiforov & N.N. Bakham, "The Effect of Aluminum Additives on the Operational Effectiveness of the Catalytic Combustion Agent Fe_2O_3", Rept No **FTD-HT-23-627-74** (1973) 11) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants", JSciIndRes **32** (6), 279–99 (1973) & CA **80**, 121565 (1973) 12) C.C. Allen et al, "Studies in Radiation-Induced Polymerization of Vinyl Monomers at High Dose Rates. II. Methyl Methacrylate", JAppPolymSci **18**, 709–25 (1974) & CA **81**, 4309 (1974) 13) O.P. Korobeinichev et al, "On the Mechanism of Catalyst Action on the Combustion of Condensed Systems", Rept No **FTD-HT-23-1222-74** (1974) 14) L.A. Romodanova & P.F. Pokhil, "Effect of Metal Additives and Their Borides on Combustion Rate of Mixed Systems", Rept No **FTD-HT-23-1237-74** (1974) 15) G.L. Wilkes, "Synthesis of Novel Polymers with Unusual Properties by Radical Polymerization", USARO Rept, Contract DA-ARO-D-31-124-73-G27, Princeton Univ, Princeton (1974) 16) O.P. Korobeinichev et al, "Structure of the Extinguished Surface of a Catalyzed Ammonium Perchlorate-Poly(Methyl Methacrylate) Mixture", FizzGoreniyaVzryva **10** (3), 345–53 (1974) & CA **81**, 172449 (1974) 17) C. Shabani et al, "Hybrid Combustion of Poly (Methyl Methacrylate)", CahTherm (Fr) **4**, 57–61 (1974) & CA **82**, 158337 (1975) 18) R.M. Price, "Propellants Plasticized with High Energy Compounds and Having High Energy Polymers as Binder", USP 3829336 (1974) & CA **82**, 75150 (1975) 19) V.S. Ilyukhin et al, "Role of Heterogeneity of the Composite Solid Fuel in the Mechanism of Pulsating Combustion", FizGoreniyaVzryva (Russ) **11** (3), 498–501 (1975) & CA **83**, 118018 (1975) 20) V.S. Ilyukhin et al, "Low-Frequency Pulsations of Gunpowder Combustion in Vacuum", FizGoreniyaVzryva (Russ) **11** (4), 660–62 (1975) & CA **83**, 208114 (1975) 21) G.L. Wilkes

& J.H. Grezlak, "The Preparation and Physical Properties of Polyester-Poly(Methyl Methacrylates) Triblock Copolymers", TR for Jan 1–March 1, 1975, Contract N00014-67-A-0151-0011, Princeton Univ, Princeton (1975)
22) R. Wisnieff & D. Longo, "Laser Cartridge Concept Development Study", Rept No **ECOM-74-0376-F**, Contract DAAB07-74-C-0376, United Technologies Corp, Norwalk (1976)
23) S.A. Marolo, "Conference on Aerospace Transparent Materials and Enclosures", **AFML-TR-76-54** (1976)

Polynitramides. Several compds of the type $C_6H_{11}[NNO_2CH_2CH_2]_nNNO_2C_6H_{11}$, where n=1 to 4, were prepd and examined by Harpham et al (Ref 1). These dicyclohexylethylene-polynitramides are high melting (171.5° avg), highly insol solids, exceptionally difficult to detonate, which do not respond to the Granchimont test for the nitramino group

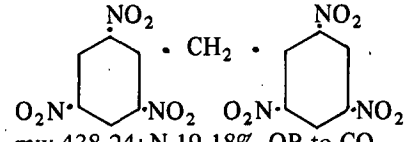
Other polynitramides have been synthesized by Frankel and Klager (Ref 2). These compds are of the type $RC(O)NHCH_2[AN(NO_2)]_nCH_2A'NHC(O)R'$, where R and R′ are alkyl radicals, A and A′ are alkylene radicals, and n is 1–4. Their prepn consists of condensing the appropriate polynitrodiamines derived from nitrazadiisocyanates and strong mineral acids with acid anhydrides. These compds are considered by their inventors to be suitable for use as the main expl charge in shells, missiles and blasting charges, or as O donors and modifiers for proplnt fuels. To date, little ordn use has been found for them

For more information on "Nitramides", see this entry in this Vol, N28-R to N29-L
Refs: 1) J.A. Harpham, et al, "Linear Secondary Polynitramides (Polynitramines)", JACS **72**, 341–43 (1950) & CA **45**, 1048 (1951) 2) M.B. Frankel & K. Klager, "Polynitramides", USP 2967198 (1961) & CA **55**, 7842 (1961)

Polynitroamines. A series of compds developed by Frankel and Klager (Ref) as expls and O donors in proplnt fuels. These compds are prepd by condensing β-geminal polynitro alcohols with ammonia or polynitro amines. The compds produced are of the type, $RC(NO_2)_2(CH_2)_nNH(CH_2)_xC(NO_2)_3$, and yield Pb block values of approx 140 (TNT=100) and Ballistic Mortar values of approx 140 (TNT=100). See also "Amines, Nitrated and Nitrited" in Vol **1**, A174-R to A177-R
Ref: M.B. Frankel & K. Klager, USP 2978507 (1961) & CA **55**, 15933 (1961)

Polynitrocellulose. See under "Cellulose Nitrates" in Vol **2**, C100-L to C126-L

Polynitrodiphenylmethanes. See "Diphenylmethane and Derivatives" in Vol **5**, D1464-L to D1466-L. Hexanitrodiphenylmethane had not been synthesized as of 1966. However, since then the work of Shipp and Kaplan (Ref 2) in 1976 allows the following entry to be made:
2,2′,4,4′,6,6′-Hexanitrodiphenylmethane.



mw 438.24; N 19.18%, OB to CO_2 –62.07%. Prepn is by treating TNT in tetrahydrofuran with a mixt of methanol-KOH, and then with picryl chloride in the presence of Me_2SO. The prod of this step is then oxidized with chromic oxide in a nitric acid–oleum mixt to yield the polynitrodiphenyl methane. The compd is expl
Refs: 1) Beil – not found 2) K.G. Shipp & L.A. Kaplan, "Substituted Polynitrodiphenylmethanes", USP 3941853 (1976) & CA **84**, 150325 (1976)

Polypropylene. The lowest density homoplastic obtd by stereoselective catalysts
Monomer
Propylene(Propene). $CH_3.CH:CH_2$; mw 42.08; colorl gas; mp –185.25°; bp –47.4°; d 0.5193 at 20/4° (liq at satn press); RI 1.3567 at –40°. V sol in acetic acid, ethanol and w. Prepn is by dehydration of propan-2-ol over Al oxide at 330°. It is also obtd as a pyrolysis product of propane and as a fraction of petr well head gases

Propene has a Q_c of 460.47kcal/mole; the expln limits with air are 2.0 to 11.1% (Ref 2); it has an autoign temp of 927°F. Under unusual conditions, such as 955 atms press and

327°, propene has been known to expld (Ref 5a)

Propene is a simple asphyxiant. Rapid evapn from the liq can cause skin burns due to its refrigerant effect on tissue

For the "Propenes and Derivatives" of ordn interest, see under that title in this Vol

Polymer

Polypropylene was first produced commercially in Italy and called "Moplene" (Ref 2),

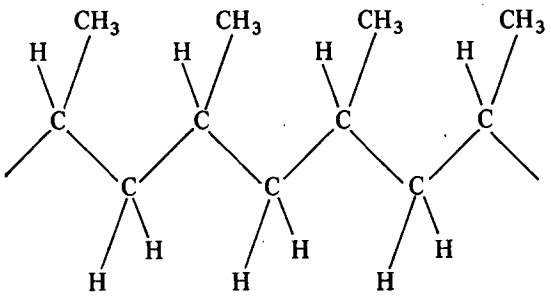


Fig 1 Schematic diagram of an isotactic polypropylene chain in the extended conformation (Ref 4)

$(C_3H_6)_n$, mw > 40,000; crystn wh powdr; mp 165–70° (isotactic); d 0.90–0.91g/cc; max breaking strength 300–50kg/cm^2; impact strength (extension) 80kg/cm/cm^2, (compression) 600–700kg/cm/cm^2; max useable temp is 150°. Sol in aromatic hydrocarbons such as benz or toluene at temps > 80°; insol in all organic solvents at RT. Prepn is by the use of Ziegler-type catalysts at an optimum temp of 120° (Refs 2 & 3). The polymerization is accomplished using a mixt of 30/70 (liq) propylene/propane or pure propylene dissolved in n-heptane with an Al alkyl (triisobutyl or trihexyl) titanous chloride catalyst (Ref 2)

Polypropylene (film) has a Q_c of 11074.5 cal/g (Ref 5)

The ordn uses for polypropylene are varied. It is used in the fabrication of personnel body armor (Refs 6 & 7); in slurry-type expls for the demolition of concrete structures (Ref 11); as a microporous hydrazine-air (cathode) separator in fuel cells (Ref 9); as a proplnt binder matl, particularly in caseless ammo, (Refs 5 & 8); and as a candidate to act as a proplnt aging inhibitor for the 155mm RAP round (Ref 10)

Refs: 1) Beil **1**, 196, (82), [167], {677} and ⟨725⟩ 2) A.V. Topchiev & V.A. Krentsel, "Polyolefines", Pergamon Press, NY (1962), 6, 73 thru 89 3) S. Hoshino et al, "The Kinetics of Crystallization of Polypropylene Fractions and Polybutene-1-Part I", **ONR Tech Rept 43**, Contract Nonr 3357(00), Univ of Mass, Amherst (1962) 4) A. Opschoor, "Conformations of Polyethylene and Polypropylene", Rotterdam Univ Press, NY (1966), 31 5) G.C. Sinke & D.R. Stull, "Investigation of the Thermodynamic Properties of Propellant Ingredients", Rept No **AFRPL-TR-68-80**, Contract F04611-67-C-0025, Dow Chem Co, Midland (1968) 5a) Sax (1968), 1035 & 1059 6) M.W. Olson & G.H. Brice, "Bicomponent and Biconstituent Fibers in Ballistic Fabric for Personnel Armor", Rept No **USA-NLabs, C/-PLSEL-TR-71-48CE, TS-173**, Contract DAA17-70-C-0032, Uniroyal Inc, Wayne (1971) 7) W.D. Claus et al, "Evaluation of the Mechanical Properties of Yarns for Ballistic Applications", Rept No **USA-NLabs, C/PLSEL-TR-73-60-CE, 113**, Contract DAA G17-70-C-0086, Fabric Research Labs Inc, Dedham (1973) 8) A.D. Craig & C.A. Luksch, "Propellant Charge for Caseless Ammunition", USP 3723203 (1973) & CA **80**, 49963 (1974) 9) W.A. Armstrong, "Operation of Air Cathodes in the Presence of Hydrazine", Rept No **DREO-TN-74-13**, Def Res Est, Ottawa (1974) 10) W. Brenner & B. Rugg, "Feasibility Studies Relative to using New Polymers and Plastics as Inhibitors to Replace Composition Presently Being Used With Rocket Propellant Grains of 155mm HE RAP (Rocket Assisted Projectile)", Final Rept – May-Dec '75, Contract DAAA21-75-C-0267, NY Univ, NY (1975) 11) T. Takayama, JapP 7518052 (1975) & CA **83**, 195956 (1975) 12) Chem-RubHdbk (1975), C-457

Polynitrostilbenes. See under "Nitrostilbene" thru ". . . HNS . . ." in Vol **5**, D1454-L thru D1457-R, and under HNS in Vol **7**, H162-L

Polystyrene. A thermoplastic used as a binder and fuel in expls and rocket proplnts. See "Plastic fuels" (Vol **3**, C465-L) under "Composite Propellants"; also "Dinitropolystyrene" in this Vol, N143-L to N144-R under "Nitro Polymers"; and "Propellants, Solid", also in this Vol

Addnl Refs: 1) B.I. Stoops & C.L. Moder, "Development of Plastic Rocket Propellant", PATR **1655** (1947) 2) E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR **2062** (1954) 3) B.J. Zlotucha et al, "Characteristics of Polystyrene-Bonded RDX (Pb-RDX)", PATR **2497** (1958) 4) G.D. Clift & K. Ablas, "Evaluation of Mononitropolystyrene and Dinitropolystyrene as Explosives", **CRDLR 3009** (1960) 5) N.W. Ryan et al, "Thermal Effects of Composite-Propellant Reactions", Tech Rept, AF Grants AFOSR 40-66 & 40-67, Univ of Utah (1967)

Polysulfide Polymers. These polymers are made up of aliphatic hydrocarbon units connected by di-, tri- or tetrasulfide links. The synthetic rubber found useful in ordn has hydrocarbon units linked by either O or formal segments. The polymers are usually prepd by the condensation of a suitable organic dihalide, usually the chloride, with aq Na polysulfide. According to Ref 8, the most practical organic dichloride is dichlorodiethylformal; viz, *Bis[2-chlor-ethoxy]-methane* (Dichlorodiethylformal or Formaldehyde-[bis-(2-chlor-ethyl)-acetal]); $CH_2Cl.CH_2.O.CH_2.O.CH_2.CH_2Cl$; mw 173.06; liq; bp 218.1°, d 1.2339g/cc; RI 1.4540. Sol in and forms an azeotrope with w. Prepn is by treating a mixt of paraformaldehyde and 2-chlorethanol with aq HCl (Ref 1)

Polymer

Liquid Polysulfide (Pre) polymer. $HS-[C_2H_4.O.CH_2.O.C_2H_4SS]_n-C_2H_4.O.CH_2.O-C_2SH$; mw (range of avgs) 500 to 7500; mobile amber liq; d 1.27 to 1.31g/cc. Sol in a wide variety of solvents such as alcohols, ethers, ketones, etc. Prepn is by treating dichlorodiethylformal with Na polysulfide (Refs 2, 3, 4 & 8). The **Thiokol LP-3** (Thiokol Chem Corp) version of the liq polymer is prepd by the reaction of 98 mole % dichlorodiethylformal and 2 mole % trichloropropane with an excess of Na polysulfide. The aq layer is treated with Na hydrosulfide and Na sulfite, bringing about a controlled cleavage of the high mw polymers to liq prepolymers of low mw (Ref 15). For information on **Thiokol** Proplnts see "Composite Propellants" in Vol **3**, C467-L and "Propellants, Solid" in this Vol. The liq prepolymer ignites upon contact with dry Ca peroxide (Ref 11). Open cup fire pt is 465°F and flash pt is 418°F (Thiokol LP-3, Ref 10)

The liq prepolymers are *cured* or polymerized by heating them with oxides or peroxides such as ZnO, Zn peroxide, PbO, or p-quinone dioxime. A high mw cryst polymer is produced which has a useful temp range of −65° to 350°F, an outstanding resistance to swelling in oils and solvents such as carbon tetrachloride, and an impermeability to vapors, gases, ozone, oxygen and light (Ref 4)

By far the greatest ordn application for polysulfide polymers is in **Thiokol** proplnts (Refs 1, 2, 4, 5, 8, 14 & 15). However, other applications exist, ie, in expls (Refs 9 & 16), in other types of proplnts (Ref 12), and in pyrots (Thiokol LP-2, Ref 13)

The US Mil Spec covering liq polysulfide polymers for use in the 3.0-inch, Mark 32 Mod 0 Rocket Motor, **MIL-P-23702 (WEP)**, (10 May 1963) contains the following requirements and criteria (Tables 1 and 2)

Table 1
Chemical Requirements

Characteristic	Requirement	
	Min	Max
Mercaptan (as SH), % [a]	5.0	6.5
Moisture, % [b]	—	0.1
Acidity (of w extract), pH [c]	5.8	8.9

a – By iodometric titration
b – By absorption of the w using dry toluene from the polymer followed by distn of the toluene plus w into a cold finger moisture measurement trap
c – By electrometric detn of pH

Table 2
Physical Requirements for the Liquid Polymer and Cured Compounded Test Sheet

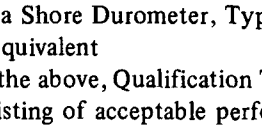
Characteristic	Requirement	
	Min	Max
Viscosity of Liq Polymer, Cps [a]	1300	1800
Tensile Strength, psi [b]	350	–
Tensile Stress at 500% elongation, psi [c]	200	300
Ultimate Elongation, % [d]	800	1100
Hardness, Shore A [e]	32	38

a – By means of a Brookfield Helipath, Model RFV viscometer at 80°F (Brookfield Engrg Co, Stoughton, Mass)
b – By means of an Instron testing machine
c – Ibid
d – Ibid and calcn
e – By means of a Shore Durometer, Type A, or approved equivalent

In addition to the above, Qualification Tests are required consisting of acceptable performance when incorporated with other satisfactory matls in a test batch of N-26 Propellant Composite [Spec **MIL-P-23735 (WEP)**]

Refs: 1) Beil **1**, 595, {2573} & ⟨3028⟩ 2) E. Müller, Ed, "Methoden Der Organischer Chemie" **9**, G Thiema Verlag, Stuttgart (1956), 91 3) C.E. Schildknecht, "Polymer Processes", Interscience, NY (1956) 4) H.L. Fisher, "Chemistry of Natural and Synthetic Rubbers", Reinhold, NY (1957), 94 thru 97 5) W.W. Howard & B.J. Alley, "Determination of Ferric Oxide, Aluminum, and Magnesium Oxide in Polysulfide Propellants", **ARGMA TR-1D2R** (1960) 6) Anon, "Polysulfide, Polymer, Liquid (For Rocket Motor, 3.0 Inch, Mark 32 Mod 0)", **MIL-P-23702 (WEP)** (1963) 7) A.V. Tobolsky, "Polymer Sulfur and Other Polysulfide Polymers", ONR Tech Rept **RLT-80**, Contract Nonr-1853(07), Princeton Univ, Princeton (1964) 8) Urbański **3** (1967), 368–80 9) T. Takei & S. Fujihira, JapP 7008676 (1970) & CA **73**, 68164 (1970) 10) H. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vol **5**, J. Wiley, NY (1970) 11) Anon, "Manual of Hazardous Chemical Reactions–1971", NFPA No **491M** (1971), 57 12) N.G. Burton, "Effects of Propellant Composition Variables on Acceleration-Induced Burning-Rate Augmentation of Solid Propellants", **NASA TND-6923** (1972) 13) G.W. Hastings, USP 3706611 (1972) & CA **78**, 113580 (1973) 14) H.R. Ferguson, "Composite Polysulfide Propellant Cured with a Monofunctional Mercaptan", USP 3706610 (1972) & CA **78**, 149439 (1973) 15) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants", JSciIndRes **32** (6), 279–99 (1973) & CA **80**, 121565 (1973) 16) W.O. Munson, "Specialty Explosive Development", ProcIntConfCentHighEnergyForm **4**, 7.1 (1973) & CA **82**, 142284 (1975)

Polytetrafluoroethylene (Teflon, PTFE, Fluon, Fluoroflex, Polytef, TFE). A thermoplastic homopolymer composed of long chains of $-CF_2-$ units. Colorl to grey powder, flakes or



$n \approx 1000$

grains. Grayish white transparent thin sheets. Useful temp range –75° to 250°. Gels at 325° and at 400° reverts to the gaseous monomer. D 2.25g/cc; Shore hardness 55–56; tensile strength 3500–4500psi; flexural strength 2000psi; brittle pt below –80°; dielectric const (at 60 to $3x10^9$ cycles) 2.0–2.05. Prepd by polymerization of tetrafluoroethylene

Not affected by w, aqua regia, chlorosulfonic acid, acetyl chloride, B fluoride, hot nitric acid, boiling solns of NaOH and organic solvents. Not wetted by w. No substance has been found which will dissolve the polymer, but prolonged contact with fluorine, hot plasticizers and polymeric waxes is not recommended (Refs 1 & 6)

In ordn applications, powdered PTFE has been used primarily in pyrot and proplnt areas. Infrared pyrot flares have been based on pressed Mg/PTFE formulations since the 1950's (Ref 3). Allen (Ref 2) obtained a high regression rate by supplementing the surface energy of the solid fuel compn of hybrid rocket motors with Mg/PTFE used at approx 10% by wt. Kaufman and Roy (Ref 4) used 2–10% PTFE powder in composite proplnt compns; during extrusion it was cold-drawn to form fibers which strengthened the product. Igniter compns contg 20–50% Mg powder, 20–30% small particle size PTFE and 10% silicone rubber have also been patented

(Ref 7)

PTFE has also been used in some expl nuts, where a PTFE insert provides a self-locking feature of the thread and a gas-tight seal between thread segments, bolt and housing (Ref 5). It has also been used to make inert seals or containers for pyrot compns (Ref 1)

Powdered Teflon for use in pyrots is covered by US Mil Spec **MIL-P-48296(PA)** (1 May 1974), "Polytetrafluoroethylene (TFE)". Three classes of material are specified (1, 2 & 3). The requirements are: purity, 99.4% min; infrared spectrum, peaks consistent with figure shown; color, TFE shall be opaque and the color shall range from white to gray; moisture, 0.05% max; ash, 0.1% max; mp, 337° ± 10°C; packing density, Class 1 – 1.18 ± 0.13g/cc, Class 2 – 1.25 ± 0.02g/cc, Class 3 – 1.14 ± 0.09g/cc; particle size by sieve analysis, Class 1 – 95 ± 15 microns, Class 2 – 237 ± 27 microns, Class 3 – 200 ± 30 microns; particle size distribution by sieve analysis, as specified in Table 1

Table 1
Particle Size Distribution Requirements for TFE

US Standard Sieve Size	Percent Retained On		
	Class 1	Class 2	Class 3
40	–	None	–
50	–	13–24	0–6
60	0.8 max	15–35	2–18
70	–	10–22	–
80	–	8–14	38–57
100	5 max	7–16	–
120	11–29	–	20–37
140	15–26	–	–
170	11–21	–	–
200	7–16	7–16	1–13
325	9–25	–	–
Pan	9–26	6–12	6 max

Particle shape, as indicated in figure under 100X magnification; shall be free from hair shape or needle shape particles

Refs: 1) Anon, EngrgDesHndbk, "Military Pyrotechnics Series, Part Three – Properties of Materials Used in Pyrotechnic Compositions", **AMCP 706-187** (1963), 232–35 2) P.L. Allen, USP 3309249 (1967) & CA **66**, 97085 (1967) 3) Ellern (1968), 412 4) M.H. Kaufman & E.M. Roy, USP 3853645 (1974) & CA **83**, 12971 (1975) 5) K.O. Brauer, "Handbook of Pyrotechnics", ChemPublishing Co, NY (1974), 130 6) Merck (1976), 985-R (No 7361) 7) F. Shroeder, GerP 2530209 (1976) & CA **84**, 138053 (1976)

Addnl Refs: (limited distribution): 1) C.E. Vest, "Transfer Film Lubrication of Ball Bearings", Rept No **MTR-764-001**, NASA, Greenbelt, Md (1972) 2) R.M. Giannini & W.G. Thelen, "Development of Self-Lubricating Piston-Seal Materials for High-Pressure, Oil-Free Air Compressors", Rept No **PAS-75-21**, Naval Ship R&D Center, Annapolis (1975) 3) T. Toshiaki & E. Fukada, "Depolarization Current and Molecular Motion in Polyethylene and Polytetrafluoroethylene Electrets", Rept No **AST-18401-120-75**, **FSTC-1901-75**, Army For Sci & Tech Center, Charlottesville (1976)

Polythiocyanogen. $(SCN)_x$; mw $(58.08)_x$; N 24.12%; brick red solid; mp, decomps when heated over 300°. Insol in w and the usual organic solvents as well as weak acids and alkalies. Comm prepn (Ref 3) is from thiocyanic acid and/or thiocyanates either by anodic oxidation or by interaction with hydrogen peroxide or halogens. The yield is impure because it contains both H and O. The S content varies between 45 and 55%. Lab prepn of the pure polymer is by reacting the Na salt of 5-chlor-3-mercapto-1,2,4-thiodiazols with either acet, ethanol or w (Refs 1 & 2)

Audrieth (Ref 3) patented the use of $(SCN)_x$ as a fuel in primers, ignition and fuze time trains (see Table below). A significant advantage of the invention for fuze time train useage over BlkPdr is the greater control evidenced in the rate of burning

Table 1
Examples of $(SCN)_x$ Useage in Energetic Materials

Composition	Ordnance Applications, % of Contents						
	Primers		Igniters			Fuze Time Train Mixtures	
$(SCN)_x$	10	10	25	5	10	50	50
K chlorate	51	64	75	–	–	–	–
Sb trisulfide	34	21	–	–	–	–	–
Pb azide	5	5	–	–	–	–	–
Ba peroxide	–	–	–	95	90	–	–
K nitrate	–	–	–	–	–	50	40
K perchlorate	–	–	–	–	–	–	10

Refs: 1) Beil **3**, 143 & [127] 20 S.S. Bhatnagar et al, JIndChemSoc **17**, 529–36 (1940) & CA **36**, 3409 (1942) 3) L.F. Audrieth, USP 2410801 (1946) & CA **41**, 866 (1947)

Polyurethanes. See Vol **3**, C464-L under "Composite Polyurethane Propellants", and C465-L under "Composite Propellants". In this Vol see under "Nitro Polymers", N145-R to N147-L; N148-L to N150-L and N150-R to N157-R; also under "Propellants, Solid"

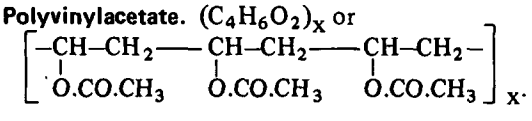
Addnl Refs: 1) W.G. Joseph, "Use of Foamed Polyurethane in Decreasing Erosion in Guns", PATR **2520** (1958) 2) Anon, "Polymer, Urethane, Liquid", **MIL-P-38683 (USAF)** (13 Aug 1970) 3) J. Wright, "An Assessment of Recently Developed Thermoplastic Polyurethane and Polyester Elastomers", **ERDE TR 136** (1973) 4) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants", JSciIndRes **32** (6), 279–99 (1973) & CA **80**, 121565 (1973) 5) D.L. Granatstein & H.L. Williams, "Nonreinforcing Filler-Elastomer Systems. I. Experiments Based on Model Systems", JApplSci **18**, 1–20 (1974) & CA **80**, 109562 (1974) 6) R.L. Duerlsson & J. Cohen, "High Specific Impulse Propellants", BritP 1326721 (1973) & CA **80**, 17079 (1974) 7) R.W. James, "Propellants and Explosives", Noyes Data Corp, Park Ridge (1974) 8) J.L. Eisel et al, "Combustion of Ammonium Perchlorate-Polyurethane Propellants. Pressure, Temperature, and Gas-Phase Composition Fluctuations", AIAAJ **10** (12), 1655–61 (Engl) (1972) & CA **81**, 172450 (1974) 9) L. Laire et al, "Ignition or Propulsion Device for Rockets", FrP 2181178 (1974) & CA **81**, 15272 (1974) 10) A.J. Hammond & C.J. Strickler, USP 3811967 (1974) & CA **81**, 108114 (1974) 11) A. Reichel et al, GerP 2335926 (1975) & CA **82**, 173248 (1975) 12) A.W. Benbow & C.F. Cullis, "Combustion of Flexible Polyurethane Foams. Mechanism and Evaluation of Flame Retardance", Combust&Flame **24** (2), 217–30 (1975) & CA **83**, 82287 (1975) 13) A.E. Oberth et al, USP 389111 (1975) & CA **84**, 108000 (1976) 14) A.F. Oberth & R.S. Bruenner, USP 3919011 (1975) & CA **84**, 108001 (1976) 15) M.H. Kaufman, "Inhibitor System for Double-Base Propellant", USPAppl 530916 (1974) & CA **84**, 7208 (1976)

Polyvinylacetate. A thermoplastic primarily used as a binder in non-metallic cartridge cases (see Mil Spec below)

Monomer

Vinyl Acetate. $CH_3.C(O).O.CH:CH_2$; mw 86.09; colorl, mobile liq; mp –93.2°, –100.2°; bp 72.2°, 73°; d 0.9335g/cc; RI 1.3959. Sol in hot w, ethanol, eth, acet, benz, chlf and CCl_4. Prepn is by addn of acetic acid to acetylene in the vap phase at 200° over Zn or Cd acetate catalyst (Refs 1, 4, 6a & 7). Autoign temp 800°F; flash pt 18°F; expl limits (in air) are 2.6–13.4%. Exposure of vinyl acetate to light produces the *polymer* (Ref 2a)

Polyvinylacetate. $(C_4H_6O_2)_x$ or



The resins as a class are colorl,odorl, non-toxic and have v good aging characteristics. The initial mp (or glass transition temp) is 28° (Ref 4). The polymer of 24,500 mw is sol in chlf, benz, py, dioxane and acet; insol in carbon disulfide, carbon tetrachloride, cyclohexane, hexane, etc

Polyvinylacetate has found use as a binder in expls (Refs 2, 3 and 6)

Polyvinylacetate aq emulsion for use as a binder in non-metallic cartridge cases is covered by US Mil Spec, "Polyvinyl Acetate Aqueous Emulsion (PAAE) (For use in Ammunition)", **MIL-P-50855(MU)** (31 March 1971). The requirements and criteria are in Table 1

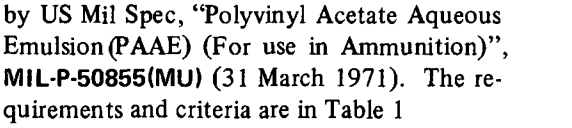
Table 1
Polyvinyl Acetate Aqueous Emulsion Copolymer Requirements

Property	Requirement
Total Solids, % range [a]	50–53
Viscosity, cps range [b]	4500–7500
Baked Insolubles, % min [c]	94
Chromic Nitrate Catalyst, % range [d]	43–46
Color	dark green
Specific Gravity, °Bé range [e]	48.5–49.5
Workmanship [f]	Free of impurities such as wood chips, oil and solvents not specified

a – Gravimetrically
b – By use of a Brookfield Viscosimeter
c – Gravimetrically
d – By any acceptable procedure
e – By using a std Baumé hydrometer calibrated for the specified range
f – By inspection

Refs: 1) Beil **2**, (63), [148] & {276} 2) Anon, "Plastic Explosive", FrP 947052 (1949) & CA **45**, 3599 (1951) 2a) Sax (1968), 1226 3) E.J. Nolan, "Water-Degradeable, Cap-Sensitive, Self-Supporting Explosive Compositions", USP 3586551 (1971) & CA **75**, 99598 (1971) 4) C.E. Schildknecht, Ed, "Polymer Processes . . .", Interscience Pub, NY (1956) 5) Anon, "Polyvinyl Acetate Aqueous Emulsion (PAAE) (For Use in Ammunition)", **MIL-P-50855(MU)** (31 March 1971) 6) W.L. Evans, "Vinyl Acetate Copolymer Binders for Crystalline Explosives", USP 3428502 (1969) & CA **70**, 79660 (1972) 6a) ChemRubHdbk (1975), C-80 7) N.L. Allinger et al, "Organic Chemistry–Second Edition", Worth Publishers, NY (1976), 660 & 932

Polyvinylalcohol (PVA, Alvyl, Resistoflex, Solvar). A polyhydric alcohol polymer used chiefly as the starting matl for Polyvinyl Nitrate (PVN) (qv), $(C_2H_4O)_X$ or

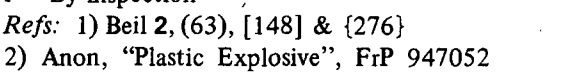


mw $(44.065)_X$; white to cream colored powd; softening pt at 200° with decompn; d 1.329g/cc. Sol in hot and cold w; insol in petr solvents. Prepn is from polyvinyl acetates by replacement of the acetate groups with hydroxyl groups. Using an alkali or mineral acid catalyst the alcoholysis will proceed quickly in a methanol-methyl acetate mixt. The alcohol has a flash pt of 175°F (open cup)

PVA is also used as a polar polymer binder for rocket proplnts (Ref 4)

Refs: 1) Beil **2**, [149] & {1855} 2) J.A. Monick, "Alcohols – Their Chemistry, Properties and Manufacture", Reinhold, NY (1968) 3) Sax (1968), 1036 4) R.W. James, "Propellants and Explosives", Noyes Data Corp, Park Ridge (1974), 185–86 5) Merck (1976), 986

Polyvinyl Chloride. (Chloroethene homopolymer, Chloroethylene polymer, PVC, Vybak, Geon, Breon, Welvic, Deckor, Vinacort, Ultron, Vinylite, Koroseal, Marvinol). A synthetic thermoplastic polymer; white powder or colorl granules;



avg mw about 60000 to 150000; tasteless, odorless, nontoxic; combustible but self-extinguishing; d 1.406g/cc. Solvents for unmodified PVC of high mw: cyclohexanone, methyl cyclohexanone, dimethyl formamide, nitrobenzene, tetrahydrofuran, isophorone, mesityl oxide. Solvents for lower polymers: dipropyl ketone, methylanyl ketone, methyl isobutyl ketone, acetonyl acetone, methylethyl ketone, methylene chloride. Prepn by polymerization of

vinyl chloride by suspension, emulsion and soln methods. May be copolymerized with up to 15% of other vinyls (Refs 6, 8 & 12)

PVC is used in pyrots as a chlorine donor for improved color saturation in flare, signal and tracer formulations (Refs 1, 2, 3, 4, 5, 9 & 11)

PVC is also employed in Polyvinyl chloride *Plastisol Propellants.* In many ways plastisol proplnts are similar to the many composite proplnts which have binders comprised of polyesters, acrylates, epoxies, polysulfides, polyurethanes, or polybutadiene-acrylic acid. They all contain 75–80% by wt of finely divided inorganic solids uniformly dispersed in a continuous matrix of organic elastomeric binder. They all utilize the same inorganic oxidizer (normally Amm perchlorate) and the same powdered metals (usually Al) to enhance performance, and they all are made by thoroughly mixing the solid ingredients in a nonvolatile liq to form a viscous slurry, deaerating the mixed slurry to remove entrapped air or other gases, casting the deaerated slurry into molds of the desired shape, and solidifying the mass

It is in the technique of solidifying the mass that plastisol proplnts differ so markedly from composite proplnts. In composite proplnts, the nonvolatile liq is comprised of monomers or low mw prepolymers. Solidification is accomplished by completion of the polymerization reactions. Much attention must be given to the degree of completion of these reactions during manuf so as to minimize changes in physical properties as a consequence of continued slow polymerization, so-called "post-cure", following manuf

In plastisol proplnts, however, all polymerization reactions are complete before proplnt manuf begins. Solidification is accomplished thru solvation (or soln) of the solid resin (or polymer) particles in the nonvolatile liq, which has been selected to be a plasticizer for the resin. Solvation or "curing" is accomplished by heating to a temp at which the resin particles dissolve rapidly (within a matter of a few minutes) in the plasticizer to form a gel which on returning to room temp has the characteristics of a rubbery solid (Ref 7)

Ref 7 reviews the characteristics and manuf of PVC plastisol proplnts. Information is given on compn, uncured proplnt flow, curing time, variation of physical properties with temp of cure and use, combustion products, safety characteristics, and manufg techniques. Effects of oxidizer content (Amm or K perchlorate) on specific impulse, flame temp, d, and burning rate are shown. Burning rate is correlated with oxidizer particle size. Wide variation of burning rate by use of additives and fine metal wires is demonstrated, and the effects of Al and Mg on specific impulse and burning rate are covered

PVC plastisol proplnts are employed in sounding rockets, jets, aircraft, control motors, tactical weapons and ship models. However, they are not case-bondable (Ref 10)

The requirements of the US Armed Forces for PVC are covered by two Military Specifications: "Polyvinyl Chloride (For Use in Pyrotechnics)", **MIL-P-10307A** (15 May 1965); and "Polyvinyl Chloride, Plasticized", **MIL-P-47136** (24 May 1974)

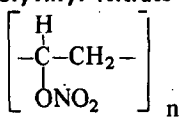
The requirements of **MIL-P-20307A** are as follows: color, white; loss in wt at 135°C, 0.5 percent (max); ash, 0.1 percent (max); chlorine, 55.7 to 57.7 percent; specific viscosity, 0.50 to 0.70 centipoises; bulk density, 0.40 to 0.60g/ml; granulation, 95 percent min thru US Standard Sieve No 100, and 30 percent max thru US Standard Seive No 325

MIL-P-47136 covers one formulation of plasticized PVC used in the production of flexible tubing, cord, film, sheet, and other various extruded shapes. The Specification requirements are concerned with electrical, mechanical and physical properties and shelf life

Refs: 1) D. Hart, PATR **1592** (1946) 2) H.J. Eppig, PATR **1669** (1947) 3) W.J. Nolan, PATR **1943** (1953) 4) Anon, EngrgDes-Hndbk, "Military Pyrotechnics Series, Part Three – Properties of Materials Used in Pyrotechnic Compositions" (1963), 236–7 5) Ellern (1968), 125 6) H.A. Sarvetnick, "Polyvinyl Chloride", VanNostrand Reinhold, NY (1969) 7) K.E. Rumbel, "Polyvinyl Chloride Plastisol Propellants" in "Propellants Manufacture, Hazards, and Testing", ACS Advances in Chemistry Series 88, Washington (1969) 8) CondChemDict (1971), 714 9) R. Lancaster, T. Shimizu, R.E.A. Butler & R.G. Hall, "Fireworks Principles and Practice", Chemical Publishing Co, NY (1972), 45–6 10) R.P. Rastogi & K. Kishore, "Polymers as Fuel Binders in Composite Solid Propellants",

JSciIndRes **32**, 279–99 (1973) & CA **80**, 121565 (1973) 11) A.P. Hardt & P.V. Phung, "Study of Reaction Mechanism in Tracer Munitions", FrankfordArs **TR-74047** (1974) 12) Merck (1976), 986-R

Polyvinyl Nitrate (PVN). $(C_2H_3NO_3)_n$; mw $(89.05)_n$; theor N 15.75%; OB to CO_2 –45%; OB to CO –9%; with a low degree of polymerization the product is a white powder, while nitrates of a high degree of nitration are in the form of tough white strands; the color is white to buff depending on method of prepn; softening pt 30–50°; deflagration pt ca 175°; Q_f^v –275.6kcal/kg; Q_e 1180kcal/kg; it is readily inflammable and burns without melting (Ref 16)



PVN was first prepd in Ger in 1929 (Ref 1) by the nitration of polyvinyl alc with mixed nitric-sulfuric acid. The highest yield was 80% but the product contained only 10% N, against a theoretical value of 15.75%. It detonated when heated

Burrows and Filbert (Ref 2) improved the process of nitration by using straight nitric acid and keeping the oxidation to a minimum by conducting the operation in an atm of inert gas such as N_2 or CO_2. They claimed that products with as high as 15% N could thus be obtained

Noma, Oya and Nakamura (Ref 5) examined the reaction of nitrating polyvinyl alc and concluded that neither nitration with a mixt of nitric and sulfuric acid, nor nitration with nitric and acetic acid can bring about the esterification of all of the hydroxyl group, probably due to simultaneous hydrolysis. They recommend nitrating either with a compn of nitric acid and acetic anhydride or a soln of nitric acid in carbon tetrachloride, whereby a higher nitrated product, softening at a temp of 40–50° is obtained

Deans and Nicholls (Ref 8) prepd polyvinyl nitrates with nitrogen contents ranging between 13–15%. They found its structure to be unstable, apparently decompg at RT. The Abel heat test at 70° was more sensitive than for NC. The Trauzl Pb block test indicated high explosive power (153–341cc vs 255cc for TNT). The impact test using a Rotter Impact app gave values of 30 to 335cm vs 158cm for TNT. On standing, the impact values decreased, indicating increased sensitivity. The ignition pt range of 160–78° was below that of NC (ca 200°)

Chédin and Tribot (Ref 6) conducted extensive investigations on methods of prepn of PVN, after WWII, in the Laboratoire Central des Services Chimiques de L'Etat Paris. They claimed that products with N content as high as 15.7% were obtained

LeRoux and Sartorius (Ref 10) studied PVN prepd from both low and high viscosity polyvinyl alcs. With low viscosity PVN, a max N content of 14.48% was obtained compared with 13.43% for high viscosity PVN. They reported Trauzl Pb block values ranging from 102cc for high viscosity to 113.5cc for low viscosity material. They also found that the detonation of PVN is propagated with a rate similar to that of NC of the same N content. The rate of detonation of PVN contg 13.4% N, in 30mm diameter cardboard cartridges was:

Density, g/cc	Detonation Rate, m/sec
0.3	2030
0.6	3450–3520
1.0	4920–5020
1.4	6090
1.5	6560

Preparation (Typical procedure). Five g of pulverized polyvinyl alc (contg 10% moisture), previously screened thru a No 30 sieve (metric), were gradually introduced during about 1 hr into 100ml of 99–100% nitric acid. The acid was stirred and maintained at –8° by cooling thruout the addition, and for an additional 2 hrs (a total of 3 hrs). The resulting slurry was slowly drowned in an equal volume of ice w, vigorously stirred. After filtering off the white powder, it was washed with w to neutrality, and then allowed to stand for 12 hrs in pure w. The same operation (washing and standing for 12 hrs) was repeated using 95% alc, and then 12% Na bicarbonate soln. Finally, the powder was washed with distd w until neutral, dried in air and then in vacuum; yield 96%

Note: The N detn was made by the Dumas method as modified by P. Jovinet and S. Courtecuisse [MemServChimÉtat **32**, 16 (1945) and État Francais, FrP 510911 (1946)], because other methods, such as the nitrometer or the Kjeldahl, did not give reliable results

This product was sol in acet, NG and DEGDN;

insol in 95% alc. Its thermal stability, as judged by the 72° Abel heat test and the Bergmann-Junk test, was satisfactory.

It was recommended for use in double base proplnts, eg, in the combinations NC+NG+PVN or NC+EGDN+PVN

PicArsn PVN, Preparation and Properties. Polyvinyl alc was mixed with acetic anhydride and the mixt cooled to −5°; a large excess of nitric acid was added gradually with cooling and stirring, maintaining the temp below 20°. When the nitration was completed, the mixt was poured slowly into a large amt of cold w. The resulting white ppt was filtered off, and purified by boiling in frequent changes of w

The dried product had the following properties:

Nitrogen content. 14.86%
Explosion temperature. 265° (5 sec)
Friction pendulum test. Steel shoe, crackles; fiber shoe, unaffected
Hydrolysis test. 240 hrs; 5.07% calcd as nitric acid
Hygroscopicity. At 30°, 90% RH, 0.62% wt gain
Heat of combustion. 2960cal/g at C_V
Heat of explosion. 900cal/g; gas vol 838cc/g
100° Heat test. % loss 1st 48 hrs, 1.9; 2nd 48 hrs, 2.1; no expln in 100 hrs
134.5° Heat test. Salmon pink color in 20 mins; red fumes in 25 mins; expln in 300+ mins
Impact sensitivity. Using PicArsn app with 2kg wt, 4″ vs 5″ for dextrinated Pb Azide and 3″ for pure Pb Azide
65.5° KI test. 60+ mins
Sand test. Using a 200g bomb, 49.9g vs 48.0g for TNT
100° Vacuum stability test. 11+cc in 16 hrs
120° Vacuum stability test. 11+cc in 16 hrs (Ref 13)

Daume and Breitenmoser, in a 1972 patent (Ref 14), describe a process to prepare stabilized PVN from the crude product. They found that pure and stabilized PVN, usually with a N content greater than 15% can be produced from raw, decomposable PVN, resulting in a free-flowing, noncaking powder. Their process consists of (a) providing a soln of raw acid contg PVN in an org solvent; (b) neutralizing or rendering the soln slightly alkaline; (c) separating the soln from nondissolved products of the neutralization; introducing the purified soln of step (c) into a hot pptg bath in which the organic solvent is insol or only partially sol, whereby the solvent is stripped and stabilized PVN is pptd. The rate of introduction of the purified soln corresponds to the stripping rate of the solvent so that steady-state conditions are maintained. A solvent is selected in step (a), the bp of which, or the azeotropic bp of which, with the pptg bath is below the bp of the pptg bath. As the pptg bath, either pure w or an aq medium which contains certain additives is preferably used. With aq pptg baths, such solvents are preferably used in the PVN soln which form with the w an azeotrope with min bp, this usually being the case when using solvents which are not or only partially miscible with w. Examples of such solvents are esters and ketones, such as ethyl and butyl acetate or methylethylketone and methylisobutylketone

The solubility of PVN depends on its viscosity (degree of polymerization). The products of low viscosity are entirely sol in all proportions in acet, nitrobenzene and liq nitrate esters. Those of high viscosity are only partially sol, causing strong coloring of the soln

The ease of N determination in PVN samples appears to be a function of the degree of polymerization. The nitrometer method gives consistent results, but are about 0.6% lower than the true values (Ref 6). Difficulty is experienced with high viscosity PVN. These products dissolve slowly in sulfuric acid, and give scattered results. Analytical methods based on titanous chloride, Devarda's alloy, or the Dumas method appear to be applicable for all products (Refs 6 & 11)

PVN is a highly energetic substance which computer simulation calcns indicate would have higher impetus, similar flame temps, and a lower avg mw of combustion product gases compared to conventional NC in several proplnt compns. Table 1 gives such data for WC846 and M9 proplnts

Table 1
Comparison of Nitrocellulose vs Polyvinyl Nitrate in Propellant Formulations

Ingredients	WC846 Proplnt %	
Nitrocellulose (13.15%N)	82.0	–
Polyvinyl nitrate	–	82.0

(continued)

(continuation)

Nitroglycerin	10.2	10.2
Dinitrotoluene	0.7	0.7
Dibutylphthalate	6.1	6.1
Diphenylamine	1.0	1.0
Total volatiles	0.8	0.8
Flame temp, °K	2805	2811
Force, ft-lbs/lb	329200	372200
Gas vol, moles/g	0.04219	0.04753
Avg mw gas products	23.70	21.02
Heat of expln, cal/g	859	875

Ingredients	M9 Proplnt %	
Nitrocellulose (13.25% N)	57.75	–
Polyvinyl nitrate	–	57.75
Nitroglycerin	40.00	40.00
Potassium nitrate	1.50	1.50
Ethyl centralite	0.75	0.75
Ethyl alc (residual)	0.50	0.50
Flame temp, °K	3799	3772
Force, ft-lbs/lb	382000	415000
Gas vol, moles/g	0.03618	0.03955
Avg mw gas products	27.64	25.28
Heat of expln, cal/g	1295	1303

An investigation was conducted to determine the effect of addition of PVN to solventless colloidal proplnts (Refs 7 & 9). In general, the tensile strength is decreased, but the elongation at break is increased. There is an increase in flexibility. PVN has only a slight effect on the burning rate constant, but it increases the pressure exponent. In general, the addition of PVN complicates manuf without offering any worthwhile advantage over the standard colloidal NC proplnt

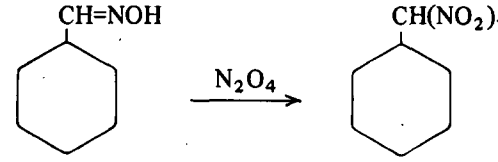
Two factors have militated against its application – first, the tendency of atactic PVN to flow when mixed with other materials, and second, the inherently sticky nature of atactic PVN proplnt blends, leading to problems in the extrusion or molding of proplnt grains

PVN was studied extensively by the Fr (Refs 6, 10 & 11), who found that, while PVN had expl properties comparable to NC and Nitrostarch, it could not be recommended for use in the expls industry

The above comments were directed against atactic PVN, in which the nitrate groups are randomly oriented about the backbone of the polymer. Compositions contg atactic polymer are tacky or semi-solid at RT. The introduction of stereoregularity into the PVN chain results in a more crystalline material. The feasibility of prepg stereoregular PVN has been demonstrated (Ref 15), and studies are currently being directed toward its evaluation

Refs: 1) G. Frank & H. Kruger, GerP 537303 (1929) & CA **26**, 1125 (1932) 2) L.A. Burrows & W.F. Filbert, USP 2118487 (1938) & CanadP 385037 (1938) 3) S.A.V. Deans, Doctoral Thesis, McGill Univ, Montreal (1942) 4) F.H. Foxlee, Doctoral Thesis, McGill Univ, Montreal (1946) 5) K. Noma, Sh. Oya & K. Nakamura, ChemHighPolymers(Japan) **4**, 112 (1947) 6) J. Chédin & A. Tribot, MP **30**, 359–71 (1948) 7) J.P. Picard & A.M. Pennie, CARDE Tech Memo **25/48** (1948); **32/48** (1948); addendum to 32/48 (1949) 8) S.A.V. Deans & R.V.V. Nicholls, CanJRes **27B**, 705–15 (1949) 9) B.J. Holsgrove, A. Ouellet, I.R. Cameron & R.W. Gordon, CARDE Tech Rept **267/49** (1949) 10) A. LeRoux & R. Sartorius, MP **34**, 167–77 (1952) & CA **48**, 9063 (1954) 11) P. Aubertein & P. Lafond, MP **35**, 133–47 (1953) 12) Urbański **2** (1965), 173 13) Anon, EngrDesHndbk, "Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 315–17 14) E. Daume & J.B. Breitenmoser, USP 3669924 (1972) 15) R.A. Strecker & F.D. Verderame, USPAppl, FrankfordArs (1973) 16) R. Meyer, "Explosivstoffe", Verlag Chemie, Weinheim (1975), 197

Ponzio Reaction. The formation of phenyldinitromethane from benzaldoxime by oxidation with nitrogen dioxide in eth (Refs 1 & 2)



The nitration of phenyldinitromethane yields m-nitrophenyldinitromethane, m-$O_2NC_6H_4$.$CH(NO_2)_2$, which was reported by Milone and Mass [Gazz **70**, 196 (1940)] to be a more powerful expl than TNT or 3,5-dinitrophenylnitromethane, $(O_2N)_2C_6H_3.CH_2(NO_2)_2$

Refs: 1) G. Ponzio, Gazz **27** [1], 171 (1897); JPraktChem **73** [2], 494 (1906); Gazz **36**

[2], 288 (1906); **38** [2], 509 (1908); & **39** [1], 326 (1909) 2) L.F. Fieser & W. vonE. Doering, JACS **68**, 2252 (1946)

Popped Corn. Ground popped corn is used for producing Dynamite of low d; other ingredients include NG, AN, Na nitrate, etc
Ref: N.G. Johnson & S.G. Baker, Jr, USP 1687023 (1928) & CA **22**, 4821 (1928)

"Popping": A term used to designate the heat treatment of empty or fired small arms ammo cartridge cases prior to shipping them as scrap. This treatment is necessary to insure that no unfired primers remain among the cartridges

Poseidon. A submarine-launched missile with about twice the payload of a Polaris A3 (qv). The Poseidon C3 is built by Lockheed and can be fired from existing Polaris launch tubes with very little modification of the tubes. It has a length of 34 ft, a diameter of 6 ft, a launching wt of about 60,000 lbs, and a range of 2875 miles. The Poseidon has already been tested with a MIRV payload, reported to consist of more than ten separate warheads, each with a yield of some tens of kilotons
Refs: 1) E. Luttwak, "A Dictionary of Modern War", Harper & Row, NY (1971), 155 2) J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 355

Potassium. K; aw 39.102; at no 19; valence 1; soft, silvery metal, rapidly oxidized in moist air; body-centered cubic structure; mp 63°; bp 770°; d 0.862g/cc. Sol in liq ammonia, aniline, Hg and Na

K is highly toxic by inhalation and ingestion, and is a strong irritant. It is a dangerous fire risk; reacts with moisture to form K hydroxide and hydrogen. The reaction evolves much heat causing the K to melt and splatter, also igniting the oxygen: K metal will form the peroxide and superoxide at room temp even when stored under mineral oil; it may expld violently when handled or cut. More than 150 reported hazardous reactions involving K with other chem species are documented in Ref 6

Metallic K in admixtures with Ag or Hg oxides or chlorides, or in contact with chlf or carbon tetrachloride, can be expld by strong impact (Ref 3). Such mixts were proposed by Staudinger (Ref 1) for use as initiating expls for blasting or in bursting projectiles

Davis and McLean (Ref 2) studied the expl reaction between metallic K or Na and chlf more closely. They stated that if a test tube contg some chlf, and an ampule with K or Na, were dropped onto a concrete surface from a height of about 6 ft, a loud report is produced accompanied by a bright flash
Refs: 1) H. Staudinger, ZElectrochem **31**, 549 (1925); USP 1547076 (1925) & CA **19**, 2879 (1925) 2) T.L. Davis & J.O. McLean, JACS **60**, 720 (1938) 3) Davis (1943), 402–3 4) Merck (1968), 851 5) CondChemDict (1971), 717 6) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, Natl Fire Protection Assn, Boston (1975) **491M**, 329–36

Potassium Azide. See Vol **1**, A594-R to A596-R

Potassium Dinitrobenzfuroxan (KDNBF). See Vol **2**, B68-R

Potassium Dinitroethane. See under 1,1-Dinitroethane in Vol **6**, E164-L

"Potassium" Dynamites (Dynamite à la Potasse). A series of expls proposed in 1873 by the British Dynamite Co, Ltd (which later became the Nobel Explosives Co, Ltd), which consisted of NG 15, saltpeter 70–75, plus paraffin and powdered charcoal 7–17%. Another mixt contained NG 18, saltpeter 71, charcoal 10, and paraffin 1%

In Fr, three varieties were manufd: *Arles;* NG 25, K nitrate 63 and charcoal 12%; *Cugny* or *Dynamite No 2;* NG 48, K nitrate 39, and cellulose 12%; *Arles et Cugny* or *Dynamite No 3;* NG 22, K nitrate 66, and charcoal 12%
Ref: Daniel (1902), 636

Potassium Ethylenedinitramine. See in Vol **6**, E244-L

Potassium Fulminate. See in Vol **6**, F223-L

Potassium Nitrate. See in this Vol, N34-R

Potassium Nitride. See under Potassium Azide in Vol **1**, A594-R to A596-R

Potassium Nitrite. See in this Vol, N108-L

Potassium Nitroethane. See in Vol **6**, E146-L

Potassium Picrate. See under Picrates in this Vol

Potatomeal or Potatopulp Explosives. Expls made by drying raw potato pulp, mixing it with about 80% of its wt of K chlorate, granulating and drying the mixt, and tumbling with graphite to coat the granules
Refs: 1) D.M. Stirton, USP 995579 (1911) & CA **5**, 2725 (1911) 2) G.M. Peters, USP 1048578 (1912) & CA **7**, 703 (1913)

Pot de Feu (Fire Pot). See under Cannon in Vol **2**, C26-L

Potentite. A smokeless powder, prepd in the 1880's by the Cotton Powder Co, Ltd of Engl by mixing wet NC (59.5% on a dry basis) with 40.5% K nitrate. It was also called "Cotton Powder of Liverpool" (Ref 1). Pepin Lehalleur (Ref 2) refers to Potentite as being an NC expl used prior to WWI in demolition blocks, contg Guncotton 50, K nitrate 50%
Refs: 1) Daniel (1902), 636 2) Pepin Lehalleur (1935), 354

Powder-Air Explosions and Detonations. Two-phase detonations involving fuel drops or solid particles and a gaseous oxidizer have been observed (Refs 8, 9 & 11). Detonations in fuel drop and gaseous (air or pure oxygen) mixts have been studied in greater detail because of their relevance to FAE (see Vol **6**, F3-L to F4-R) and liq rocket engine instabilities (Refs 8, 11, 12, 13 & 16). It has been shown that the fuel drop size and number density can affect the ignition and detonation characteristics

Currently, liq fuels are used in all fuel-air munitions (Refs 8 & 12). The fuel drops are created by the techniques of expl dissemination. Due to the large effect of the drop size and drop distribution on the detonation characteristics, many restrictions are placed on both the method of dissemination and the final design of the munition. In the case of solid fuels, the particle size can be accurately controlled, allowing other dissemination techniques to be utilized. This flexibility in design criteria can lead to improvement in overall munition performance. Solid fuels also have other practical advantages over liqs. Higher charge densities can be achieved in loading with solids than with liqs, and thermal expansion problems during storage can be minimized

Solid particle-gaseous oxidizer systems have been studied because of applications to proplnts and expls (Refs 5 & 14), and hazards due to dust explns (Refs 1, 3, 4, 6, 7, 10 & 15). Strauss (Ref 9) reported on a heterogeneous detonation in a solid particle and gaseous oxidizer mixt; the study concerned Al powder and pure oxygen in a tube. Detonations initiated by a weak source were obtained in mixts contg 45–60% fuel by mass. Measured characteristics of the detonations agreed with theoretical calcns within about 10%, and detonation pressures of up to 31 atms were observed. With regard to solid particle-air mixts, detonations have not been reported; only conditions for expln have been studied (Ref 2)

Lu, Vyn, Sandus and Slagg (Ref 17) conducted ignition delay time and initiation studies on solid fuel powder-air mixts in an attempt to determine the feasibility of solid-air detonations. The materials investigated included Al, Mg, Mg-Al alloy, C and PETN. Ignition delay time was used as a method of screening the candidate fuels for further work in initiation studies which determined detonation wave speed, detonation pressure, detonation limits, initiation requirements, and the effect of particle size and confinement. The testing showed the importance of large surface area per unit mass, since the most

promising materials were those with small particle sizes and nonspherical shapes such as Al flakes. Shock tube initiation studies were performed on Al flake-air suspensions using an H_2-O_2 driver and in a chamber with central point ignition. The results gave strong though inconclusive indications of the occurrence of detonations

Refs: 1) I. Hartman & H.P. Greenwald, "The Explosibility of Metal-Powder Dust Clouds", Mining Metallurgy **26**, 331 (1954) 2) M. Jacobson, A.R. Cooper & J. Nagy, "Explosibility of Metal Powders", BuMines Rept **6516** (1964) 3) J. Nagy, A.R. Cooper & J.M. Stuper, "Pressure Development in Laboratory Dust Explosions", BuMines Rept **6561** (1964) 4) J. Nagy, H.G. Dorsett & M. Jacobson, "Preventing Ignition of Dust Dispersions by Inerting", BuMines Rept **6543** (1964) 5) M.H. Friedman, "Shock Tube Measurement of Explosive Sensitivity", Combstn&Flame **10**, 112 (1966) 6) A.A. Borisov et al, "Ignition of Powder Fuels Behind Shock Waves", FizGoreniya i Vzryva **3**, 308 (1967) 7) M.A. Nettleton & J.R. Stirling, "Ignition of Clouds of Particles in Shock Heated Oxygen", ProcRoySoc(London), 62 (1967) 8) K.W. Ragland, E.K. Dabora & J.A. Nicholls, "Observed Structure of Spray Detonation", Physics of Fluids **11**, No 11 (Nov 1968) 9) W.A. Strauss, "Investigation of Aluminum Powder-Oxygen Mixtures", AIAAJournal **6**, 1753 (1968) 10) K.N. Palmer & P.S. Tonkin, "Explosibility of Dusts in Small-Scale Tests and Large-Scale Industrial Plant", InstrChemEngrs(London), JChemE SympSeries No 25 (1968) 11) E.K. Dabora, K.W. Ragland & J.A. Nicholls, "Drop-Size Effects in Spray Detonation", 12th Symp Combstn (1969) 12) C.W. Kauffman & J.A. Nicholls, "Shock Wave Ignition of Liquid Fuel Drops", AIAA-Journal **9**, No 5 (1971) 13) T.H. Pierce & J.A. Nicholls, "Two Phase Detonations with Bimodal Drop Distribution", 3rd Intern Colloq Gas Dynamics of Explns and Reactive Systems (1971) 14) N.M. Laurendean & I. Glassmar, "Ignition Temperatures of Metals in Oxygen Atmospheres", CombstnSci&Technol **3**, 77 (1971) 15) J.T. Bryant, "The Combustion of Premixed Laminar Graphite Dust Flames at Atmospheric Pressure", CombstnSci&Technol **2**, 389 (1971) 16) P.M. Collins, "Critical Energy Threshold for Detonation Initiation in Unconfined Fuel-Air Mixtures", 4th Intern Colloq Gas Dynamics of Explns and Reactive Systems, Univ of Calif, San Diego (1973) 17) P. Lu, W. Vyn, O. Sandus & N. Slagg, "Studies of Powder-Air Explosions and Detonations", PATR **4825** (1975)

Powder Bags. See Cartridge Bags in Vol **2**, C77-L

Powder, Black. See Black Powder or Gunpowder in Vol **2**, B165-R ff

Powder Chamber Pressure Measurements. See Chamber Pressure in Vol **2**, C147-R

Powder Explosions. See under Coal Dust; Explosion Hazards from its Uses in Vol **3**, C359-R; Dust Explosions in Vol **5**, D1578-R; and Powder-Air Explosions and Detonations in this Vol

Powder Metallurgy. The content of this article is a verbatim reproduction of the ref

"Conventional powder-metallurgy (PM) processing is a fabrication method characterized by high productivity and low-cost yields. Parts are produced to 'net/near-net' shapes having good dimensional accuracy and surface finish

The method of producing components from metal powder is to prepare a PM compact by pouring blended metal powders into a die cavity and applying pressure. The cold-pressed (green) compact is then heated for an appropriate time at a temperature such that the metal particles 'sinter' or fuse together, being densified to approximately 85 per cent theoretical

Consequently, the mechanical properties normally are characterized by lower strength, lower ductility, lower impact strength, and reduced fatigue endurance

The use of PM products in Army materiel fulfills a variety of special applications. These products would include magnetic materials, refractory metals, controlled-porosity materials,

nonalloyable metals, friction materials, metallic-nonmetallic mixtures, hard materials, etc. However, military weapon systems contain many small structural components generally made of low-alloy or plain carbon steel and the use of PM products for these components is quite limited

PM steel-processing techniques have not been used for the fabrication of structural parts or critical components because, as stated previously, the properties of sintered steel parts have not approached the mechanical properties or reliability of wrought materials. The reason for this is attributed to residual porosity and chemical inhomogeneity inherent in pressed and sintered 'blended' metal powders

Advances in powder metallurgy have brought the technology to a point where it could be applied advantageously to the production of highly stressed, critical components. Specifically, PM forging now can replace the conventional forging of certain low-alloy steel components. A PM preform could be made using recently developed prealloyed steel powders, and full densification could be achieved by hot precision forging to final configurations after the sintering operation

This procedure, a logical consolidation of PM and forging methods, would resolve the inhomogeneity and porosity problems associated with PM products and combines the cost advantages of powder metallurgy with the structural integrity of forged components

Program Initiated. An Army Manufacturing Methods and Technology (MMT) program was initiated in 1969 and had two objectives. The first was to document a process for the forging of prealloyed steel powders capable of producing complex-shaped, high-performance components having quality levels equivalent to conventional forgings but at a significantly lower manufacturing cost

It is common knowledge that the use of PM processing techniques is greatly expanded as production quantities are enlarged. This is attributed to the higher tooling costs required for 'net/near-net' forgings. Since Department of Defense arsenals usually are concerned with smaller production orders compared with the private sector, full realization of potential cost savings would not be achieved

Therefore, the second objective, equally important, was to share the results of this program not only with other DOD organizations but also with the private industrial sector. Since industry is concerned with larger production orders, the DOD procurement posture would be improved substantially through the shared knowledge and established standardization specifications. This, in fact, is the goal of all MMT programs

A 2-phase program was conducted. The first phase was a materials and process study. The second phase dealt with the manufacture of a selected high-performance weapon component in prototype quantity to demonstrate the applicability of the developed PM forging process. A processing specification and an economic evaluation of the developed manufacturing process also was included

The compressibility and sinterability of a large variety of 4,600 prealloyed steel powders, mixed with sufficient graphite to give 0.40 per cent carbon, were investigated. Sintered compacts were forged at selected temperatures over the range of 1,400 to 2,200 degrees Fahrenheit using both conventional and minimum-deformation (flash-free) tooling. Apart from forging temperature, the variables investigated were preform porosity, protective coating, and forging pressure or amount of reduction

The forgings were evaluated by density, microstructure, surface finish, tensile strength, notched impact strength, ductility, and fatigue strength measurements

For further process optimization, the minimum-deformation forging was selected primarily because it was capable of producing a high-quality flash-free forging with no draft angles, thus eliminating subsequent machining steps

Results of the forging study on the selected 4640 composition have shown that PM forgings were competitive with wrought materials from a property standpoint. Tensile and yield strength were density dependent and comparable to wrought materials in the range of 98 per cent or higher density. Ductility and impact properties were very sensitive to minor amounts of residual porosity

However, PM forgings with near-theoretical density (99 per cent plus) when combined with microstructure uniformity and low interstitial

content provided notched impact strength and ductility comparable to bar-stock forgings

The viability of the developed minimum deformation PM forging process was demonstrated in the production of the accelerator for the M85 caliber .50 machine gun. Through the use of PM forging methods, the production sequence for the accelerator was reduced from 6 to 2 forging operations and from 23 to 7 machining operations. This resulted in reducing the cost of the accelerator from $95.00 (using conventional forging sequences) to an estimated cost of $30.00 for the PM accelerator

It was concluded that any candidate component can be produced using PM forging techniques at a cost at least 50 per cent lower compared with conventional forging processes. The accelerators were endurance-tested and exceeded all requirements in the standard room-temperature tests. The accelerators also withstood the test firing of more than 10,000 rounds at minus 65 degrees Fahrenheit with no failures being experienced

A Military Specification (MIL-F-45961), the first of its kind, for prealloyed steel powder forgings was then drafted and has been accepted as a standard by Department of Defense and commercial organizations. The significance of this work is that the improved PM manufacturing technology is applicable to all weapon systems which require complex-shaped steel forgings

Future Prospects. Evaluations were made of the M85 weapon, and it has been determined that 26 components could be made at greater than 50 per cent cost reductions if PM forged products, rather than conventionally forged parts, were used. Engineering Change Proposals (ECP's) have been processed, and PM forgings are now specified as alternate products for the 26 components. Evaluation of the M60 machine gun has shown that 22 components can be produced more cheaply when PM products are used

The significance of this work is that this new technology is applicable to all weapon systems which require complex-shaped components made of steel forgings. Evaluation of all future weapon systems will continue to determine which components can be produced more economically using PM forged products

To assist the transition to a more versatile production capability, an MMT program entitled 'Computerized PM Forging Design' is proposed for fiscal 1977. This program will provide the required die design technology to expand this new manufacturing method. In other words, there are many components which could be more economically produced by PM forging if a production order called for, say, 15,000 pieces

Through the use of computer-aided graphics, the trial-and-error method of forging-die development would be eliminated and tool setup costs would be minimized. Consequently, the minimum 'go/no-go' production order for PM forged products could be reduced to 7,500 pieces or even less"

Ref: J. DiBenedetto, "Machine Gun Parts from Steel Powder", NatlDefense **LXI**, No 340 (Jan-Feb 1977), 264–66

Addnl Refs: 1) J.D. Dale, Ordn **37**, 525–28 (1952) [PowderMetallurgy for Better Ordnance] 2) K.H. Roll, Ordn **38**, 873–75 (1954) 3) J.D. Dale, Ordn **40**, 714–18 (1956) [Powdered Metals in War] 4) R.A. Powell, Ordn **44**, 952–53 (1960) [Powdered Metal Bullets]

Power Cartridge. Initiators in which a proplnt compn is used for initiation and for generating heat and pressurized gas for a short duration. Power cartridges contain an ignition primer and a main charge of a pressure producing proplnt, mounted in one casing. The ignition primer initiates the main proplnt charge which consequently generates gas in the required quantity and temp. The gas thus produced can be used for numerous work functions, for example, for pushing a piston, inflating a flotation device, or fracturing a diaphragm

The amt of gas generated is relatively small, the major energy results from the gas temp. A typical power cartridge produces a pressure of 4400psi in a closed test chamber of 10cc volume in 5 to 10 millisec after initiation of the cartridge. Pressure ranges in these cartridges are generally from 100psi to 10000 psi, although those with a pressure capacity of 70000psi have been developed for special applications

Power cartridges are ideally used for the actuation of separation nuts and bolts, valves, ejection systems, pressure-actuated pumps, switches and piston devices, such as pyrotechnic

cutters for cables, straps, reefing lines, hoses and tubes. In spacecraft and missile systems they have been utilized for umbilical release, airborne emergency separation systems, thrusters, pin pullers, drogue chute mortars, line cutters, thrust reversal systems, termination devices, and separation systems for fairings and nose cones
Refs: 1) K.O. Brauer, "Handbook of Pyrotechnics", Chemical Publishing Co, NY (1974), 46–52 2) Anon, EngrgDesHndbk, "Propellant Actuated Devices", **AMCP 706-270** (1975)

Power of Explosives. In its normally used context, *power* of an expl is a misnomer. It is generally accepted that *power* of an expl is a measure of its strength, its blasting action or available energy, and not necessarily a measure of its rate of energy delivery, which is indeed the true definition of *power*. Further confusion arises because another frequently used expl term, called *brisance,* is sometimes erroneously equated with *power*. Brisance is a measure of the ability of an expl to shatter material in its immediate vicinity. The fundamental property of an explosive that determines brisance is its detonation pressure (see Vol **2**, B265-L). The power of an expl (we bow to accepted usage and will keep referring to *power* rather than the correct terms such as *strength* or *blasting ability*), on the other hand, is a measure of the ability of an expl to do work such as blasting down rock or propelling a chunk of metal. The fundamental expl property that determines its power (or better, available work) is its *heat of detonation,* Q (see Vol **7**, H38-L), or the related quantity, $n_j T_j$, where n_j is the number of moles of gas under steady (Chapman-Jouguet) detonation conditions and T_j is the detonation temp [a]. As will be shown below, a more exact dependence is that power is proportional to Q–q (rather than just Q), but q, the residual heat of the detonation products, is usually quite small compared to Q

According to Cook (Ref 2), the energy available to do external work (we continue to miscall it *power*) is

$$A = -\int_{V_i}^{V_f} PdV = \int_{T_o}^{T_i} c_V dT - \int_{T_o}^{T_f} c_V dT = Q - q \qquad (1)$$

where P=pressure, V=volume, T=temp, c_v= specific heat of the detonation products, and the subscripts o, i & f refer to ambient, initial and final states respectively. The initial state is usually taken to be that achieved in a constant volume expln for which $P_v \simeq P_j/2$; $T_v \simeq (\Gamma+1)(T_j)/2\Gamma \simeq 4/6\ T_j$; and $n_v \geq n_j$. [b] The final state is the state of product expansion, after which no more useful work is available

As pointed out by Cook (Ref 2), there is no unequivocal method of computing A for expls that produce appreciable amts of condensed phase (solid) products. Cook suggests the use of an empirical relation

$$A \simeq Q' + \tfrac{1}{2}Q'' \qquad (2)$$

where Q' is the heat of detonation computed solely for gaseous detonation products; Q'' is the heat of detonation computed solely for condensed phase products

Andreev & Belyaev (Ref 4) show that

$$A \simeq Q\ [1 - (P_f/P_i)^{\Gamma-1/\Gamma}\ ] \qquad (3)$$

For military expls $(P_f/P_i)_{max} \simeq 10^{-3}$, which for Γ=3 gives $A \simeq 0.99Q$. For commercial expls such as ANFO, $p_f/P_i \simeq 5 \times 10^{-3}$ and $\Gamma \simeq 2.1$ (Ref 8), therefore $A \simeq 0.94Q$. Thus $A \simeq Q$ appears to be a rather good approximation

Expl Power is always measured in relative terms, ie, relative to a standard expl and expressed as a percentage. For military explosives the consensus standard is TNT, and for commercial expls the standard is usually Blasting Gelatin (see Vol **2**, B211-R). Three measurement methods are in common use: 1) Ballistic Mortar; 2) Trauzl block; 3) Underwater explns; and 4) one method – cylinder expansion – that is now used at Lawrence Livermore Laboratories

The ballistic mortar method is described briefly in Vol **1**, p VII. Basically this test consists of firing a standard weight of expl (usually 10g) in a suspended mortar closed with a tightly fitting steel projectile. The angle of recoil of the mortar is measured and compared to the recoil produced by the same weight of a standard

[a] Not quite correct; see discussion below

[b] In reality, since most explosives are oxygen deficient, $n_v \geq n_j$ because $p_v < p_j$ and less solid carbon will be formed (see article on *Products of Detonation* in this Vol). Consequently $n_v T_v \simeq n_j T_j$ since $n_v > n_j$ but $T_v < T_j$

expl. Although the measurements are capable of high precision, the power or strength thus obtained is difficult to relate to the ability of the test expl to break rock, propel metal, etc. The loading d in the ballistic mortar is much lower than that used in practice. Consequently, neither the initial nor the final states obtained in the mortar correspond to what is obtained in actual practice. Gas leakage from the mortar results in additional uncertainty. It is also unfortunate that TNT is commonly used as the standard mortar charge. TNT detonation product compn depends very strongly on pressure and thus on loading d. However, for nearly oxygen-balanced Dynamites which generate mostly gaseous detonation products, the ballistic mortar should provide fairly reliable data on the performance of these Dynamites in actual blasting

Commercial expls have a percentage power or strength rating marked on the expl cartridge. For straight NG Dynamites this strength rating is exactly equivalent to the NG content of the Dynamite. With other energy developing ingredients in the Dynamite (AN for example) the strength is no longer directly proportional to the NG content. Thus a 60% weight strength Dynamite may contain only 10–15% NG with most of its strength contributed by AN and other ingredients

Comparisons between ballistic mortar strengths and heats of detonation relative to TNT are shown in Table 1 (the mortar values were taken from Ref 5 and the heats of detonation from Vol **7**, H41–42). Agreement is generally quite good

Table 1
Comparison of Ballistic Mortar Strength with Observed [c] Heats of Detonation

Explosive	Ballistic Mortar Relative to TNT	Heat of Detonation Relative to TNT
HMX	1.50	1.48
RDX	1.50	1.51
PETN	1.45	1.49
NG	1.40	1.48
Comp B	1.33	1.20
Tetryl	1.30	1.14
50/50 Pentolite	1.26	1.23
Picric Acid	1.12	1.03
DATB	1.00	0.98

[c] Based on calorimetrically measured values given in Ref 7. We have arbitrarily used 1.00 kcal/g as the heat of detonation of TNT. For highly confined TNT ΔH_d = 1.09kcal/g and 1.03kcal/g for partially confined TNT

Some additional mortar strengths are shown in Vol **2**, B266–95

In the Trauzl-block test the expl is loaded into a Pb block at a loading d near 1.0g/cc and stemmed or sealed in with a screw cap. Theoretically these measurements should correlate well with practical conditions because initial and final states in the measurement and in practice should be similar. Unfortunately the Trauzl method is not very reproducible (in part because of rupture of portions of the block by reflected shocks). Consequently no further discussion of the Trauzl-block measurements will be made in this article. Interested readers are referred to Vol **2**, B266–95 and Ref 5 for Trauzl block data for many expls

Cole (Ref 1) described methods and presented data for measuring the underwater effects of expls. Price (Ref 3) suggested that the underwater effectiveness of an expl can be indicated by the sum of its shock wave and bubble energy equivalent wts (in her paper relative to 50/50 Pentolite). In Table 2 we compare such indices of underwater performance (but relative to TNT rather than Pentolite) with relative heats of detonation. We used 1.09kcal/g for the heat of detonation of TNT under the assumption that deep water provides good confinement. Note that agreement is not as good as in Table 1, but

Table 2
Comparison of Underwater Effectiveness of Explosives with their Heat of Detonation

Explosive	Relative Underwater Effectiveness	Relative Heat of Detonation
TNETB	1.28	1.35
PETN	1.25	1.37
HMX	1.19	1.36
RDX	1.16	1.38
Comp B	1.11	1.10
50/50 Pentolite	1.09	1.13
Tetryl	1.08	1.05
TNT	1.00	1.00

there is certainly a correlation trend, ie, expls with large heats of detonation have a greater underwater effectiveness than expls which have smaller heats of detonation. The effectiveness of aluminized expls cannot be correlated with their heat of detonation since there are no reliable values for the latter

Incidentally, air blast effects correlate much better with computed Q's rather than calorimetrically measured Q's (Ref 6)

A fairly recent method of measuring expl energy (power in our convention) depends on accurate determination of the expansion of an explosively-driven metal cylinder (Refs 7 & 8)

Table 3
Correlation of Cylinder Expansion Energy with Heat of Detonation

Explosive	Relative Cylinder Expansion Energy (Tangential)	Relative Heat of Detonation (on a volume basis)
HMX	1.79	1.72
BTF [d]	1.72	1.61
PBX 9404	1.66	1.56
PETN	1.615	1.61
LX-04	1.51	1.50
Comp B	1.36	1.26
50/50 Pentolite	1.29	1.28
XTX-8003 [e]	0.974	1.11
TNT	1.00	1.00
NM	0.764	0.860

[d] Benzotrifuroxanhexanitrosobenzene
[e] Extrudable PETN composition
For TNT ΔH_d taken to be 1.63kcal/cc

Available expln energy is then correlated with the kinetic energy of the metal cylinder. In Table 3 we see that relative cylinder expansion energies (from Ref 7) correlate fairly well with relative heats of detonation if the latter are taken on a per unit volume basis

Thus we see that there is reasonable correlation between power of an expl, measured in a variety of ways, and its heat of detonation. Earlier in this article it was mentioned that power can also be correlated with n_jT_j. The latter correlation follows directly from Eq (1) if $c_v \neq f(T)$. With this restriction, the two middle integrals of Eq (1) give

$c_v(T_i-T_o) - c_v(T_f-T_o) = c_v(T_i-T_f) = n_vR(T_i-T_f)/\gamma-1 \simeq \text{const} \cdot n_vT_v$ if $T_i \gg T_f \simeq$ const $\cdot n_jT_j$, since R and γ are constants

Written by **J. ROTH**

Refs: 1) R.M. Cole, "Underwater Explosives", Princeton Univ Press (1948) 2) Cook (1958), 265–70 3) D. Price, ChemRev **59**, 821 (1959) 4) Andreev & Belyaev (1960), 654 5) Anon, EngrgDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971) 6) Anon, EngrgDesHndbk, "Principles of Explosive Behavior", **AMCP 706-180** (1972) 7) B.M. Dobratz, "Properties of Chemical Explosives & Explosive Simulants", **UCRL-51319** (1972) 8) M. Finger et al, 6th SympDeton Preprint (1976), 188

Praepositer (or Präposit). An expl similar to BlkPdr, manufd in the 1870's by the International Praeposite Co Powder Works, Millville, NJ, until the plant expld. The compn was K nitrate, S, charcoal, and "Hipposine", the latter ingredient being finely pulverized dried horse dung. The same expl was manufd in Ger by the Deutsche Präpositwerke G.m.b.H., Karlsruhe in Bavaria (Ref 1)

Refs: 1) Anon, SS **9**, 55 (1914) & CA **8**, 1508 (1914) 2) Van Gelder & Schlatter (1927), 28

Precession. A change in the direction of the axis of a rotating body, as a spinning top, or gyroscope, the effect of which is to rotate this axis (axis of precession) perpendicular to its original direction and to the axis of the twisting forces producing the change

When a symmetrical projectile leaves a gun barrel, it travels along the "line of fire" (also called the "line of no precession"), and at the same time spins rapidly around its long axis of gravity. The resistance forces are parallel to the line of fire, the center of pressure is at or near the apex of the projectile, there is no precession, and the projectile flies without yaw. As the force of gravity begins to draw the projectile away from the line of fire onto its curved trajectory, the direction of the resistance forces start to change, causing the center of pressure to move slowly from the apex toward the base along the ground side of the flying projectile. The change in the direction of the resistance

forces away from the line of fire will start the precession on the long axis. From that time on, the projectile will be flying with "yaw". The greater the precession and yaw, the greater is the air resistance. They can be minimized if the projectile is symmetrically constructed (uniform wall thickness) and uniformly loaded
Refs: 1) C. Cranz, "Handbook of Ballistics" (Engl translation), Vol **1**, HMSO, London (1921), 243 2) H.V. Wagner, "The Projectile in Flight", Ordn **37**, No 194 (1952), 341–44 3) OrdTechTerm (1962), 230-L

Preisenhammer Explosives. Mining expls, patented in 1864, consisting of mixts of hydrogen and oxygen
Ref: Daniel (1902), 651

Premature Explosions. See Vol **6**, E380-L to E383-R

Addnl Refs for In-Bore Prematures: 1) D. Price & J.F. Wehner, Combstn&Flame **9**, 73 (1964) (Closed pipe DDT study) 2) R.T. Schimmel, "Setback Sensitivity of Composition B Under Conditions Simulating Base Separation in Artillery Projectiles", PATR **3857** (1969) 3) J. Eadie & P.J. Hubbard, "A Comparison of the Setback Sensitiveness of TNT and Composition B", AustralianDefStandLabs Rept **341** (1969) 4) R.T. Schimmel & G. Weintraub, "Effect of Base Separation and Loading Density on the Setback Sensitivity of Composition A-3", PATR **4147** (1970) 5) V.F. DeVost, "Premature Simulator for Projectile Explosives" **NOLTR-72-1190** (1972) 6) R.R. Bernecker & D. Price, Combstn&Flame **22**, 111, 119 (1974) (Closed pipe DDT study)

Pressling. See 1,3,5,7-Tetranitrophenothiazine under Phenothiazine in this Vol

Pressure and Its Measurement in Ordnance. See under Closed Bomb (or Vessel) and Instruments for Measuring Pressures Developed by Explosives or Propellants in Vol **3**, C330-L to C345-R

Pressure, Detonation. Detonating condensed expls develop very high pressures. For most military expls and many of the commercial expls the pressures attained within the expl column do not depend on confinement, provided the column diameter is appreciably larger than the critical diameter of the expl. This confinement-independent pressure associated with a steady detonation is called the Chapman-Jouguet pressure or P_{CJ}

References to detonation pressure are scattered thruout Vol **4**, eg, D230–35, D265, D463–64, and D483–93. The present article is primarily an up-date of the Vol **4** entries. However, its additional purpose is to bring together ina single article pertinent information on detonation pressure

Detonation pressure may be computed theoretically or measured exptly. Both approaches are beset with formidable obstacles. Theoretical computations depend strongly on the choice of the equation of state (EOS) for the detonation products. Many forms of the EOS have been proposed (see Vol **4**, D269–98). So far none has proved to be unequivocally acceptable. Probably the EOS most commonly used for pressure calcns are the *polytropic* EOS (Vol **4**, D290–91) and the *BKW* EOS (Vol **4**, D272–74 & Ref 1). A modern variant of the *Lennard-Jones-Devonshire* EOS, called *JCZ-3*, is now gaining some popularity (Refs 11 & 14). Since there is uncertainty about the correct form of the detonation product EOS there is obviously uncertainty in the pressures computed via the various types of EOS

The situation in exptl measurements of detonation pressure is hardly more satisfactory than that encountered in theoretical computations. Although there may be reasonably good agreement among pressure measurements made by a given technique, agreement among measurements made by different techniques for the same expl is often unsatisfactory. This state of affairs has led to what has been called *"Kamlet's Complaint"* (Ref 13) which in effect states that no single P_{CJ} measurement is universally accepted as being correct to within 5%

The different pressure measurement techniques alluded to in Kamlet's complaint may be grouped into particle velocity measurements, transmitted shock velocity measurements, pres-

sure transducer measurements and detonation product density profiles. Among the particle velocity measurements are the various free surface velocity (u_{fs}) measurement techniques (Vol 4, D483–91; Ref 10, pp 5-7 to 5-10 and 5-15 to 5-18; & Ref 3), the magnetic probe techniques (Refs 7, 8 & 13), and the flash X-ray technique (Refs 2 & 3). Measurements of shocks transmitted into inert solids or water (aquarium method) have been used to obtain P_{CJ} (Refs 4, 6 & 8). Pressure transducer methods are described in Ref 10, pp 5-10 to 5-15, Ref 14, and Refs 5 & 17. The flash X-ray technique is also claimed to give density profiles of detonation products (Refs 2 & 3)

A good illustration of the discordance observed among several of the above methods is given in the following tabulation taken from Ref 3:

Table 1
Measured Pressure for Composition B-3

Technique	Pressure–kbar
Rarefaction velocity (X-ray)	268 ± 6
Embedded foils (X-ray)	275 ± 4
Protected flash gap (u_{fs})	292 ± 5
Reflection–change flash-gap (u_{fs})	312 ± 5

Table 2
The "Aquarium Technique" as a Pressure Gage
Single Shot Results for Ten Explosives (All Charges d=7.2cm, L=11.4cm)

Explosive	Density (g/cc)	Det Vel (cm/μ sec)	Transmitted Shock Vel, U_s (cm/μ sec)			Measured Detonation Pressure, P_{det} (kbar)			LLL Values[1]		
			St Line Fit 2mm	Model I	Model III	St Line Fit 2mm	Model I	Model III	Density	Det Vel	P_{det} ±5 (kbar)
PBX 9404[a]	1.844	.881	.677	.676	.686	370	369	377	1.846	.882	375
TNT[p]	1.638	.692	.561	.553	*	201	195	*	1.632	.694	190
Pentolite[2,p]	1.644	.752	.618	.624	.630	257	262	250	1.644	.752	252
Comp. B[3,c]	1.729	.798	.641	.637	.647	297	294	302	1.733	.800	300
LX-04-1[4]	1.858	.846	.654	.688	.660	338	372	344	1.867	.848	345
LX-07[5]	1.850	.859	.694	.684	.694	381	370	381	–	–	–
LX-09[6]	1.861	.882	.662	.682	.682	354	372	373	–	–	–
LX-10[7]	1.841	.881	.679	.675	*	374	370	*	–	–	–
Cyclotol[8,c]	1.757	.830	.644	.659	.668	312	325	333	1.760	.830	316
RX-11-AY[9]	1.876	.625	.540	.639	.541	190	187	191	–	–	–

[1] Values determined by the LLL "Standard Test for Detonation Pressure Measurement"
[2] 50/50 PETN/TNT average PETN particle size 10μ
[3] 60/40 RDX/TNT
[4] 85/15 HMX/Viton
[5] 90/10 HMX/Viton
[6] 93.3/4.2/2.5 HMX/DNPA/FEFO
[7] 95/5 HMX/Viton
[8] 72/25 RDX/TNT
[9] HMX/Potassium Perchlorate Formulation

Model I: $R = A_1 + A_2 t + A_3 e^{A_4 t}$

Model III: $R = A_3 t + 4A_1 A_2 \tan^{-1}(t/2A_1)$

} See Ref 6

[a] Average of two shots
[p] Pressed
* Model III failed to converge to a solution
[c] Cast

For Comp B of slightly lower density, Jameson and Hawkins (Ref 4) measured $266 \leq P_{CJ} \leq 284$ kbar using a shock transmission technique. The aquarium method of Rigdon and Akst (Ref 6) gave $294 \leq P_{CJ} \leq 304$kbar for a Comp B of slightly higher density than that of Ref 3. Clearly Kamlet's complaint is well justified, since measured P_{CJ} for Comp B vary from 266 to 312kbar.

A good compilation of recent measurements of P_{CJ} for many military expls is given by Dobratz (Ref 11). This compilation relies heavily on measurements made at the Lawrence Livermore Laboratory (LLL). Particularly extensive measurements of P_{CJ} as a function of packing density were made at that laboratory for PETN (Ref 9)

In Table 2 the "aquarium" measurements of Rigdon & Akst (Ref 6) are compared with LLL measurements. Agreement is surprisingly good

Some interesting results for very low density foamed PETN or expanded NC were obtained by Austing et al (Ref 5). These are shown in the tabulation below:

System	Initial Explosive Density, g/cc	Foam Density, g/cc	CJ Pressure, kbars
Foamed PETN	0.176	0.136	4.8
Expanded NC	.252	–	4.8
	.141	–	2.8
	0.104	–	1.2

Austing's PETN measurement is in reasonable accord with the measurements of Ref 9

In recent years the most commonly used expl in mining has been ANFO (94/6 AN/Fuel Oil). Ref 16 quotes $55 \leq P_{CJ} \leq 61$kbar for very large charges of ANFO

The preceding paragraphs have been primarily devoted to a brief description of the methods of measuring detonation pressure and the presentation of selected measurement data. We have emphasized that both theory and measurements entail considerable uncertainty. Thus comparison between theory and observation is at best rather risky. Nevertheless, the P_{CJ} vs loading

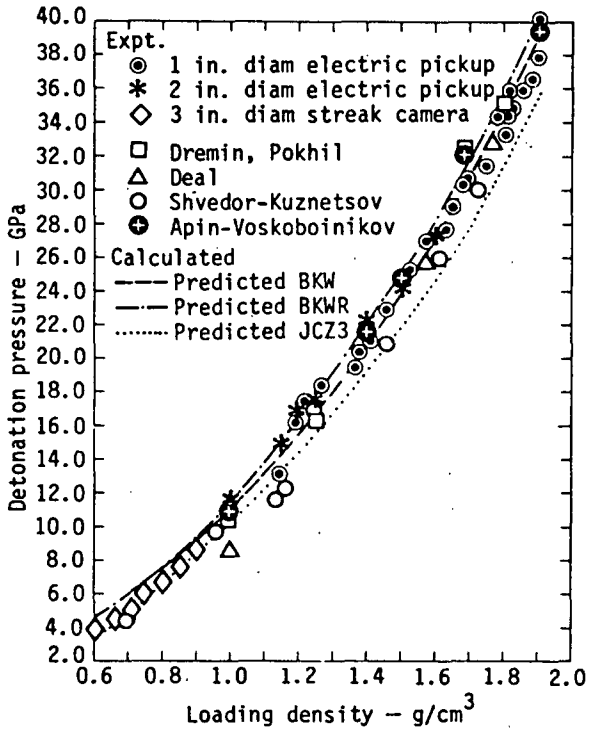


Fig 1 HMX C-J pressure dependence on loading density

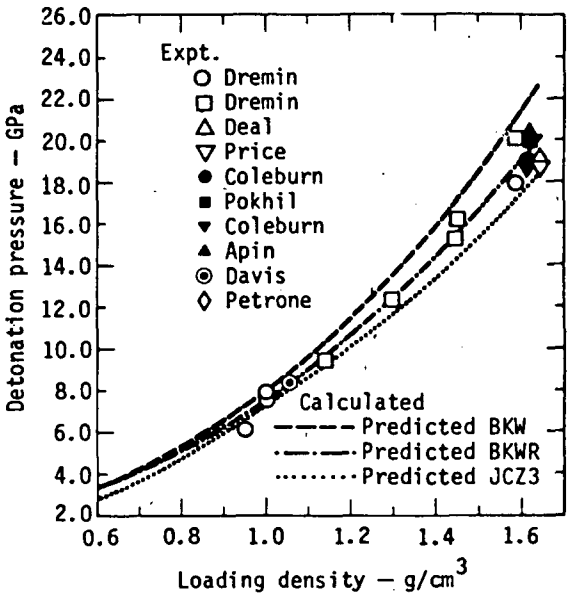


Fig 2 TNT C-J pressure dependence on loading density

density curves shown below (from Ref 15) are of considerable interest (Figs 1 & 2). They suggest that reasonable accord exists between the more popular types of theoretical calcns and exptl measurements. Indications are that pressure computations based on the *BKW* EOS are generally somewhat too high, while those based on the *JCZ-3* EOS are a little too low. The *BKWR* is a modified *BKW* EOS which apparently has been curve-fitted to the exptl data

Written by **J. ROTH**

Refs: 1) C.L. Mader, **LA 2900**, Los Alamos Scientific Lab, Los Alamos (1963) 2) W.C. Rivard et al, 5th ONRSympDeton (1970), 3 3) W.C. Davis & D. Venable, Ibid, 14 4) R.L. Jameson & A. Hawkins, Ibid, 23 5) J.L. Austing et al, Ibid, 47 6) J.K. Rigdon & I.B. Akst, Ibid, 59 7) S.J. Jacobs & D.J. Edwards, Ibid, 413 8) B. Hayes & J.N. Fritz, Ibid, 447 9) H.C. Hornig et al, Ibid, 506 10) Anon, EngrgDesHndbk, "Principles of Explosive Behavior", **AMCP 706-180** (1972) 11) B.M. Dobratz, "Properties of Chemical Explosives & Explosive Simulants", **UCRL-51319** (1972) 12) M. Cowperthwaite & W.H. Zwisler, SRI final Rept Contr N60921-72-C-0013 (1973) 13) W.C. Davis, Preprints 6th ONRSympDeton (1976), 144 14) K. Burrows et al, Ibid, 149 15) M. Finger et al, Ibid, 173 16) M. Finger et al, Ibid, 192 17) A.J. Tullis, Ibid, 623

Pressure Effect of Explosives. See under Blast Effects in Air, Earth and Water in Vol **2**, B180-L to B184-R

Pressures, Gun. Pressures within a gun tube or barrel, as used in design practices. Because of the wide variations in size, wall ratios, heat dissipation, required safety factors, etc, design practices vary for the different types of weapons. Some pressure terms have significance in the design of (a) all tubes and barrels, (b) cannon tubes, (c) recoilless rifle tubes, and (d) small arms barrels, viz:

(a) **For All Tubes and Barrels:**

Chamber Pressure. The pressure existant within the gun barrel at any time as a result of the burning of the proplnt charge. This pressure normally varies from atm pressure at the time of ignition to a peak pressure which is attained when the projectile has traveled a very short distance, decreasing steadily until the projectile emerges from the muzzle. It then drops quickly to atm pressure again (Fig 1)

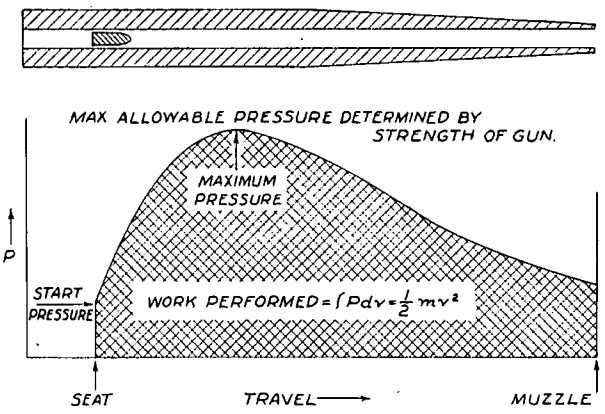


Fig 1 Chamber Pressure

(b) **For Cannon Tubes:**

Elastic Strength Pressure (ESP). Computed true internal gas pressure in a gun at any given cross section thereof that will stress the metal at the inner layer of the wall at that section tangentially up to the max elastic limit of the metal from which the inner layer is made. Normally required to be at least 1.5 times the computed max pressure

Maximum Pressure. Max value of the pressure exerted by the proplnt gases on the walls of a gun during the firing of a round

Computed Maximum Pressure (CMP). Value of max pressure computed by means of interior ballistic formulas. It will be developed when a new gun of a particular type is fired under standard conditions with a propelling charge which will give to the projectile its rated muzzle velocity

Rated Maximum Pressure (RMP). Value of max pressure specified in the proplnt specifications as the upper limit of avg pressure which may be developed by an acceptable proplnt in the form of propelling charges which will impart the specified muzzle velocity to the specified projectile. Normally about 2000psi above the computed max pressure, subject to determination at the time of development

Lower Acceptable Mean Maximum Pressure (LAMMP). Value of max pressure specified in

the proplnt specifications as the lower limit for the avg of the max pressures developed by acceptable proplnt in propelling charges that will impart the specified muzzle velocity to the specified projectile. Normally about 4000psi under the computed max pressure, subject to determination at the time of development

Permissible Mean Maximum Pressure (PMMP). Value which should not be exceeded by the avg of the max pressures developed in a series of rounds fired under any service conditions. Normally established as 1.08 times the rated max pressure

Permissible Individual Maximum Pressure (PIMP). Value which should not be exceeded by the max pressure developed by any individual round under any service condition. Normally established as 1.15 times the rated max pressure

(c) **For Recoilless Rifle Tubes:**

Elastic Strength Pressure (ESP). The gas pressure that will produce an equivalent stress (based on distortion-energy criteria) at some point in the gun that is equal to the min elastic limit of the material at ambient temp

Elastic Strength Pressure (Hot). (ESP [Hot]). A reduced elastic strength pressure; the reduction is made to allow for the decreased elastic limit of the gun materials at elevated temps

Computed Maximum Pressure (CMP). The gas pressure which is computed by means of interior ballistic formulas to be the max gas pressure developed by the gun under standard conditions and rated muzzle velocity

Rated Maximum Pressure (RMP). The gas pressure which should not be exceeded by the avg of the max pressures developed by a group of firings which will impart the specified muzzle velocity to the specified projectile. If the RMP is exceeded, the proplnt lot is considered unacceptable

Lowest Acceptable Mean Maximum Pressure (LAMMP). The gas pressure which should be equalled or exceeded by the avg of the max pressures developed in a series of rounds which meet the muzzle velocity requirements

Permissible Mean Maximum Pressure (PMMP). The gas pressure which should not be exceeded by the avg of the max pressures developed in a series of rounds fired under any service conditions

Permissible Individual Maximum Pressure (PIMP). The gas pressure which should not be exceeded by the max pressure developed by any individual round under any service condition

(d) **For Small Arms Barrels:**

Maximum (or Peak) Chamber Pressure. Max value of pressure induced in the chamber as detd with the help of a Cu crusher gage or with a piezoelectric gage. Comparison has shown that Cu pressures should be multiplied by 1.2 to give true peak pressures

Residual Chamber Pressure. Pressure in chamber from time of bullet exit

Barrel Pressure. Value of pressure induced by the proplnt gases at any barrel position and at the time that the bullet bypasses the particular position. May be calcd with the help of the simultaneous chamber pressure

Maximum Barrel Pressure. Value of pressure induced by the proplnt gases at a barrel position just passed by the bullet, and at a time that peak pressure exists in the chamber

Proof Pressure. This pressure is about 20% larger than that induced by the service round. If used for barrel design purposes, it provides some margin of safety

Refs: 1) Anon, OrdTechTerm (1962), 231–32 2) Anon, EngrgDesHndbk, "Ballistic Series, Interior Ballistics of Guns", **AMCP 706-150** (1965)

Pressure, Influence of on Combustion of Propellants. See under Burning and Burning Characteristics of Propellants for Artillery Weapons and Small Arms in Vol **2**, B346-L ff

Pressure, Influence of on Decomposition of Explosives. See under Decomposition of Explosives in Vol **3**, D23-L to D25-R

Pressure Measurements in Closed Bombs and Weapons. See under Closed Bomb (or Vessel) and Instruments for Measuring Pressures Developed by Explosives or Propellants in Vol **3**, C330-L to C345-R

Prilled Ammonium Nitrate. See under Ammonium Nitrate in Vol **1**, A314-R, A315-R, A317, A340-L, A354, etc

Primacord. See under Cord, Detonating; Cordeau Fuse or Detonating Fuse in Vol **3**, C529-R to C531-L, and Detonating Cords or Detonating Fuses in Vol **3**, D103-R to D107-L
Addnl Refs: 1) Blasters' Hndbk (1969), 103–05, 175–84 & 365 2) C.E. Gregory, "Explosives for North American Engineers", Trans Tech Publications, Cleveland (1973), 99–102 3) R. Meyer, "Explosivstoffe", Verlag Chemie, Weinheim (1975), 228–29

Primary Explosives. See under Initiating Explosives in Vol **7**, I105-L to I106-L

PRIMERS

Introduction – History.

The successful initiation of high energy material, which would include an entire variety of substances such as BlkPdr, smokeless or NC-type powder, pyrot or display powder, and HE material, is accomplished by the application of a small external stimulus, provided by a suitable source of energy

This small initiating mechanism is available in a variety of forms and is generally referred to as a "primer" or a "detonator". The choice depends on the nature of the major high-energy material to be ignited. In most general terms, primers are used to effect the ignition and proper propagation of a burning process (Ref 13); eg, propInt powder. Detonators serve an entirely different role and are intended to cause the functioning of a HE material (Ref 12). (Also see under "Detonators, Igniters, Primers and Other Initiating Devices Used for Nonmilitary and Military Purposes" in Vol **4**, D733 ff)

Obviously, there are many combinations and variations of the use of primers and detonators. There are instances where primers are used to ignite detonators, the output of which is then used either to cause directly the operation of a main expl charge or to ignite a slow-burning delay column, followed by a detonator and an expl charge

Figure 1 represents the difference in the two sequences of events (Ref 13)

High-energy materials such as BlkPdr and a wide variety of pyrots (truly "fireworks") have been known since before Christ; and, consequently, some primitive form of initiation for these was utilized

It is remarkable that little is known about the development of the art of initiation until the invention of the first modern primers by Forsyth in 1807 (Ref 2). His formula was based on a mixt containing 70.6 parts of K chlorate, 11.8 parts of charcoal, and 17.6 parts of sulfur. It is equally remarkable that modern primers are very much the same as the early ones designed by Forsyth and that the mixts still remain a heterogeneous group of granular substances, capable of taking fire when struck

The development of the first HE, NG, by Sobrero in 1846 and the later successful development of the means for utilizing NG as a practical expl by Nobel prompted invention of more efficient methods of initiating these HE's (Ref 6). It remained for Nobel to accomplish this task; and from this point on, the expl community, both commercial and military, would witness an ever-expanding family of initiating devices, beginning with Forsyth's early primer and extending to the highly sophisticated exploding bridgewire initiators.

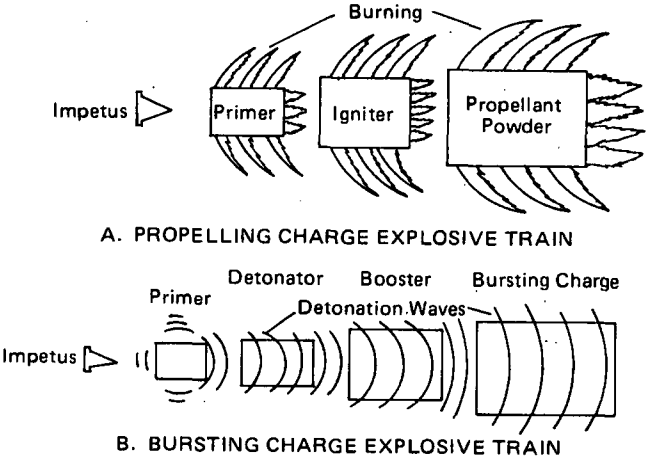


Fig 1 Schematic Representation of Explosive Trains

These bridgewire devices are relatively safe from initiation by direct application of heat and external mechanical influences or from most electrical inputs. They are designed for highly specialized electrical impulses (Ref 13)

MECHANICAL INITIATORS PERCUSSION PRIMERS, STAB DETONATORS, AND FRICTION PRIMERS

Although it is evident that initiators represent a broad spectrum of items and designs, both percussion and electric, the contents of this treatise will deal only with three selected types of percussion items; ie, percussion primers, stab primers and/or detonators, and friction primers

Percussion Primers

Percussion primers are used for the ignition of proplnt powder, thereby ejecting a projectile from a weapon. Thus, a relatively small percussion primer containing a small amount of sensitive priming mixt, upon being struck by a sufficient blow from a firing pin, causes ignition of the proplnt. In small arms ammo, the output of the primer is of sufficient magnitude to ignite the proplnt directly. In larger-caliber rounds, particularly artillery rounds, an igniter or booster material (usually BlkPdr) is used to amplify the primer; and it is then the burning of the booster material which effects proper ignition of the proplnt (Ref 6)

Percussion primers (also referred to as "caps" by the Brit) are either rimfire or centerfire (Ref 20). The use of rimfire priming is restricted to 0.22 cal ammo, which is almost exclusively commercial for sporting ammo, even though it is utilized to a minor extent by the military for training purposes. Rimfire priming is, in effect, an integral part of the small cartridge case. Centerfire ammo, as the name imples, contains a primer (which is either a separately manufd piece or a pertially completed item), located centrally in the head of the cartridge case

There are four different types of percussion primers; and these are recognized by name as Boxer, Berdan, Bloehm, and Battery Cup. These centerfire primers and the rimfire type are shown in Fig 2

Here are brief descriptions of these percussion primers. The Boxer primer consists of a metallic cup and anvil (both made from brass alloy: 70/30; Cu/Zn). Compressed priming mixt is contained between the cup and anvil. This primer is separately manufd and then inserted into a cavity in the base or "head" of the cartridge case. This cavity is commonly known as the "primer pocket". Neither Berdan nor Bloehm primers (which, incidentally, are seldom used in the USA, either for military or commercial ammo) contain anvils and are not complete until inserted into the cartridge cases. With the Berdan primer, the primer cup is charged with mixt and covered with protective foiling paper. The anvil is an integral part of the cartridge case, being formed in its original position in the base of the primer pocket

The Bloehm primer is a slight variation of the Berdan type. The anvil is not an integral part of the cartridge case, but takes the form of a "spade" which is inserted into the centrally located primer vent in the cartridge case, after which the charged cup is inserted

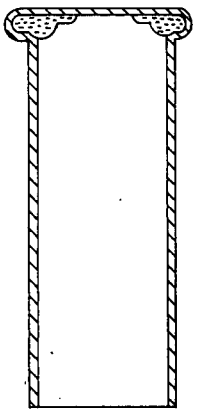
The primary mixt widely used by the US Army for small arms ammo in the early period of 1900 was based on Mercury Fulminate (MF) and is believed to be of Austrian origin (Ref 2). The most widely used formula is reported to have been as follows:

Early (1900) US Army Priming Mixture	
Mercury Fulminate	13.7%
Potassium Chlorate	41.5%
Antimony Sulfide	33.4%
Powdered Glass	10.7%
Gelatin Glue	0.7%

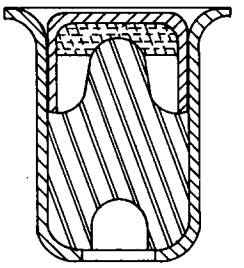
Some time later, circa 1917, the US Army changed to a non-mercuric formula, which eventually was known as FA70 (Ref 20) (the "FA" signifying Frankford Arsenal)

FA70	
Potassium Chlorate	53.0%
Antimony Sulfide	17.0%
Lead Thiocyanate	25.0%
TNT	5.0%

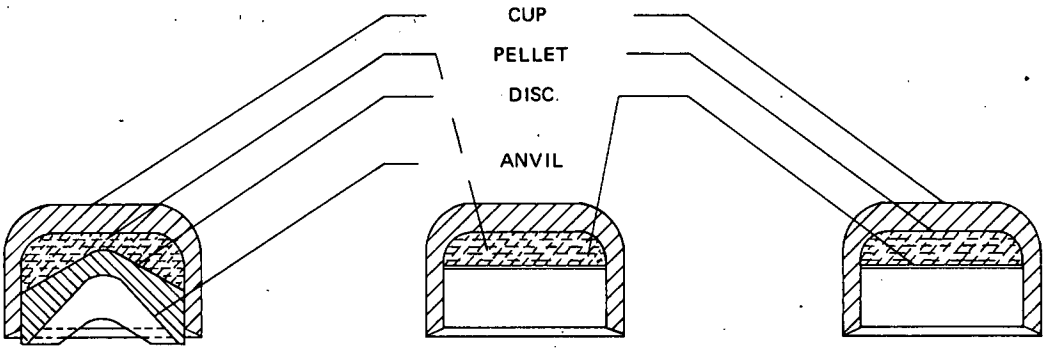
It is interesting to note that, from the time of the adoption of FA70, its use was continued as the standard mixt for cal .30 and cal .45 primers all thru WWII. A variation of FA70, known as FA90, was used in cal .50 (Ref 20)



RIM FIRE PRIMER



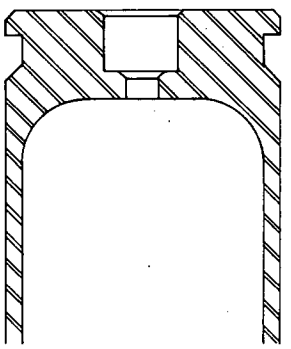
BATTERY CUP PRIMER



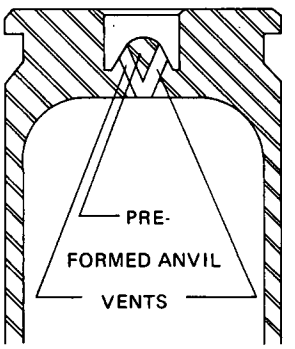
BOXER

BERDAN

BLOEHM



STANDARD CASE WITH CENTRAL VENT



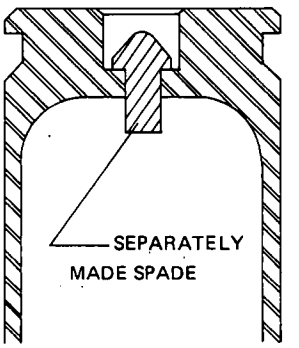


Fig 2 Various Types of Percussion Primers

FA90

Potassium Chlorate	53.0%
Lead Thiocyanate	25.0%
Antimony Sulfide	12.0%
PETN	10.0%

Except for special application, especially primers intended for use in high-temp environments, K chlorate priming mixts have been abandoned. The main reason for this change is that K chlorate primers are corrosive. After firing, hygroscopic K chloride, resulting from the decompn of the K chlorate, is deposited in the gun barrel. This causes immediate and extensive rusting of the barrel

Many types of non-mercuric, non-chlorate priming compns have been investigated for use in small arms ammo. Despite the many years of study and testing of many mixts, Lead Styphnate (LSt) compns, originally conceived by Rathsburg in 1926 (Ref 1), were adopted by the US Army in 1948. Initially, small arms LSt primers were purchased from commercial vendors, while the US Army proceeded to develop a standardized mixt. This was accomplished in the formulation of FA956 mixt, which is used in all military ammo today. It is similar to the mixt used by commercial vendors for sporting ammo (Ref 20)

FA956

Lead Styphnate, Normal	37.0 ± 5%
Tetracene	4.0 ± 1%
Barium Nitrate	32.0 ± 5%
Antimony Sulfide	15.0 ± 2%
Aluminum Powder	7.0 ± 1%
PETN	5.0 ± 1%
Gum Arabic	0.2% *

* 105ml of 1% soln used per 3500g of priming mixt

A review of the vast amt of work performed in the field of percussion primers reveals what is essentially an empirical approach to the development of both primer designs and priming mixts. It is recognized that a percussion primer must perform two vital functions: (1) it must "fire", "ignite", or otherwise function when provided with the proper mechanical stimulus – a firing pin (with optimum contour to its striking end); and (2) it must perform its other function by which the "flame", "fire", or "output" will ignite the propInt properly so as to provide the projectile with the specified velocity and within a specified range of gun chamber pressures; ie, proper ballistic performance

In order to fire reliably in a gun or other weapon device, a percussion primer must possess impact sensitivity which is in consonance with the mechanical energy delivered by the firing pin. In all cases, a factor of safety is built into the system in such a manner that the firing pin energy usually exceeds the max energy requirement of the primer by approx 20%

In small arms percussion guns, the firing pin energy has been detd by having the firing pin impinge on a standard Cu cylinder inserted in the primer pocket. A variation of this technique is the use of "dummy primers", loaded with an inert mixt, the consistency and resistance to crushing thought to be more related to the actual firing process of the primer vis-a-vis the impact of the firing pin (Refs 2 & 20). In either case, the indentations produced are measured and compared to values produced in a "sensitivity drop-test machine". With a knowledge of the sensitivity of live primers and the use of a standard drop-test machine, the following relationships are established: (a) height of drop (inches) vs indentation (inches); and (b) height of drop vs percentage of firing (ie, sensitivity data). From this, the relationship between indent and sensitivity for any specified primer can be obtained. It is an easy step to add a factor of safety, which the designer must decide upon, and then specify the minimum indents that the firing pin of the gun must produce for high reliability of firing (Refs 3 & 20)

The sensitivity of a primer for a given firing pin/weapon system is then designed into the primer by the proper choice of the thickness of the base of the primer cup, the point radius of the anvil, and the degree of compression of the mixt between the anvil point and the cup. This is controlled by the degree to which the anvil is compressed into the cup during manuf of the primer. In addition, some influence or further compression can be achieved when the primer is inserted into the cartridge case and crimped. This latter effect is minimal with the LSt mixts (as compared to FA70 or FA90), and is further minimized by the use of flat-bottomed primer cups

The choice of an available primer for a cartridge is dependent on the energy available in

the firing-pin system of the weapon (which can be altered within limits by changing the strength of the firing spring), and by the output required to efficiently ignite the proplnt (Ref 3)

The output of a primer includes hot gases, hot particles, a pressure pulse (which, in some cases, may be a strong shock), and thermal radiation (Refs 6, 12 & 13). Some of the aspects of primer output which have been measured as a means of characterization include the following: (a) vol of gas emitted; (b) the impulse imparted to a column of Hg by the pressure pulse; (c) the light impulse as measured by a photocell; (d) the temp rise of a thermocouple in the stream of output gases and particles; (e) the ionic conduction between a pair of probes exposed to the output; (f) the pressure rise in a chamber in which the output is confined; (g) the propagation of the air shock; and (h) the "hangfire", namely, the time lapse between supply of mechanical energy to the primer and the initial primer output and flame duration

Some of the brisant primers emit pressure pulses of sufficient magnitude to give measurable results in either the sand test or the Pb-disc test. Although many of these quantities are related to some aspects of primer performance, insofar as output is concerned, no general quantitative relationship of overall value has been developed which can be used as a means of acceptance

Primers are designed for specific applications, and the mixts chosen are largely based on precedent. Speaking very broadly, it can be said that the output must be characterized so that both gaseous products and hot particles are produced, both assuming important roles in ignition. The effectiveness of the gaseous products increases directly with temp and pressure; and, since pressure is related inversely to the enclosed vol, an increase in this vol or a venting of the system may call for primers of greater output

It has been shown exptly that the heat of an enclosed body of gas is distributed quite uniformly over the surface to which it is exposed (Ref 4). Thus, the insertion of baffles or the introduction of irregularities which increase the total surface (both inert and reactive) exposed to the primer gases may necessitate the use of a primer with more output energy. Hot particles of solids or globules of liqs are very effective in the ignition of materials with high thermal diffusivities (such as those contg appreciable proportions of metal) or of those whose melting points are well below their ignition temps. Hot particles and globules establish a number of reaction nuclei, rather than burning along a uniform surface. This action may be undesirable in proplnt grains designed for selected burning rate. Where the particles or globules are large or penetrate too deeply into the proplnt, serious problems may result. One very dangerous effect would be over-ignition of the proplnt, resulting in an extremely sharp rise in chamber pressure. This could be of sufficient magnitude to cause swelling or even rupture of the cartridge case and subsequent damage to the gun mechanism (Ref 20)

The blast effects of pressure pulse and accompanying gas movement are capable of producing both positive and negative effects. Although they result in more rapid heat transfer between gases and solid materials which are to be ignited, they may also extinguish the flame by moving the hot, gaseous products from contact with the individual proplnt grains (ie, individual particles of proplnt)

Shock waves from primers, quite often referred to as "brisance" or the "brisant effect", may cause rupture of proplnt grains (Refs 19 & 20). This effect is accentuated at low temps, at which condition the NC grains become more brittle and subject to fracture. This effectively results in the burning of much smaller proplnt particles, radically increasing the burning rate. This then produces very high gun chamber pressures, which have been known to cause guns to expld

The reproducibility of the time of a delay element is related to the reproducibility of the primer used for initiation. The times of short obturated delay elements are very sensitive to variation in primer output (Refs 7 & 12). Although primers of this type have been additionally tested for blast and gas vol, some opinions have held that, provided the priming mixt is maintained within the prescribed limits, the output is a mere reflection of the pellet wt

When a percussion primer is used to drive a firing pin to cause a series of events to occur, an important aspect of primer output is the moment-

um it is capable of imparting to a firing pin. Where the output gases are reasonably well contained, the impulse is measured in the gas vol and impulse apparatus. Again, this seems to be another cogent argument for the necessity of maintaining primer pellet wt within very close tolerances

In dealing within the confines of a standard priming mixt which has been used successfully in other cartridges, the kind of primer required for a different application requires essentially the solution of two problem areas: (a) the design of the primer in terms of mechanical aspects so that it will properly interface with the weapon; this would include but not necessarily be limited to a knowledge of the kinematics of the firing rate of the weapon, etc; and (b) the amount of priming mixt required for proper ignition and burning to obtain specified internal and external ballistic characteristics

Generally speaking, the ordnance designer works backwards from the target. Target effects translate to projectile parameters; ie, mass, diameter, ballistic coefficient, and velocity. Exterior ballistics dictate interior ballistics, and the end result is a choice of the primer-propInt combination. With the propInt type and charge calcd, it is possible, based on precedent, to make a reasonable estimate of the amt of standard type of LSt mixt, preferably FA956, required (Ref 20)

Working around this estimated pellet wt, a series of primers with different but known pellet wts are prepared. In a well-conducted investigation, a group of five different lots of primers, with 30 primers to a lot and the exact pellet wt of each primer recorded, are assembled into complete cartridges with the same charge of propInt. These rounds are then fired at +70°F, +165°F, and −60°F, single shot in a test weapon, recording velocity, pressure, and barrel time (the time interval between beginning of pressure rise due to propInt ignition to exit of the projectile from the gun barrel). The barrel time versus pellet wt is plotted for each temp, and curves similar to that in Fig 3 are obtained

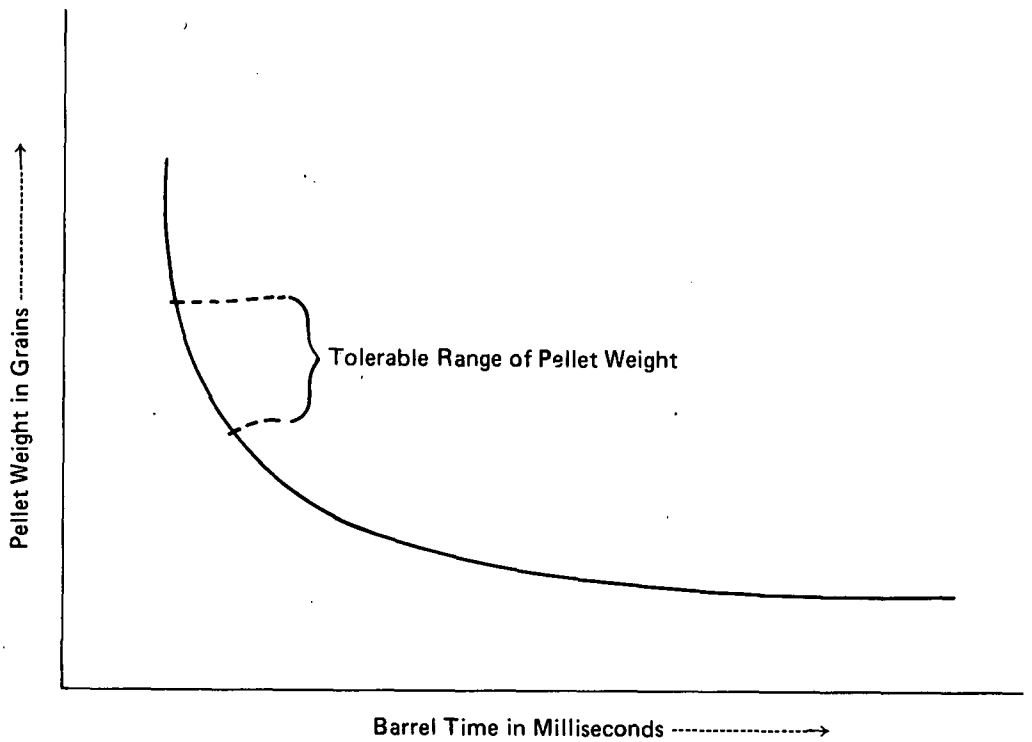


Fig 3

Examination of these curves will show a flat portion, where further increase in pellet wt causes little or no change in barrel time. This portion of the curve is examined judiciously; and a pellet wt is chosen which, with the normal variations that can be expected in the primer manuf, will have minimal effect on barrel time

Sensitivity testing of primers (Refs 3 & 15) is conducted with the primers inserted into the specified cartridge case in which they are to be used. The primer is inserted into the primer pocket of the cartridge case so that the surface of the primer cup, when measured from the center of the primer, is within the tolerance specified on the applicable cartridge drawing. The test is performed in accordance with the complete run-down method described in **TECP 700-700**, Volume III.; **AMCR 717-505**, Volumes 3 and 5; or **AMSMU-P-715-501 FA1**, as applicable

The sensitivity testing is conducted using a standardized app, which is known as "Fixture, Testing, Primer Sensitivity", US Army Ordnance Department Drawing **No 81-3-44**. Briefly, this is a very sturdy iron stand which is easily adjusted and leveled, and contains a lower base where the test cartridges are inserted in suitable holding dies, over which is a firing pin holder in a swing-over latch. This secures the firing pin directly over the primer. A vertical member, with suitable graduations in inches, allows a solenoid to be fixed at variable heights and holds the steel ball which, upon release, impinges directly on the vertical firing pin. The mass of the ball used depends on the primer to be tested, and the mass is specified in the appropriate primer specification. These steel ball bearings are usually used in 1-, 2-, 4-, 8-, or 16-ounce wts

The actual test procedure generally prescribes a sample of 400 primed cases. Fifty sample primed cases are tested at each height (where the drop-height is measured as the distance from the bottom of the ball to the top of the firing pin). The number of primers that fire – or fail to fire – is recorded, and this procedure is repeated at successively increasing heights of fifty primed cases at each height until a height is reached at which all test samples in the group being tested fire. The test procedure is repeated at successively decreasing heights of one inch each, using a new group of fifty test cases at each height, until a height is reached at which all primers tested fail to fire

The raw data of fires and "no-fires" is translated into meaningful sensitivity data by use of a calcn sheet shown in Table 1

The data thus calcd, $\bar{H}$, the height at which 50% of the sample fired and σ, the standard deviation, can then be used to calc the height at which all primers will be expected to fire at a chosen confidence level:

$\bar{H} + 5\sigma$ = All Fire Height (height at which not more than 3 out of 10,000,000 would misfire)

and also to determine the height at which all will misfire:

$\bar{H} - 2\sigma$ = All Misfire Height (height at which not more than 1 out of 50 will fire)

The skewness is calcd to determine whether or not the particular lot of primers under test manifest a normal distribution. As a general rule, skewness is often recognized at the high drop heights, where the sensitivity curve tends to lengthen. This tendency may be observed in the study of exptl mixts or designs. When observed, lowering of the value to obtain normal distribution can be achieved by adjustment of the formula of the priming mixt or a change in metallic components. Standard primers which have long and successful records of manuf and sensitivity normally exhibit low and acceptable skewness values (Ref 3)

Currently, the official US Army category of small arms ammo comprises cartridges ranging from 5.56mm up to and including 30mm. The following (Table 2) is a list of these primers and the matching US Armament Command Drawings applicable to these percussion primers. (It should be noted that this entire family of primers requires the use of "styphnate" priming compns. Further definition of "styphnate" means normal LSt (Ref 11) and, in most cases, FA956 primer compn)

Table 1
Calculation Sheet for Primer Sensitivity and Skewness

H = Ht	p_i = Fraction Misfiring	k_i = Variance Factor	$k_i p_i$ = Variance Factor times Fraction Misfiring	s_i = Skewness Factor	$s_i p_i$
		1		1	
		3		7	
		5		19	
		7		37	
		9		61	
		11		91	
		13		127	
		15		169	
		17		217	
		19		271	
		21		331	
		23		397	
		25		469	
		27		547	
Σp_i =		$\Sigma k_i p_i$ =		$\Sigma s_i p_i$ =	
$^*H_{100\%} + .5$ =		$-(\Sigma p_i)^2$ =		μ_3 =	
$\bar{H}$ =		σ^2 =		α_3 =	
$^*H_{100\%}$ = 1st ht at which 100% misfire		σ =			

$\mu_3 = \Sigma s_i p_i - 3\,\Sigma k_i p_i\,\Sigma p_i + 2(\Sigma p_i)^3$

$\alpha_3 = \mu_3/\sigma^3$ = skewness value

Table 2
US Army Armament Command Drawings

B8595819 - Primer (Styphnate) for Caliber .30 Match

C7645332 - Primer (Styphnate) for Caliber .30 and Caliber .30 Blank

B6200959 - Primer (Styphnate) for Caliber .30 Carbine

C11751131 - Primer (Styphnate) for Caliber .30 Carbine

B10534279 - Primer (Styphnate) for 5.56mm

B8594094 - Primer (Styphnate) for 7.62 Match

B10522621 - Primer (Styphnate) for 7.62mm, 7.62mm Blank, 7.62mm Grenade, 7.62mm Match, and Caliber .30

B1053489 - Primer (Styphnate) for 7.62 Match, 7.62mm Blank, Caliber .30, and Caliber .30 Match

B7645336 - Primer (Styphnate) for Caliber .45 and Caliber .45 Blank

B7645339 - Primer (Styphnate) for Caliber .50

Since the quantity of small arms ammo manufd and expended is extremely high, greater emphasis has been placed on an explanation of the primers used in these rounds. However, this in no way is intended to diminish the importance of additional types of percussion primers which find wide use in artillery ammo (Table 3)

Table 3
Percussion Primers Used in Artillery Ammunition

Primer	US Army Armament Command Drawing	For Use In
M36A2	D7259094	20mm Percussion Ammo
M61*	8831157	Ignites BlkPdr Tubes in a Number of Artillery Rounds
M29A1**	8798312	Fuses
M42***	See McDonnell Aircraft Company Report #MDCA0514 of 30 June 1970	Fuses

* Loaded with FA70 Composition
** Loaded with PA101; contains basic Lead Styphnate
*** Loaded with either FA70 or Lead Styphnate compns

The firing pin mechanisms used in both small arms weapons and artillery guns produce firing pin energies of considerable magnitude. As a matter of illustration, the spring-actuated firing pin of the M-14 rifle has a striking energy of at least 100 inch-ounces; whereas, the primers for these 7.62mm cartridges require 60 inch-ounces. This favorable situation results from the fact that no excessive restriction is placed on the weight, volume, or geometry of the firing mechanism. Consequently, the primers used in these weapons are considered to possess a normal degree of sensitivity. This allows the ordnance to be handled safely, yet insures reliable performance in the weapon (Refs 2, 5 & 9)

In mechanical fuses, where percussion primers are required, it seems fairly obvious that space requirements impose limits on the size of spring mechanisms or other physical modes of causing firing pins to move. The result is that, for fuses and other applications of this type, it becomes necessary to use primers of greatly increased sensitivity (Refs 6 & 8). This condition is illustrated with the M29A1 primer which is required to fire with an applied energy of 16 inch-ounces. This increased sensitivity is achieved by the use of thinner primer cup metal of softer alloy. Sensitivity can be further enhanced by the use of more sensitive priming mixt (Refs 2, 6 & 20)

Table 4 shows the approved and standardized priming mixts which possess greater sensitivity than FA70, FA90, or FA956, previously listed (Refs 8, 12, 13, 17 & 20)

High-Temperature-Resistant Percussion Primers

Until the USA became seriously involved with the space program in 1957, little emphasis was placed on the performance of ordnance, particularly high energy materials, after exposure to significant periods of high temps. Firing of ammo at −65°F and +165°F had been a routine procedure in research and developmental phases, but no requirements had ever been enunciated for performance criteria at higher than +165°F or for prolonged exposure to this or even higher temps (Ref 9)

The motivation to develop high-temp-resistant primers is well documented by McDonnell Aircraft Company (Ref 15), based on early work by

Table 4
Standardized Priming Mixtures

Ingredients	PA100	PA101	793	NOL160	NOL130
Lead Styphnate, Basic	–	53%	39%	60%	40%
Lead Styphnate, Normal	38%	–	–	–	–
Barium Nitrate	39%	22%	44%	25%	20%
Lead Azide	–	–	–	–	20%
Tetracene	2%	5%	2%	5%	5%
Lead Dioxide	5%	–	–	–	–
Calcium Silicide	11%	–	14%	–	–
Aluminum Powder	–	10%	–	–	–
Antimony Sulfide	5%	10%	–	10%	15%

the Frankford Arsenal (Ref 9) and Remington Arms Company, Inc (Ref 14). It is important to note that these primers were required for proplnt-actuated devices (PAD) used in military aircraft to perform a variety of functions. The most important illustration of this type of device is the pilot ejection system, which includes many proplnt devices, each activated by percussion primers. The entire system culminates in the ejection of the pilot from the aircraft

It was found that the primers used in these systems, which contained FA70 priming mixt, were subject to solar radiation in closed areas (in some locations in the aircraft), which produced temps of up to +235°F. In addition, it was predicted that certain devices would be exposed to temps estimated at +400°F. As a result of the consideration of these factors, a goal of successful functioning after 2000 hours at 400°F was established

The development of a reliable high-temp-resistant primer was a problem of considerable challenge and technical effort. It was found that none of the available expl-type priming mixts would survive. Eventually, mixts based on the use of K chlorate evolved. Two high-temp mixts were developed as shown below (Refs 14 & 20)

Ingredient	G-11	G-16
Potassium Chlorate	53% *	53%
Antimony Trisulfide	25%	30%
Calcium Silicide	12%	17%
TACOT **	10%	–

* The percentages shown are by wt

** TACOT is the trade name for a duPont high-temp-resistant secondary expl

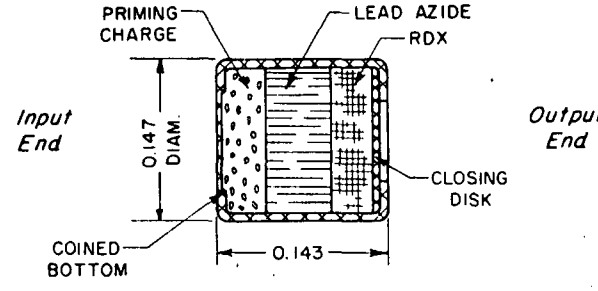
Mixture G-11 has been demonstrated to be the more preferable of the two mixts and has been manufd in three different types for various applications. This is a relatively brisant primer, will withstand 400°F for prolonged periods, and will continue to operate. Depending on the metal components used (cups and anvils), the energy to fire will vary as follows (Ref 15):

Primer	Energy Input
44-G11	90 inch-ounces
49-G11	85 inch-ounces
72-G11	100 inch-ounces

Stab Detonators

It is becoming increasingly clear that the preponderant amt of modern ordnance requiring the initiation of HE charges utilize electric initiation. However, there still remains a continued requirement for the use of percussion initiation. The use and description of sensitive artillery primers, eg, M29A1, etc, to accomplish this has previously been discussed

In instances where the expl is to be detonated without a primer and whose output will not reliably initiate secondary HE charges, the initiator takes the form of a stab detonator (Refs 8, 12 & 13), a diagram of which is shown in Fig 4



STAB DETONATOR (M55)

Fig 4

As shown in Fig 4, the stab detonator is a small, sensitive component which is capable of reliably initiating high-order detonation in the next HE element in the expl train. It differs from the primer in that its output will initiate reliably secondary HE charges

Stab detonators are made in the form of cylindrical cups of Al, stainless steel, Cu, or gilding metal. The open end is sealed with a closing disc of metal or of paper over which the end of the cup is crimped

Whereas primers contain a single heterogeneous expl charge of priming mixt, detonators and especially stab detonators contain three charges, primary, intermediate, and base, although sometimes two or three are combined. The primary charge is near the input or acceptor end and the base charge is near the output end. With stab detonators, the percussion sensitivity is a function of the type of priming compn used (see Table 4), the loading pressure exerted on the mixt during manuf, and the thickness and

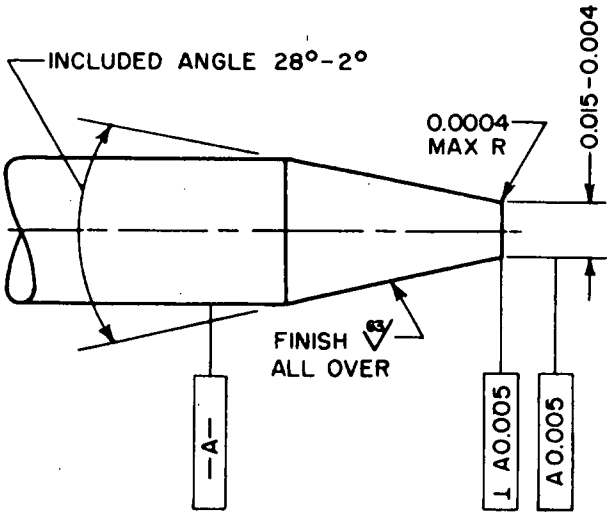


Fig 5 Standard Firing Pin for Stab Initiators

rigidity of the metal at the input end. In addition – and of vital importance – is the configuration of the striking end of the firing pin, the standard design of which is shown in Figure 5

The functioning of a stab detonator involves the conversion of mechanical energy into concentrated heat, with the energy necessary being nearly proportional to the amt of material (priming mixt) which is heated (Ref 4). The standard firing pin is a truncated cone. It has been found that the less sensitive the priming mixt, the larger the optimum diameter of the flat. It has also been determined, both by experience and expt, that the most compact shape for a cylinder is one whose length is equal to its diameter. Thus, as the energy required for initiation is increased, it is advantageous to distribute it over a large enough area to limit the effective length to nearly its diameter. The flat diameter as shown serves the standard priming mixts in use. Both steel and Al alloy firing pins are used, but Al results in a significant but not serious decrease in sensitivity. The effect of eccentricity of the firing pin is such as to cause a decrease in sensitivity

Since stab detonators contain no restraining anvil as do percussion primers, the resistance to penetration of the firing pin becomes quite important. This is the role of compression or density of the mixt. With higher density, the kinetic energy of the firing pin is dissipated over a shorter distance, so that a smaller quantity of expl is heated to a higher temp (Table 5)

Table 5
Effect of Loading Pressure on Initiator Sensitivity *

Loading Pressure (1000psi)	Drop Test Height (inches)
15	1.31
25	0.91
40	0.77
60	0.68
80	0.57

* NOL priming mix in MARK 102 cups; 2-ounce ball.

Since the resistance of solids to deformation does not change very much with moderate changes of deformation rate, the power dissipation by the displacement of compressed priming mixt by a firing pin is nearly proportionate to its velocity (Ref 19)

Pb Azide (LA), which is the most important expl used in detonators (Ref 11), although extremely sensitive to shock, heat, and friction, is not sufficiently sensitive to stab action to insure 100% reliability in firing from the stab action. Consequently, the priming mixt is used as a first-fire layer in these units. RDX (cyclotrimethylenetrinitramine), also known as Cyclonite, is contained as the output charge of the typical stab detonator. Its output results in a detonation of other expls (Ref 11)

The selection of a stab detonator for a specific application requires a consideration of both input and output (Ref 7). The situation exactly duplicates the problems encountered in the selection of a percussion primer. However, as previously discussed, the end purpose of a detonator is different: the input energies are significantly lower, and the output is intended to initiate a high expl. In addition to the main criteria, consideration must also be given to size, weight, cost, and reliability

When designing a stab detonator, the engineer will select the firing pin so that the entire initiation mechanism is under control. This permits close coordination with other systems designers involved in the weapon development, and thus insures that the stab detonator will receive the proper stimulus

The output of a stab detonator is a detonation. Unfortunately, available output data are more nonspecific than input data so that firm, quant choices of output are difficult to make. Consequently, comprehensive testing is usually required (Refs 6 & 12)

In addition to the type of output, the functioning time of the detonator, which is the interval from delivery of the input to the stab detonator until the output of the initiator is realized, is of considerable importance. Where fast initiation is required, the use of LA is essential and, in addition to being used as the intermediate charge, is sometimes incorporated in the initial priming charge in minor percentages to decrease the operation time of the LSt mixt

The sensitivity requirements of stab detonators, like percussion primers, are specified in terms of wt and height of a falling ball, measured in a standard drop-test machine (Refs 8, 12 & 13). The actual test detonators are contained in an enclosed but vented housing. The actual sensitivity can be detd by using the complete rundown method, which has been described under "Percussion Primers". Although requiring a relatively large sample, it provides an excellent assessment of the distribution of the underlying population. The data are treated in the same manner as previously described, which permits the calcn of the all-fire and all-misfire heights or energies

In the case where the number of samples is more limited, the staircase or Bruceton test is applied. This is one in which a predetermined set of steps in the magnitude of the initiating stimulus is established before starting and in which the magnitude for each trial is determined by results of previous trials. In the Bruceton test, the magnitude of stimulus used in each trial is determined by the result obtained in the immediately preceding trial. If the preceding trial resulted in a misfire, the stimulus to be used in the present trial is one step higher than that in the previous trial. If it fired, the stimulus of the present trial should be of a magnitude one step lower. The test is continued in this manner for a predetermined number of trials

The validity of the results of this procedure depends on whether the assumption is valid that the steps are of uniform size in a system in which the frequency of explns is normally distributed. The Bruceton test is most applicable to systems for which extensive tests have established the nature of a generic normalizing function. Unfortunately, it is often applied to systems for which it is not economically feasible to carry on such a program. The Bruceton exptl technique is often used as a convenient means for the collection of data in situations where the assumption of normality is known to be false and where it is intended to use other methods of analysis. An objection which has been raised to this practice is that the strong tendency of the Bruceton technique to concentrate testing near the 50% point reduces the value of the data in estimating the nature and deviation of the distribution. However, it is pointed out, the sample sizes available are usually so small that a reasonable estimate of the mean and a rough guess of the deviation is the most which can be expected

The output of detonators, regardless of the mode of initiation, is intended to induce detonation in a subsequent charge. The two features of output which are useful for this purpose are the shock wave it emits and the high velocity of its case (fragments). Although it is possible to imagine detonator designs which are effective in inducing detonation without detonating themselves, the output effectiveness of detonators is directly related to the quantity of the explosive which detonates, and to the strength of this detonation. These quantities are somewhat less predictable than in most other components because the transitions from burning to detonation and from low-order to high-order detonation take place in the detonator. These transitions may require anything from one hundredth of an inch to the whole length of the detonator, depending upon such factors as loading density, compn, particle size, confinement, and column diameter. Recent improvements in LA production have resulted in materials in which these transitions require so little expl that the output of a detonator can be predicted with a fair degree of confidence (Ref 17). The effective output of a stab detonator includes factors of pressure, duration, and area over which the pressure acts

Detonator output is difficult to characterize except in terms of the characteristics of a subsequent charge. This is to be expected because the transmission of detonation involves the interaction of quantities associated with the acceptor

as well as with the donor. Output is measured by means of gap or barrier tests, sand test, Cu block test, Pb disc test, steel plate dent test, Hopkinson bar test, and in terms of the air shock produced. These tests are described in various publications (Military Standards **316, 317 & 320**)

Both the Pb disc test and the steel dent test are of particular significance to stab detonators. As a matter of illustration, the steel dent test (Ref 10) consists of firing a detonator in direct end-on contact with a steel block. The depth of the dent produced is a measure of output. The depth, or better, the volume of the dent correlates well with initiation effectiveness. The low-rate detonation, which crushes nearly as much sand as high-order detonation, makes no dent in a steel plate. It has been demonstrated that the depth of the dent is proportionate to the excess of pressure over the yield strength of the steel of the dent block, integrated over the volume of the detonation head. It has been found that a detonator of 0.190-inch diameter or larger, which produces a dent 0.010 of an inch deep in a mild steel block, will initiate a lead of Tetryl or RDX under favorable conditions. Specification requirements for detonators to be used in fuses are usually at least 0.015 to 0.020 inch in depth, and many produce dents up to 0.060 inch deep

Stab detonators, as a subclass of initiators, in general are loaded by pressing powdered expls into the cup. Although most initiators are loaded at between 10,000 and 20,000psi, stab priming mixts are pressed at between 30,000 and 80,000psi. This increment is loaded first, since the priming mixt is the most vulnerable to moisture and other atm gases; consequently, it is farthest from the crimped end in a coined-bottom cup. The intermediate charge of the stab detonator is LA, which is used exclusively in this application due to its demonstrated superiority over other expls. Although most detonators have previously used dextrinated LA, the variation in performance in the growth of detonation has caused a preference of other forms such as RD1333, a development of Brit origin (Ref 13)

The base charge of stab detonators had usually been Tetryl but present designs use RDX

The total energy released by a stab detonator is the sum of the heat of detonation and the quantities of the various expls used. Of this energy, only that from the expl which detonates high-order is effective initiation output obtained. In general, this includes the base charge and part of the intermediate charge. The azide which actually detonates must be sufficient to initiate the base charge. In current detonator designs, this is assured by the use of at least 100 milligrams of LA. It is common practice to require 0.10-inch minimum column heights. Although the use of RD1333 (Ref 12) permits smaller quantities of this type of LA, sufficient data has not been accumulated to provide reliable minimum quantities

A final and important factor in the output of a stab detonator or, as a matter of fact, any type of detonator, is the confinement afforded by the containing structure. This is difficult to describe in quant terms because different properties of the confining structure are involved in the promotion of detonation growth and in increase of the output of stable detonation; the confinement provided by surrounding fuse structures as well as that of the detonator itself can contribute significantly to the effective output of a detonator. In the detonation process, tightness is the most important factor in the early stages; whereas, as the growth continues, the strength of the container becomes important. As a stable rate of detonation is achieved, the pressure exceeds the bursting strength of any normal type of container and confinement is chiefly a matter of inertia

A list of some of the more commonly used stab detonators, together with a short compilation of some important factors for each, is shown in Table 6

Table 6
Stab Primer Data

Item No.	Primer No.	Diameter (Max) Inches	Length (Max) Inches	Functioning		Cup Matl	Primer Mix (MG)	Inter Chg (MG)	Base Chg (MG)
				Wt of Ball (Oz)	Ht of Drop (Inches)				
1.	M26	.193	.115	4	15	GM	116 PA #100	–	–
2.	M41	.241	.248	4	3	GM	180 PA #100	–	225 Lead Azide
3.	M45	.241	.342	4	3	GM	105 PA #100	117 Black Powder	73 Black Powder
4.	M55	.193	.115	4	3	GM	70 PA #100	–	57 Lead Azide
5.	M56	.302	.172	4	3	GM	365 PA #100	–	–
6.	M72	.241	.245	2	2	SS	350 PA #100	–	–
7.	M97	.192	.115	1	4	SS	85 NOL #130	–	200 Lead Azide
8.	T96	.192	.500	2	3	AL	120 NOL #130	180 Lead Azide	165 Lead Azide
9.	T97	.108	.106	2	6	GM	22 PA #100	–	–

Friction Primers

The importance of frictional heating in the initiation of expls is a subject of considerable importance. The frictional sensitivity is directly involved in the handling hazards of all high-energy materials; and considerable attention has been directed toward gathering of frictional sensitivity data on almost all mil expls, in addition to an entire host of pyrotechnic mixts and certain proplnts (Refs 6 & 17)

Although a significant quantity of this information has been obtained, initiating devices operating on this principle and known as friction primers appear to be anachronous

Friction primers are devices for the production of fire, where the mechanical stimulus is either a push or pull of a roughened rod or wire thru a pellet of priming compn. These were used for firing artillery in situations where the proplnt charge was loaded separately and not enclosed in a brass case, complete with ignition tube and percussion element (percussion primer). They have also been used by being crimped to the end of a Bickford fuse as a means of ignition. This latter system has been replaced by a mechanical fuse lighter which operates by first removing a safety pin and then pulling a handle back which compresses a spring with attached firing pin. At the end of the rearward stroke, the pin and spring are released, moving forward to strike a conventional percussion primer

Friction primers have also been used for igniting flares which were then thrown overboard from aircraft. It would appear obvious that any application in which ordnance is manually ejected from aircraft would conjur up thoughts of WWI systems. In any event, the pull element of the primer was attached to the aircraft by a suitable length of twine or wire; and the mass of the falling flare pulled and then broke it off

The mixts which were most favored for friction primers were as follows (Ref 6):

Table 7
Friction Primer Compositions

Ingredient	Type 1	Type 2	Type 3
K Chlorate	67%	56.2%	44.6%
Sb Sulfide	33%	24.6%	44.6%
Sulfur	–	9.0%	3.6%
Meal Powder	–	–	3.6%
Ground Glass	–	10.2%	3.6%

All ingredients were in the powdered form except in the Type 1 mixt, where half the K chlorate is powdered and the other half is in granular form. Apparently, the first mixt was considered best; the sulfur contained in the second and third mixts served to increase sensitivity but compromised the storage life. Mixts of sulfur with K chlorate were subject to decompn in moist atms. Although efforts were made to decrease the decompn by the additional anti-acid agents, eg, Ca carbonate, trimethylamine, etc, and the use of high percentages (5%) of gum arabic, these mixts soon disappeared from the scene. This is in the same time frame in which the US Army abandoned the use of sulfur with K chlorate in percussion primers and adopted FA70, in which the sulfur was replaced by K thiocyanate

What has been described so far constitutes only one half of the friction primer, ie, the main charge, contained in a cylindrical cup. Centrally located in the K chlorate mixt was a loop of braided wire, coated with red P (90%) and dried shellac (10%). Any mixt of red P with K chlorate was, and still is, very sensitive, hazardous, and unpredictable. There is ample reason to understand why friction primers were abandoned and replaced with spring-actuated firing pins to fire percussion primers and carry the sequence thru a suitable expl train

Attempts to find any present application have not been fruitful. It is possible that, in the vast array of ordnance, some type of friction primer device may still be in use

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Prism or Prismatic Powder. See under Black Powder or Gunpowder in Vol **2**, B167-R
Addnl Ref: Davis (1943), 41–42

PRODUCTS, DETONATION

Detonation is universally defined as a chemically supported shock wave. It is a cooperative process in which the shock wave activates an exothermic chem reaction and the chem reaction, in turn, supports the shock. The products generated in such detonation reactions are the subject of this article. A very cursory description of detonation products was given in Vol **4**, D494-R. Below we will consider the main equilibria that control the compn of detonation products, and present examples of product compns calcd theoretically as well as observed exptly

Detonation Equilibria. Most of the commonly used expls are compds or mixts whose elemental compn consists of C, H, N, O. If the expl is reasonably *oxygen-balanced* (see *Oxygen Balance* in this Vol) then the detonation product compn is primarily detd by the *water gas equilibrium:*

$$CO_2 + H_2 = CO + H_2O \quad (1)$$

Note that there is no net change in the number of moles of gas in this equilibrium. Therefore, by Le Chatelier's principle, this reaction will be independent of external pressure (ignoring second-order effects due to gas imperfections). Under these conditions the N of the expl will appear as N_2 in the detonation products

For oxygen-rich expls NO will be produced according to the reaction

$$N_2 + O_2 = 2NO \quad (2)$$

This equilibrium is also independent of pressure

In oxygen-poor expls the so-called soot reactions become important. These are:

$$2CO = CO_2 + C_{(s)} \quad (3)$$

$$CO + H_2 = H_2O + C_{(s)} \quad (4)$$

Note that the right-hand terms of reactions (3) and (4) contain fewer moles of gas than their respective left-hand terms. Consequently increase in pressure will drive both these reactions to the right

If the expls contain excess H the reactions

$$N_2 + 3H_2 = 2NH_3 \quad (5)$$

and

$$C_{(s)} + 2H_2 = CH_4 \quad (6)$$

will also come into play, but will not influence product compn as much as reactions (1), (3) and (4). Reactions (5) and (6) as written are also favored by high pressure

Except for O_2 (a product in oxygen-rich expls), equilibria (1) thru (6) account for all major detonation products of condensed CHNO expls. In gas detonations (ie, at low detonation pressures) such species as OH, H etc may also exist. In "experimental" measurements of detonation products (to be discussed later) HCN frequently appears as a minor product

For expls containing halogens (X), there is some controversy about the form in which these appear in detonation products. Some theoretical calcns (Ref 2) indicate that halogenated expls produce CX_4. Exptl measurement (Ref 4),

however, suggest that the main product is HX and very little CX_4 is formed

Metallized expls or expls containing metal salts produce metal oxides. For example, in aluminized expls the Al reacts with any available oxygen to form Al_2O_3

Experience has shown that the oxygen distribution in the products of a *metallized military explosive* favors the formation of the metal oxide. Any remaining oxygen then forms steam with the H of the expl. If any oxygen is still available it forms CO_2, and any unreacted C atoms then show up as free carbon in the products. (Confinement of the expls favors the formation of CO_2 and C at the expense of CO). In halogenated expls HX appears to be formed in preference to H_2O and H_2

We have noted that an increase in pressure tends to shift all the above reactions, except (1) and (2), to the right. We will now show that an increase in temp shifts equilibrium (1) to the right, but rather mildly, whereas it shifts all the other equilibria strongly to the left. Thus for reactions (3) thru (6) to be important, the effect of pressure must override the effect of increasing temp

The effect of temp on chemical equilibria is conventially determined via the free energy function $\Delta G^\circ/RT$ and the ideal equilibrium constant K. Table 1 gives the free energy function G°/RT for the important detonation products of CHNO expls. From these data $\Delta G^\circ/(RT)$ can be obtained for different temps for the reactions of interest, and ideal equilibrium constants computed according to:

$$\ell nK = -\Delta G^\circ/(RT) \qquad (7)$$

where

G° = standard state Gibbs free energy
R = gas content
T = absolute temperature

Table 1

Ideal Gas Free Energy Functions $[G^\circ/(RT)]$ for Detonation Products

T, °K	CO_2	CO	H_2O	H_2	$C_{(s)}$	NH_3	N_2	CH_4	H	O
1000	−75.69	−38.88	−53.94	−17.49	−1.522	−31.70	−24.95	−34.17	–	–
1400	−63.66	−36.03	−46.77	−18.39	−2.064	−31.44	−25.97	−33.38	–	–
1500	−61.74	−35.61	−45.66	−18.59	−2.190	−31.49	−26.20	−33.38	–	–
1600	−60.09	−35.26	−44.70	−18.78	−2.312	−31.57	−26.43	−33.41	+0.435	−2.84
1800	−57.42	−34.72	−43.17	−19.14	−2.454	−31.79	−26.84	−33.59	–	–
2000	−55.36	−34.34	−42.00	−19.47	−2.764	−32.06	−27.24	−33.85	−3.31	−7.06
2500	−51.89	−33.79	−40.11	−20.20	−3.256	−32.83	−28.12	−34.70	–	–
3000	−49.83	−33.58	−39.07	−20.84	−3.686	−33.65	−28.89	−35.67	–	–
4000	−47.70	−33.58	−38.19	−21.90	−4.406	−35.24	−30.19	−37.61	−11.41	−16.11
5000	−46.81	−33.81	−37.99	−22.77	−4.996	−36.67	−31.29	−39.41	−13.24	−18.13

From Table 1 and Eq (7) we obtain the following:

Reaction	$K_{1000°K}$	$K_{1600°K}$	$K_{3000°K}$
(1)	0.70	2.97	7.24
(3)	0.58	2.9×10^{-4}	1.2×10^{-6}
(4)	0.40	1.1×10^{-3}	8.6×10^{-6}
(5)	8×10^{-7}	3×10^{-9}	3×10^{-11}
(6)	0.097	–	6.1×10^{-5}

These data show quite clearly that increasing temp (detonation temp is expected to be in the range of 2000–4000°K) does not favor the products of reactions (3) thru (6)

For nearly oxygen-balanced expls equilibrium (1) will dominate and control the compn of the detonation products. As already stated this equilibrium is expected to be independent of pressure if the gases behave ideally. But even for ideal gas behavior and an oxygen-balanced expl, no direct comparison can be made between theoretical detonation product calcns and observed products. This is so because measurements are made at temps much lower than detonation temps, and the products reequilibrate as the temp drops. Further complications arise because the reequilibration *freezes* at some rather high temp. This is a consequence of reaction rates. At temps below some *frozen equilibrium temperature*, T_{fr}, reaction rates become so slow that for all practical purposes further reequilibration ceases even if the temp drops well below T_{fr}

To anticipate some of the results to be presented later, it is instructive to compute the equilibrium compn of PETN at 1600°K. PETN is nearly oxygen-balanced and as will be shown later its $T_{fr} \simeq 1600°K$. The empirical formula for PETN is $C_5H_8N_4O_{12}$. Let X be the number of moles of CO_2 at equilibrium, and C, H, O the original gram atoms of carbon, hydrogen and oxygen respectively. Then from mass balance and Raoult's law

$$p_{CO} = \frac{P(C-X)}{n_t}$$

$$p_{CO_2} = \frac{PX}{n_t}$$

$$p_{H_2O} = \frac{P}{n_t}(O-C-X)$$

$$p_{H_2} = \frac{P}{n_t}(\tfrac{1}{2}H+C-O+X)$$

where

n_t = total number of moles of gas at equilibrium
p = partial pressure
P = total pressure at equilibrium

The ideal equilibrium constant for reaction (1) is

$$K = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = \frac{(C-X)(O-C-X)}{X(\tfrac{1}{2}H+C-O+X)}$$

$$= \frac{(5-X)(7-X)}{X(X-3)} \quad \text{for PETN}$$

From Table 1, K=2.97 at T=1600° and X=3.50= moles CO_2 per mole of PETN; C–X=1.50= moles CO per mole of PETN; O–C–X=3.50= moles H_2O per mole of PETN; ½H+C–O+X= 0.50=moles H_2 per mole of PETN; N/2=2.00= moles N_2 per mole of PETN. This computed equilibrium mixt matches almost exactly the compn found by Ornellas (Ref 3) for unconfined, or for that matter confined, PETN

Similar computations for HMX or TNT also match the respective compns found by Ornellas (Refs 4 & 6) for *unconfined* HMX or TNT. This is to be expected since rapid pressure release in unconfined samples prevents accumulation of appreciable amounts of the products of reactions (3) thru (6)

Theoretical Detonation Product Compositions.

Except for oxygen-balanced expls, the computation of detonation products depends strongly on the choice of the equation of state (EOS) for these products. In the US the BKW EOS (see Vol **4**, D272-R) has been favored and most of the computed product compns below will be based on it. Some of these will be compared with the relatively few calcns based on a Lennard-Jones-Devonshire (LJD) EOS (see Vol **4**, D287-L)

CJ state product compns calcd via the BKW EOS are compared with compns computed with LJD types of EOS in Tables 2–4. For PETN (Table 2) an early variant of the LJD EOS (Ref 1) shows no solid C in the products and somewhat more CO than the BKW computation. Note that for PETN both EOS give product compn that show relatively little variation with ρ_o, the initial density of the expl. This is not the case for RDX and TNT (Tables 3 & 4) where a change in ρ_o results in substantial changes in product compn.

For RDX and TNT a modern form of the LJD EOS (JCZ-3) was used (Ref 5). Note that this EOS gives substantial amounts of NH_3 in the products. This is rather startling since the JCZ-3 calcns give lower pressures and higher temps than BKW calcns. Both these effects are in the direction of *reducing* rather than *increasing* the amount of NH_3 formed, unless

Table 2
PETN—CJ State

*	ρ_o=1.4g/cc		ρ_o=1.0g/cc	
	BKW (Ref 2)	LJD (Ref 1)	BKW (Ref 2)	LJD (Ref 1)
CO_2	3.47	3.29	3.04	3.19
CO	1.07	1.67	1.96	1.81
$C_{(s)}$	0.46	none	none	none
CH_4	0.0008	0.033	0.0002	0.0009
H_2O	3.99	3.73	3.94	3.77
H_2	0.006	0.20	0.050	0.23
N_2	2.00	1.99	1.99	1.98
NH_3	0.003	–	0.004	–

*All compns in moles of product/mole expl

Table 3
RDX—CJ State

*	ρ_o=1.8g/cc		ρ_o=1.0g/cc	
	BKW (Ref 2)	JCZ-3 (Ref 5)	BKW (Ref 2)	JCZ-3 (Ref 5)
CO_2	1.49	2.39	0.672	1.08
CO	0.022	0.132	1.85	1.90
$C_{(s)}$	1.49	0.478	0.45	none
CH_4	none**	0.001	0.022	0.015
H_2O	3.00	1.09	2.80	1.93
H_2	none**	0.005	0.111	0.344
N_2	3.00	2.36	2.98	2.77
NH_3	0.00003	1.27	0.029	0.46

*All compns in moles of product/mole expl
**Less than 10^{-5} moles/mole

Table 4
TNT—CJ State

*	ρ_o=1.6g/cc		ρ_o=1.0g/cc	
	BKW (Ref 2)	JCZ-3 (Ref 5)	BKW (Ref 2)	JCZ-3 (Ref 5)
CO_2	1.64	1.97	0.964	0.672
CO	0.230	0.474	1.71	2.40
$C_{(s)}$	5.13	4.42	4.31	3.40
CH_4	0.0003	0.03	0.016	0.056
H_2O	2.495	1.47	2.36	1.47
H_2	0.0013	0.033	0.085	0.379
N_2	1.499	1.155	1.492	1.306
NH_3	0.0015	0.630	0.016	0.329

*All compns in moles of product/mole expl

some drastic gas imperfection effects radically change the well-known behavior of reaction (6) (Haber synthesis) at CJ conditions

"Measured" Product Compositions.

Actual measurements of detonation products at CJ conditions do not exist for pure expls, but may be available for expl mixts with inerts. By far the best efforts to measure product compns were made by Ornellas & co-workers (Refs 3, 4 & 6) who made accurate calorimetry and compn measurements on highly confined and unconfined expl samples. The expls he studied were: PETN, HMX, NM, TNT, Bis(2,2-dinitro-2-fluoroethyl)formal (FEFO), 1,2-Bis(difluoro-amino) propane (1,2 DP), Benzotrifuroxan (BTF), LX-11-0 (80.1/19.9 HMX/Viton), XTX-8003 (80/20 PETN/Sylgard 182), and three Hydrazine Nitrate (HN) mixts. Of course, most of these measured compns are not CJ products, but reequilibrated mixts of CJ products at some frozen equilibrium temp $T_{fr} < T_{CJ}$

Ornellas found that for PETN, sample confinement had practically no effect on product compn, which in all cases was very close to that shown earlier in the article in the illustration of an ideal gas equilibrium calcn. We used T=1600°K for our calcn, which apparently corresponds quite closely to T_{fr} for PETN. Measurements on unconfined samples are not reported for NM, FEFO, 1,2 DP and the HN mixts. In all the remaining expls, product compn was strongly affected by confinement. In general, confined samples of these materials produced more $C_{(s)}$ and less CO than unconfined samples

Table 5
Comparison of Measured TNT Products with Isentropic Compositions

	Measured for ρ_o=1.53g/cc* (Ref 4)	JCZ-3 Isentropic Compositions for ρ_o=1.66g/cc (Ref 5)	
		T=2012°K	T=1811°K
CO_2 **	1.25	1.24	1.25
CO	1.98	1.97	2.13
$C_{(s)}$	3.65	3.62	3.36
CH_4	0.099	0.17	0.25
H_2O	1.60	1.55	1.36
H_2	0.46	0.47	0.55
N_2	1.32	1.45	1.47
NH_3	0.162	0.10	0.06

* Highly confined samples
** Moles product/mole expl

Table 6
Comparison of Measured RDX Products with Isentropic Compositions

	Measured for ρ_o=1.89g/cc * (Ref 4)	JCZ-3 Isentropic Compositions for ρ_o=1.8g/cc (Ref 5)		
		T=1986°K	T=1551°K	T=2344°K
CO_2 **	1.44	1.41	1.53	1.48
CO	0.80	1.06	1.13	0.94
$C_{(s)}$	0.74	0.42	0.014	0.53
CH_4	0.03	0.11	0.32	0.05
H_2O	2.39	2.12	1.80	2.10
H_2	0.23	0.29	0.43	0.19
N_2	2.76	2.88	2.96	2.79
NH_3	0.29	0.24	0.08	0.41

* Measurements were made for HMX. The values shown are 3/4 of the corresponding product in Ref 4, since RDX is $C_3H_6N_6O_6$ and HMX is $C_4H_8N_8O_8$. Highly confined samples
** Moles product/mole expl

For confined expls, Ornellas found that measured compns generally matched compns computed along CJ isentropes if the isentrope temp was between 1500 and 1800°K for BKW-type calcns, and 1800 to 1900°K for LJD calcns of the type used in Ref 1. Agreement between observed and computed values was poor for FEFO. For the three HN mixts, CJ temps are low (all below 1500°K). Quite possible these compns are close to actual CJ compns

For unconfined samples of PETN, HMX, LX-11-0, TNT, BTF & XTX 8003, calcns assuming ideal gas equilibria also match observed compns if the calcns are made for temps in the range of 1500 to 1800°K

The modern version of LJD, however, suggests that T_{fr} is greater than 1500–1800°K. As shown in Tables 5 & 6, JCZ-3 isentrope calcns indicate that $T_{fr} \simeq 2000$°K for RDX and TNT or slightly greater than the older type LJD isentrope calcns. At present no objective choice appears possible between freeze out temps in the 1500–1800°K range (BKW & ideal gas) or the 1800–2000°K range (LJD)

Written by **J. ROTH**

Refs: 1) W. Fickett, **LA 2712** (1962) 2) C.L. Mader, **LA 2900** (1963) 3) D.L. Ornellas et al, RevSciInstr **37**, 907 (1966) 4) D.L. Ornellas, JPhysChem **72**, 2390 (1968) 5) M. Cowperthwaite & W.H. Zwisler, SRI Final Report Contract N60921-72-C-0013 (1973) 6) D.L. Ornellas, Combustn&Flame **23**, 37 (1974)

Progressite. An expl patented by Turpin of Fr in 1882 contg Ba nitrate 65, Amm picrate 15, DNB 10, coal tar 6, and brown or red charcoal 4%
Refs: 1) J.P. Cundill, MP **6**, 108 (1893) 2) Daniel (1902), 651

Progressites. Permissible expls invented about 1896 by A.G. Dynamit Nobel in Ger. Typical formulations contd: (a) AN 94–95 & aniline hydrochloride 6–5%; (b) AN 89.1–92.2, amm sulfate 6.1–2.3, and aniline hydrochloride 5.5%, with or without 1.2% sulfur added
Refs: 1) Daniel (1902), 652 2) J. Sauer, SS **2**, 112 (1907) 3) Anon, SS **8**, 398 (1913) 4) Marshall **1**, 398 (1917)

Projectiles. See under Ammunition in Vol **1**, A383-L to A391-L

The following is a compilation of current (July 1976) unclassified US mil specs on projectiles:

Title	Document No	Date	Custodian
Projectile Bombs, Rockets, And Guided Missile Warheads, Inert Parts, Manufacture Of	MIL-P-16594A	30 June 55	OS*
Projectile (Alternate) For Cartridge, 40MM Practice, M385 and Cartridge, 40MM, High Velocity, Dummy Parts for	MIL-P-48071	09 May 72	PA**
Projectile Assembly For Cartridge, HE, 81MM, M374E1	MIL-P-60626B (2)	03 Apr 68	MU***
Projectile Assembly For Cartridge, Smoke, WP, 81MM, M375	MIL-P-60620B (6)	16 Mar 72	MU
Projectile Atomic Explosive 8 Inch, M422 Shipping Assembly	MIL-P-50833 (1)	22 Sep 75	PA
Projectile Body, Metal Parts Assembly For Cartridge, HE, 81MM M362A1	MIL-P-46502AB (1)	29 Jan 64	MU
Projectile Cubes, Fragment-simulating	MIL-P-46125	21 Sep 67	MR****
Projectile for Cartridge, 105-MILLIMETER, M360, Gb-filled, Without Fuze and Burster	MIL-P-46541	06 June 61	EA*****
Projectile For Cartridge, 81-MILLIMETER Mortar, Smoke, M370, WP Filling Assembly	MIL-P-46512A (1)	26 June 63	EA
Projectile HE, 37MM, M63 Metal Parts Assembly	MIL-P-46648	02 Apr 62	MU
Projectile Load, Illuminating Mk 12 Mod 0 (For 3 Inch /50 Projectile	MIL-P-21356 (1)	20 Aug 71	OS
Projectile Load, Illumination Mk 11 Mod 0	MIL-P-21355 (3)	20 Aug 71	OS
Projectile Load, Smoke, WP, 5 Inch 54 Caliber, Mk 14, Loading Assembly	MIL-P-23430	11 Sep 62	EA
Projectile Load, 5 Inch 54 Caliber, WP, MK 14, Filling Assembly	MIL-P-46658A (2)	02 Feb 72	EA
Projectile Load, 6 Inch 47 CALIBER, WP, Mk 13, Filling Assembly	MIL-P-14585A	26 Apr 62	EA
Projectile Metal Parts. Less Ball Assembly, With Fuze, Pd, M536	MIL-P-50203	12 Nov 68	PA
Projectile 155MM Illuminating M485A2 Accessories For, And Assembling And Packing	MIL-P-48249	28 Aug 75	PA
Projectile	MIL-P-11678B	02 Oct 68	EA
Projectile, Ap-t, 76MM, M339 Metal Parts Assembly	MIL-P-60603	10 Aug 66	MU
Projectile, Ap-t, 90MM, M318A1 Metal Parts	MIL-P-60814	17 Apr 67	MU
Projectile, Body, Smoke, WP, 81MM, M370 Metal Parts Assembly	MIL-P-46527B	15 May 64	MU
Projectile, Calibers .22, .30, .50 and 20 MM Fragment-simulating	MIL-P-46593A (1)	12 Oct 64	MU
Projectile, HE, 155MM, M107 Metal Parts Assembly	MIL-P-14824 (2)	12 Mar 74	MU
Projectile, HE, 8 Inch M106 Metal Parts Assembly	MIL-P-60596 (1)	25 Oct 74	MU
Projectile, HE, 4.2 Inch, M329A1 Metal Parts Assembly	MIL-P-60833 (2)	13 Feb 69	MU
Projectile, Heat-fs, 90MM, M431E1, Metal Parts Assembly	MIL-P-46490F	10 Jul 74	MU
Projectile, Heat-t, 76MM, M495 Metal Parts Assembly	MIL-P-48495	22 Apr 74	MU
Projectile, Heat, 106MM, M344A1 With FIN M8 Metal Parts Assembly	MIL-P-50308 (4)	22 Nov 74	MU
Projectile, Hep-t 105MM, M393A2 Metal Parts	MIL-P-60574B (1)	17 Mar 72	MU
Projectile, Hep-t, 106MM, M346A1 Metal Parts	MIL-P-60521 (4)	28 Feb 74	MU
Projectile, Hep, 165MM, M123A1, Metal Parts	MIL-P-60523	16 May 66	MU

Title	Document No	Date	Custodian
Projectile, Hes, 8-Inch, M424A1 Metal Parts	MIL-P-50560 (2)	22 Mar 74	PA
Projectile, High Capacity, Anti Aircraft, And Illuminating	MIL-P-18950	23 Jan 56	OS
Projectile, Illuminating, Localized Heat Treatment Of	MIL-P-18949A	05 Jan 76	OS
Projectile, Illuminating, 81MM, M301A2 Metal Parts Assembly	MIL-P-10590B (1)	26 June 67	MU
Projectile, Painting, Marking, And Greasing (By Projectile Manufacturers)	MIL-P-18948A (1)	10 May 74	OS
Projectile, Smoke, WP, T16E1 For 120MM Gun, M58, And Projectile, Smoke Wp-t, M357 for 120MM Gun, M58, Assembling, Marking and Packing	MIL-P-20601B	26 Nov 63	PA
Projectile, Smoke, WP, 57MM, M308A1 Metal Parts Assembly	MIL-P-14835A	05 May 72	MU
Projectile, Tp-t, 105MM, M468 Metal Parts Assembly	MIL-P-50793 (1)	22 Mar 74	MU
Projectile, Tp-t, 105MM, M489 Metal Parts Assembly	MIL-P-60811 (1)	02 Jun 69	MU
Projectile, Tp-t, 152MM, XM411E1 Metal Parts Assembly	MIL-P-60815A (3)	07 Apr 70	MU
Projectile, Training, 8 Inch, XM440 SHIPPING Assembly	MIL-P-50890	30 Aug 71	PA
Projectile, Training, 8 Inch M423, Shipping Assembly	MIL-P-50227A (1)	30 Nov 71	PA
Projectile, 105MM	MIL-P-14840 (1)	04 Aug 69	MU
Projectile, 105MM, Illuminating, XM314A2E1 Metal Parts Assembly	MIL-P-14852A	18 Apr 72	MU
Projectile, 105MM, Smoke, Be, M84E1 Metal Parts Assembly	MIL-P-14839 (2)	29 May 69	MU
Projectile, 105MM, HE, M1 Metal Parts Assembly	MIL-P-60547C (1)	14 Sep 73	MU
Projectile, 105MM, HE, M1 (HF-1) Metal Parts Assembly	MIL-P-50784	10 Aug 73	MU
Projectile, 105MM, Smoke, WP, M60 Metal Parts Assembly	MIL-P-60548A (1)	10 Sep 74	MU
Projectile, 105MM, Smoke, WP, M60E1, FILLING Assembly	MIL-P-51338 (1)	12 Oct 70	EA
Projectile, 105MM, Tpds-t, XM737E1 Metal Parts Assembly	MIL-P-50791A	23 Apr 74	MU
Projectile, 105MM, Wp-t, M416, Filling Assembly	MIL-P-60090A	05 Jul 68	EA
Projectile, 105MM, WP, M416 Metal Parts Assembly	MIL-P-60601A (1)	10 Oct 75	MU
Projectile, 120MM, He-t, M356, W/fuze, Pd M557, For, 120MM Gun, Loading, Assembly and Packing	MIL-P-46925A (1)	25 Jan 66	PA
Projectile, 152MM, Heat, M409 Metal Parts, Less Fluted Liner	MIL-P-14825A	03 Apr 72	MU
Projectile, 152MM, Slug, Proofing Metal Parts Assembly	MIL-P-60628 (1)	24 Feb 67	MU
Projectile, 152MM, Tp-t, M411A1 Metal Parts Assembly	MIL-P-50369A	18 Mar 76	MU
Projectile, 155 Millimeter Howitzer, M121A1, Vx-filled, Without Fuze and Burster	MIL-P-60077A	23 Jul 65	EA
Projectile, 155 Millimeter, XM454, With Accessories Dod Components Only, Assembly Of	MIL-P-50286	26 Aug 69	PA
Projectile, 155-MILLIMETER Howitzer, M121, And Gun, M122, Gb-filled, Without Fuze and Burster	MIL-P-46549A (2)	05 Aug 68	EA

Title	Document No	Date	Custodian
Projectile, 155-MM Gun And Howitzer, M104 and M110, WP, Fs, Hd And H Filling Assemblies	MIL-P-11807C	6 Jun 57	EA
Projectile, 155MM, Smoke, WP, M110 Loading, Assembling and Packing	MIL-P-60477A	30 Dec 68	PA
Projectile, 155MM, Velocity Test, T5119	MIL-P-50290 (2)	11 Jan 72	PA
Projectile, 155MM, Cs, Tactical, XM631 Assembling and Packing	MIL-P-60419	30 Jan 67	PA
Projectile, 155MM, Gas, M121A1 Assembling, Marking And Packing	MIL-P-46412C	29 Jul 66	MU
Projectile, 155MM, HE, M449A1, Body Assembly For	MIL-P-50535	07 Dec 70	PA
Projectile, 155MM, HE, M449A1, Hardware For	MIL-P-50537	07 Dec 70	PA
Projectile, 155MM, HE, M692 And M731, Non-metallic Hardware For	MIL-P-48376	01 Mar 76	PA
Projectile, 155MM, HE, M483A1 Loading, Assembling And Packing	MIL-P-48749 (2)	23 Mar 76	PA
Projectile, 155MM, HE, M107 Loading, Assembling And Packing	MIL-P-60377A (1)	26 Mar 76	PA
Projectile, 155MM, HE, M449A1 Loading, Assembling And Packing	MIL-P-50538	07 Dec 70	PA
Projectile, 155MM, HE, M449A1, Base Plug For	MIL-P-50536	07 Dec 71	PA
Projectile, 155MM, HE, M470 Loading, Assembling And Packing	MIL-P-46633A	30 Nov 62	PA
Projectile, 155MM, HE, M483A1 Adapter For	MIL-P-50979A (1)	07 Jan 76	PA
Projectile, 155MM, HE, M483A1 Metallic Hardware For	MIL-P-50936A	28 Aug 75	PA
Projectile, 155MM, HE, M692 And M731, Metallic Hardware For	MIL-P-48188	01 Mar 76	PA
Projectile, 155MM, HE, Rap, XM549 (With Warhead And Motor Body) Loading, Assembling and Packing	MIL-P-50578B	07 Feb 76	PA
Projectile, 155MM, HE, Rocket Assisted M549, Accessories For	MIL-P-50574A (3)	20 Jun 75	PA
Projectile, 155MM, HE, Rocket Assisted M549, Delay Assembly For	MIL-P-50570 (3)	06 Feb 75	PA
Projectile, 155MM, HE, Rocket Assisted M549, Motor Body Bonding Assembly For	MIL-P-50569A (4)	07 Feb 76	PA
Projectile, 155MM, HE, Rocket Assisted XM549, Delay Assembly Parts For	MIL-P-50571	14 Jul 71	PA
Projectile, 155MM, HE, Rocket Assisted, M549, Inert, Simulated Parts And Loading	MIL-P-48762	25 Apr 75	PA
Projectile, 155MM, HE, XM483 Non Metallic Hardware For	MIL-P-50944A (1)	27 Apr 76	PA
Projectile, 155MM, Illuminating, M485A2, Parts for	MIL-P-48043 (1)	25 Aug 75	PA
Projectile, 155MM, M483A1 Metal Parts	MIL-P-50345C	21 Feb 75	MU
Projectile, 155MM, Smoke (Hc and Colored), Be, M116B1 and M116E2, Assembling and Packing	MIL-P-20512B	30 Nov 67	PA
Projectile, 155MM, Smoke, Be, M116E2, Parts For	MIL-P-60340	06 May 65	MU
Projectile, 155MM, Smoke, WP, M110 Metal Parts Assembly	MIL-P-60584 (2)	15 Jan 69	MU
Projectile, 155MM, Test, M692 Loading, Assembling and Packing	MIL-P-48870	01 Mar 76	PA

Title	Document No	Date	Custodian
Projectile, 155MM, Training XM455 Shipping Configuration	MIL-P-14763 (1)	28 Oct 69	PA
Projectile, 155MM, XM687 Metal Parts Assembly	MIL-P-50702	25 Jun 73	MU
Projectile, 175 Millimeter, WP, XM510E1, Filling Assembly	MIL-P-60088A	09 Jan 70	EA
Projectile, 175MM, HE, M437 Metal Parts Assembly	MIL-P-60622A	01 Nov 71	MU
Projectile, 175MM, HE, M437E2 For 175MM Gun Loading, Assembling, And Packing	MIL-P-45455D	29 Dec 70	PA
Projectile, 20MM, Api, M53 Metal Parts	MIL-P-45172 (1)	06 Dec 74	MU
Projectile, 20MM, Dummy, M51A2	MIL-P-46547A	12 Jan 72	MU
Projectile, 20MM, Hei, M56A3, Metal Parts	MIL-P-46581C	26 Apr 71	MU
Projectile, 20MM, Hei, M97A2, Metal Parts	MIL-P-46620B (1)	30 Sep 70	MU
Projectile, 20MM, Heit-sd, XM246 Metal Parts	MIL-P-60679A (2)	23 Jan 74	MU
Projectile, 20MM, HE1 M56E5, Metal Parts	MIL-P-60295A (1)	20 Jun 72	MU
Projectile, 20MM, He1-T, M242, Metal Parts	MIL-P-60835A	06 Dec 74	MU
Projectile, 20MM, High Pressure Test, M54A1	MIL-P-46636C	26 Sep 73	MU
Projectile, 20MM, Target Practice Tracer, M221, Metal Parts	MIL-P-60608A	25 Feb 72	MU
Projectile, 20MM, Target Practice, M55A2	MIL-P-45117E (1)	30 Oct 72	MU
Projectile, 20MM, Target Practice, M55A3 And M55A3B1	MIL-P-50774 (1)	16 Aug 74	MU
Projectile, 20MM, Target Practice, M99A1	MIL-P-46530B	14 May 69	MU
Projectile, 20MM, Tp-t, M212A1, Metal Parts	MIL-P-50601A	23 Apr 76	MU
Projectile, 25 Millimeter, M379 For Trainer M32, Assembly	MIL-P-46416A	12 Apr 64	MU
Projectile, 30MM, Target Practice, 9252416	MIL-P-50949A	03 May 74	PA
Projectile, 4.2 Inch Tactical Cs, XM633 Metal Parts Assembly	MIL-P-14829 (1)	05 Feb 69	MU
Projectile, 4.2 Inch, Tactical Cs, XM633 Loading, Assembling And Packing (For Cartridge, Tactical Cs, XM630)	MIL-P-14901	16 Aug 68	PA
Projectile, 4.2 Inch, Illuminating, M335A2 Loading, Assembling and Packing	MIL-P-12764F	10 May 68	PA
Projectile, 4.2 Inch, Illuminating, M335A2 Metal Parts Assembly	MIL-P-60818B (1)	15 May 73	MU
Projectile, 4.2 Inch, Smoke, M328A1, WP Filling	MIL-P-13041E	31 Jan 69	EA
Projectile, 4.2 Inch, WP Smoke, M328A1 Metal Parts Assembly	MIL-P-60812 (2)	16 Jun 69	MU
Projectile, 4.2 Inch, HE, M329A2 Metal Parts Assembly	MIL-P-50718A (1)	14 May 75	MU
Projectile, 40MM, XM577	MIL-P-60600	04 Nov 66	MU
Projectile, 40MM, XM577E1	MIL-P-60633A (2)	28 Jan 70	MU
Projectile, 57 MM, Smoke, WP, M308A1, Filling Assembly	MIL-P-11635B (1)	22 Jun 71	EA
Projectile, 57MM, HE, M306A1, Metal Parts Assembly	MIL-P-14827A	06 Jul 73	MU
Projectile, 60MM, Mortar, M302, WP Loading Assembly	MIL-P-11633C	05 Aug 68	EA
Projectile, 60MM Metal Parts Assembly	MIL-P-14785B	23 Nov 73	PA
Projectile, 60MM, HE, M49A2 Metal Parts Assembly (Carbon Steel)	MIL-P-60605B (1)	02 Apr 71	MU
Projectile, 60MM, HE, M49A3 Metal Parts Assembly (Alloy Steel)	MIL-P-50357 (2)	30 Sep 74	MU

Title	Document No	Date	Custodian
Projectile, 60MM, HE, M49A3 Metal Parts Assembly (Ductile Iron)	MIL-P-14863 (1)	02 Apr 71	MU
Projectile, 60MM, HE, M49A4E1 Metal Parts Assembly	MIL-P-48400 (1)	13 Sep 74	MU
Projectile, 60MM, Illuminating M83A3 Parts, Loading, Assembling And Packing	MIL-P-60335C	15 Feb 72	PA
Projectile, 8 Inch, M422, Parts and Subassemblies, Beryllium	MIL-P-50891	24 Oct 72	PA
Projectile, 8 Inch, Chemical Agent Gb, M426, Without Fuze And Burster, Filling Of	MIL-P-46964A	06 Dec 65	EA
Projectile, 8 Inch, Gas, M426 Assembling, Marking And Packing	MIL-P-46678B	31 Aug 66	PA
Projectile, 8 Inch, HE, M404 Loading, Assembling And Packing	MIL-P-50257	14 Feb 69	PA
Projectile, 8 Inch, HE, M404, Hardware For	MIL-P-50585	28 Nov 70	MU
Projectile, 8 Inch, HE, XM509 Adapter For	MIL-P-48094	02 Mar 73	PA
Projectile, 8 Inch, HE, M106, Loading, Assembling, And Packing	MIL-P-46258B (2)	30 Nov 73	PA
Projectile, 8 Inch, HE, M404 Body Assembly And Base Plug For	MIL-P-50526A	23 May 74	PA
Projectile, 8 Inch, M424A1 Loading Assembly	MIL-P-50562(3)	15 Mar 76	PA
Projectile, 8 Inch, XM509 Metal Parts Assembly	MIL-P-14895B (1)	19 Aug 75	MU
Projectile, 8 Inch, Chemical Agent Vx, M426, Without Fuze And Burster, Filling Of	MIL-P-46987B	13 Dec 65	EA
Projectile, 81 Millimeter, Smoke, M375, WP Filling	MIL-P-51303A	07 May 71	EA
Projectile, 81MM, HE, M374A1 Metal Parts Assembly (Alloy Steel)	MIL-P-14830A (2)	16 Mar 72	MU
Projectile, 81 MM, HE, M374A1 Metal Parts Assembly (Carbon Steel)	MIL-P-50650 (2)	16 Mar 72	MU
Projectile, 81MM, HE, M374A1 Metal Parts Assembly (Pearlitic Malleable Iron)	MIL-P-50649 (2)	16 Mar 72	MU
Projectile, 81MM, Illuminating, M301A2 Loading, Assembling And Packing	MIL-P-13197C	15 Sep 66	PA
Projectile, 81MM, Illuminating, M301A3 Parts Loading, Assembling and Packing	MIL-P-60447A (1)	04 Oct 74	PA
Projectile, 90MM, Tp-t, M353 Metal Parts Assembly	MIL-P-60592 (1)	29 Dec 66	MU
Projectiles, Armor-piercing, Metal Parts Assembly	MIL-P-20460	04 Dec 51	PA

*OS – Commander
Naval Sea Systems Command
Engineering Support Division
Dept of the Navy
Washington, DC 20360

**PA – Commander
Picatinny Arsenal
Dover, NJ 07801

***MU – Commander
Frankford Arsenal
Philadelphia, Pa 19137

****MR – Director
US Army Materials and Mechanics Research Center
Watertown, Mass 02172

*****EA – Commander
Edgewood Arsenal, Md 21010

Prométhées (Fr). See under Explosifs 03 in Vol **6**, E363-L

Proof. A ballistic test of weapons or ammo to determine suitability. For proplnts, proof also includes chemical and stability tests. For armor, it includes a test to indicate resistance to bullets. A *proof charge* is a proplnt charge used in the initial firing tests of a gun. For test purposes, it may sometimes exceed normal pressures intended for use in the gun. A *proof firing* is the firing of certain rounds for the purpose of testing the serviceability of a weapon or its mounts. A *proofmark* is a distinguishing mark on a weapon to indicate inspection and proof firing
Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 358

Propagation Tests. See under Gap Tests in Vol **6**, G13-R and Influence Tests in Vol **7**, I98-R to I100-R

Propane and Derivatives

Propane (Dimethylmethane, Propyldihydride). $CH_3CH_2CH_3$, mw 44.09; colorl gas; mp −187.7°; bp −42.1°; d of liq at 0°, 0.53g/cc, of vap at 0° (air=1) 1.56g/cc; RI at −42.1°, 1.3397. Sol in eth & alc, sl sol in w. Derived from petroleum and natural gas

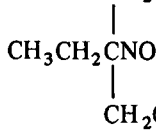
Propane is highly flammable and is considered a dangerous fire and expln risk. Fl pt −104.4°; ignition temp 468°; flammable limits 2.4–9.5%; crit temp 96.8°. It forms expl nitrocompds and nitrates
Refs: 1) Beil **1**, 104, (33) & [71] 2) CondChemDict (1971), 732-L 3) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 440

Nitropropanes. $C_3H_7NO_2$, mw 89.09, N 15.72%, OB to CO_2 −134.7%
1-Nitropropane. $CH_3CH_2CH_2NO_2$; colorl liq, mp −108°; bp 132°; d 1.003g/cc at 20/20°; RI 1.4015 at 20°; fl pt 34°; autoignition temp 789°F. Sl sol in w (1.4ml/100ml); 0.5ml w dissolves in 100ml of 1-Nitropropane; misc with many org solvents. Prepd by the vapor-phase nitration of propane (Refs 1 a & 3)

It is moderately toxic, flammable, and a moderate fire risk. Tolerance, 25ppm in air. It is a moderate expln hazard when shocked or heated (Ref 8)

1-Nitropropane has been evaluated as a solvent and plasticizer for NC (Refs 2, 4 & 6), a recrystn agent for RDX (Ref 5), an ingredient of a foamed liq expl for mine-field clearance (Ref 7), and as an intermediate rocket proplnt (Ref 9)
Refs: 1) Beil **1**, 115–16, (37) & [79]
1a) T. Urbański & M. Slón, CR **203**, 620–22 (1936) & CA **31**, 654 (1937) 2) J.D. Hopper, PATR **952** (1938) 3) H.B. Hass et al, IEC **33**, 1138–43 (1941) 4) B.T. Fedoroff, PATR **1619** (1946) 5) H.A. Aaronson, PATR **1747** (1949) 6) Ibid, PATR **1786** (1950)
7) A. Leschinsky, PATR **2113** (1955)
8) CondChemDict (1971), 625-L 9) Merck (1976), 861-L (No 6449)
2-Nitropropane. $CH_3CHNO_2CH_3$; colorl liq; mp −93°; bp 120.3°; d 0.9821g/cc at 25/4°; RI 1.3944; fl pt 24°; autoignition temp 802°F. Sl sol in w (1.7ml/100ml); 0.6ml w dissolves in 100ml of 2-Nitropropane; misc with many org solvents. Prepn, toxicity, hazard potential and uses are the same as for 1-Nitropropane

1,1-Dimethylol-1-Nitropropane Dinitrate.



$C_5H_9N_3O_8$; mw 239.17; N 17.57%; OB to CO_2 −43.5%; liq. Prepd by condensing formaldehyde with 1-Nitropropane in an alkaline medium and nitrating the product. It is a poor gelatinizer for blasting sol NC
Power. 92% blasting gelatine by BalMort
Stability. 5 minutes in 82.2° Heat Test
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

Dinitropropanes. $C_3H_6N_2O_4$; mw 134.09; N 20.89%; OB to CO_2 −59.7%
1,1-Dinitropropane. $CH_3CH_2CH(NO_2)_2$; oily

yel liq (acidic); bp 189–90°; d 1.258g/cc at 22°. Can be prepd from 1-chloro-1-nitropropane, K hydroxide and K nitrite (Ref 2). V sl sol in w, with an acidic reaction; sol in alkalies

1,1-Dinitropropane is an expl comparable in its power and sensitivity to TNT. Its thermal stability is satisfactory (does not expld to 360°; at 135°, acid in 30 mins, no expln in 300 mins) (Ref 2)

Q_c^v 3349cal/g, H_2O liq, or 3270, H_2O gas (Ref 3). Impact sensy 100cm+ with 2kg wt, BuMines app. One drop of the material was placed on a filter paper disc the same diameter as the striker of the app (Ref 4)

Refs: 1) Beil **1**, 117 & [79] 2) Blatt, OSRD **2014** (1944) 3) L.E. Newman, PicArsnChem-Lab Rept No **1123718** (1948) 4) W. Anderson & H. Vaughan, Ibid **123975** (1948)

1,3-Dinitropropane. $CH_2NO_2CH_2CH_2NO_2$; colorl or pale yel oily liq; mp −21.4°; bp 103° at 1mm; d 1.353g/cc at 25.5°; RI 1.4638 at 25°. V sl sol in w, sol in eth

It was prepd by Keppler and Meyer (Ref 2) by treating 1,3-diiodopropane with Ag nitrate; the product obtained was very unstable. Urbański and Slón (Ref 3) later prepd it in small quantities, together with 1-nitropropane, on treating n-propane vapor with gaseous nitrogen. More recently, Kispersky et al (Ref 5) prepd a product from 1,3-diiodopropane and Ag nitrate which was stable for at least 9 months

Its Na compd, $C_3H_5(NO_2)_2Na$, was prepd by Keppler & Meyer (Ref 2), and was reported to be a violent expl ("heftig explodierendes pulver" in Ger)

Refs: 1) Beil **1**, 117 & [79] 2) F. Keppler & V. Meyer, Ber **25**, 1709–12 (1892) 3) T. Urbański & M. Slón, CR **203**, 620–22 (1936) & CA **31**, 653 (1937) 4) Blatt, OSRD **2014** (1944) 5) J.P. Kispersky, H.B. Hass & D.E. Holcomb, JACS **71**, 516 (1949) & CA **43**, 3352 (1951)

2,2-Dinitropropane. $CH_3C(NO_2)_2CH_3$; white crysts with a camphor-like odor; mp 53° with subl; bp 185.5°; d 1.26g/cc; subl at RT. V sl sol in w and insol in alkalies. Was first prepd in 1876 by the oxidation of propylpseudonitrole, $CH_3C(NO)(NO_2)CH_3$, with chromic acid, or by simply heating it in air at 100° (Ref 2). Nef (Ref 3) prepd it, among other products, by treating Ag dinitroethane with methyl iodide

2,2-Dinitropropane is an expl comparable with Tetryl in power (123% TNT) and with TNT in impact sensitivity. Q_c 427.8kcal/mole. Initiation temp is 360° in 5 secs. It loses 5.6% by wt in the 75° International Test, and is efflorescent

Refs: 1) Beil **1**, 117 & [79] 2) V. Meyer & J. Lecher, Ann **180**, 145–52 (1876) 3) J.U. Nef, Ann **280**, 285 (1894) 4) Blatt, OSRD **2014** (1944) 5) Urbański **1**, 597 (1964)

1,3-Dinitro-2,2-Dimethylpropane. See under 2,2-Dimethyl-1,3-dinitropropane or Dinitroneopropane in Vol **5**, D1368-R

Propanediols and Derivatives

1,2-Propanediol (1,2-Propylene glycol, 1,2-Dihydroxypropane, Methyl glycol). $CH_3.CHOH.CH_2OH$; mw 76.09; colorl, viscous, stable, hygr liq; bp 187.3°, d 1.0381g/cc at 20/20°; RI 1.4293 at 27°; fl pt (open cup) 210°F; autoignition temp 780°F. Misc with w, alcs, and many org solvents in all proportions. Can be prepd by hydration of propylene oxide. On nitration it yields the expl 1,2-Propanediol Dinitrate (see below)

Refs: 1) Beil **1**, 472, (245) & [535] 2) CondChemDict (1971), 735-L 3) Merck (1976), 7649-L (No 7644)

1,2-Propanediol Dinitrate (Methyl Glycol Dinitrate). $CH_3.CH(ONO_2).CH_2ONO_2$; mw 166.09; N 16.87%; OB to CO_2 −28.9%; colorl, oily liq; mp −42.5°; does not freeze at −20°; bp 92° at 10mm; d 1.3774g/cc at 20/4°; RI 1.42720 at 20°; viscosity in poise, 0.0465 (20°); dielectric const 26.80 (20°) (Refs 8 & 9)

1,2-Propanediol Dinitrate was prepd by L. Henry (Ref 2) by slowly pouring propylene oxide into cooled nitric acid, followed by the addition of concd sulfuric acid. Naoûm (Ref 5) nitrated 1,2-propylene glycol with 5p of mixed acid contg 40% nitric and 60% sulfuric acids at 20° to give, in 86% yield, a product with a nitrogen content of 16.5%. A mixed acid contg 47.5% nitric, 45.5% sulfuric and 7% w was used by Matignon et al (Ref 6) at 10°. By using a

10% excess of nitric acid, they achieved a yield of 91–93%

It is insol in w; sol in alc, eth or strong nitric acid; gelatinizes NC

As early as 1904, 1,2-Propanediol Dinitrate was proposed (Ref 3) as an additive to lower the freezing temp of NG, but its practical application on a large scale was hindered by lack of the raw material, propane-1,2-diol. It is only recently that the synthesis of glycol from ethylene led to the development of a method for producing methyl glycol from propylene via chlorohydrin. Even so, propylene-1,2-glycol is somewhat more expensive than glycols derived from ethylene (Ref 9)

1,2-Propanediol Dinitrate is a HE, the properties of which were detd by Barab (Ref 4), Naoúm (Ref 5) and the Hercules Powder Co (Ref 8):

Heat of Formation. 83.1kcal/mole

Heat of Explosion. 1109kcal/kg at const vol with H_2O gaseous

Power. 540ml or 92% NG by Trauzl Pb block test with w tamping

Sensitivity to Impact. Less sensitive than NG

Stability. 60 minutes+ in 71° KI test

Velocity of Detonation. 6885m/sec and 2000 m/sec (?), as detd in 10mm ID glass tubes with 1mm wall (Ref 8)

Volatility. 3.8% loss in wt at 35° of a 10g sample in a 60mm diam dish after 24 hrs; after 3 days, 4.1%

Note: A mixt consisting chiefly of 1,2-Propanediol Dinitrate, but contg varying amts of ethylene glycol dinitrate and butylene glycol dinitrate was marketed under the trade name *Nitrobyronel* (Ref 8)

Refs: 1) Beil **1**, 473 2) L. Henry, AnnChim (Paris) [4], **27**, 261 (1872) 3) H. Claessen, GerP 179789 (1904) 4) J. Barab, USP 1371215 (1921) 5) Naoúm, NG (1928), 236–37 6) C. Matignon, H. Moureau & M. Dode, MP **25**, 176 (1932–33) 7) Davis (1943), 234 8) Blatt, OSRD **2014** (1944) 9) Urbański **2**, 3, 4 & 157 (1965)

1,3-Propanediol (Trimethylene glycol, 1,3-Dihydroxypropane). $CH_2OH.CH_2.CH_2OH$; mw 76.09; colorl to pale yel, very visc, sweet liq; mp, freezes in a mixt of dry ice and eth; bp 210–12°; d 1.0597g/cc at 20/4°; RI 1.4398 at 20°. Misc with w, alc; insol in eth, benz or chlf. Can be prepd by reduction of ethyl glycidate with LiAl hydride. On nitration it yields the expl 1,3-Propanedioldinitrate (see below)

Refs: 1) Beil **1**, 475 & (247) 2) Naoúm, NG (1928), 229 3) Merck (1976), 1246-R (No 9384)

1,3-Propanediol Dinitrate (Trimethyleneglycol Dinitrate). $O_2NOCH_2.CH_2.CH_2ONO_2$; mw 166.09; N 16.87%; OB to CO_2 −28.9%; nearly colorl oily liq with a slight aromatic odor; mp −38°; bp 108° at 10mm, decomps at about 185° with evolution of yel fumes and deflagrates at 225°; d 1.4053 at 16/16°, 1.3952 at 20/4°; RI 1.43476 at 20°; viscosity in poise, 0.0940 (6.3°), 0.0550 (20.2°), 0.0275 (54.2°); dielectric const 18.97 at 20°; dipole moment 3.50 (Ref 6)

Nearly insol in w, easily sol in alc, eth, et ac, benz; gelatinizes NC. Can be prepd by the nitration of 1,3-propanediol with mixed nitric-sulfuric acid, as described by Naoúm (Ref 4) and Blechta (Ref 3). The nitration requires a lower temp than that used for nitrating glycerin, because the central methylene group is readily oxidized at a higher temp. A temp between 0–10° is recommended since decompn is possible even at 15°, while at 20° yel fumes are evolved. Separating the product from the spent acid occurs with ease at 10°. From 100p of 1,3-propanediol, 198p of the dinitrate are produced corresponding to 90.6% of theoretical

1,3-Propanediol Dinitrate is a powerful and brisant expl which is less sensitive than NG, and has satisfactory stability. Following are some of its properties, as given in Refs 2, 3, 4, 5 & 6, and by the Hercules Powder Co:

Heat of Explosion. 1138.5kcal/kg (w as vapor)

Heat of Formation. 78.1kcal/mole

Power. 540ml or 92% NG by Trauzl Pb block test with w tamping

Sensitivity to Impact. Very low; a 2kg wt falling 100cm fails to initiate an expln

Stability. 45 minutes in 83° KI test. Storage at 75° for 25 days caused no decompn or development of acidity

Toxicity. Similar to that of NG

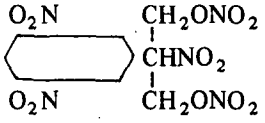
Velocity of Detonation. 6890m/sec and 2100 m/sec (?), as detd in 10mm ID glass tubes with

1mm wall
Volatility. 1.8% loss in wt at 35° of a 10g sample in a 60mm diam dish after 24 hrs; after 3 days, 4.2%
Notes: It was proposed for use as an antifreeze addition to Dynamites. A blasting gelatine consisting of 93% 1,3-Propanediol Dinitrate and 7% collodion cotton gave a Pb block expansion of 470ml, or about 80% of the effect produced by the same gelatine contg NG

1,3-Propanediol Dinitrate was present in NG prepd in Ger by nitrating synthetic glycerin, called *Protol*
Refs: 1) Beil – not found 2) J. Barab, USP 1371215 (1921) 3) F. Blechta, SS **17**, 57–8 (1922) 4) Naoům, NG (1928), 231–36 5) Davis (1943), 233–34 6) Urbański **2**, 3, 4 & 155–57 (1965)

Propanedioldinitrate (Commercial). Barab (Ref 4) patented liq expls contg varying amts of 1,2- and 1,3-Propanediol Dinitrates. These mixts were claimed to be as powerful as, but less sensitive than NG. The product was examined by the US BuMines and found to make up a 40% straight Dynamite that compared favorably with 40% straight NG Dynamite
Ref: J. Barab, USP 1371215 (1921)

2-(3′,5′-Dinitrophenyl)-2-Nitro-1,3-Propanediol Dinitrate. $C_9H_7N_5O_{12}$; mw 377; N 18.6%; OB to CO_2 –66.5%; mp 114–115°; d 1.70g/cc;



Q_C 1022.9cal/mole. Prepd by condensing phenylnitromethane with formaldehyde, and nitrating the product
Sensitivity. Slightly less sensitive than PETN
Power. 126% TNT by BalMort
Stability. Ignites at 360°; thermal stability at 135°: acid in 60 mins, no expln in 300 mins
Hygroscopicity. Gains 0.05% at 100% RH
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

1-Propanol (n-Propyl alcohol, Propylic alcohol, Optal). $CH_3CH_2CH_2OH$; mw 60.09; liq; mp –127°; bp 97.2°; d 0.8053g/cc at 20/4°; misc with w, alc & eth. Available as a by-product of the reaction between CO and H_2
Ref: Merck (1976), 1016-L (No 7630)

Dinitropropanols. $C_3H_5(NO_2)_2OH$; mw 150.10; N 18.7%; OB to CO_2 –42.7%
2,2-Dinitro-1-Propanol. $CH_3.C(NO_2)_2.CH_2OH$; crysts; mp 88°. Can be prepd by the action of formaldehyde on 1,1-dinitroethane. It is an expl comparable in power to Tetryl and in sensitivity to TNT. It is slightly hygroscopic and fairly stable
Note: A eutectic mixt of the formal and acetal of 2,2-Dinitropropanol **(DNPAF)** is used as the plasticizer in a plastic-bonded expl (PBX-9501) contg 95 wt % HMX, 2.5% Estane as the plastic bonding agent, and 2.5% DNPAF. It is claimed to have an expl energy comparable to that of PBX-9404 [94% HMX, 3% NC & 3% tris-(β-chloroethyl) phosphate (CEF)], but possesses greater temp stability and significantly better handling safety [T.M. Benziger, USP 3778319 (1973)]
1,1-Dinitropropanol (Dinitroisopropyl alcohol). $(O_2N)_2CH.CHOH.CH_3$; colorl oil; bp, deflagrates on heating above 120°; d 1.33g/cc at 15/4°; RI 1.449 at 15°; sol in w (1 p in 5–6p). Can be prepd by treating its K salt with dil sulfuric acid. The K salt is prepd from K dinitromethane and acetaldehyde
Refs: 1) Beil **1**, 366 2) Blatt, OSRD **2014** (1944)

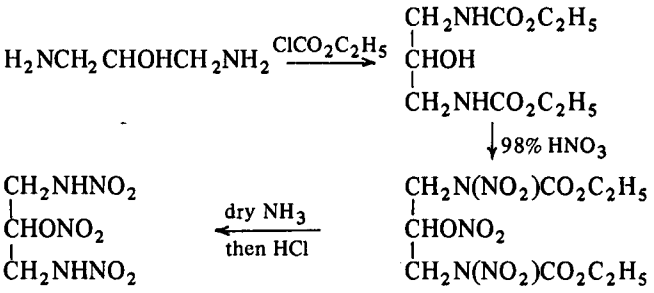
1,3-Diazidoisopropyl Alcohol (1,3-Diazidopropanol-2). $N_3.CH_2.CHOH.CH_2.N_3$; mw 142.13; N 59.14%; colorl, odorless liq; bp 88–91° at 0.6mm; d 1.2687g/cc at 21/4°. Can be prepd by reacting 1,3-dichlorohydrin with Na azide on a steam bath for 12 days in the dark. It explds on impact, when ignited, or when in contact with concd sulfuric acid. Several explns were reported when attempting to det its nitrogen content by combustion
Refs: 1) Beil **1**, (186) 2) J.C. Philip, JCS **101**, 493–96 & 1866–71 (1912)

1,3-Dinitramino-2-Propanol Nitrate. $C_3H_7N_5O_7$;

CH_2NHNO_2
|
$CHONO_2$
|
CH_2NHNO_2

mw 225; N 31.1%; OB to CO_2 −17.8%; mp 159–159.6° (decompn)

Preparation



Hygroscopicity. Gains 0.02% at 100% RH
Power. 142% TNT by BalMort
Sensitivity. Impact, with Bruceton No 3 machine, 50% positive with 5kg wt at 24cm
Stability. Deflagrates at 230°; thermal – not acid in 300 mins at 100°, acid in 105 mins at 135°; vacuum – 1.99 to 4.36cc in 48 hrs at 100°
Refs: 1) Beil – not found 2) Blatt, OSRD **2014** (1944)

Propanolamines. See under Aminopropanols and Derivatives in Vol **1**, A253-L

Propanolanilines. See under Anilinopropanol and Derivatives in Vol **1**, A436-L

Propargyl Alcohol (2-Propyn-1-ol). $HC{\equiv}CCH_2OH$; mw 56.06; colorl liq; mp −48 to −52°; bp 114–115°; d 0.97g/cc at 20°; RI 1.43064 at 20°; Flash pt 36.1°. Sol in w, alc and eth; immisc with aliphatic hydrocarbons. Can be prepd from epichlorohydrin and Na or from acetylene and formaldehyde (Refs 5 & 6)

If propargyl alcohol and similar acetylenic compds are dried with alkali before distn, the residue may expld (probably due to salt formation). Na sulphate is recommended as a suitable desiccant (Ref 2)

The addition of P_2O_5 to propargyl alcohol caused the alcohol to burst into flame (Ref 4)

Following the published procedure, hydroxyacetone was being prepd on half the scale by treating propargyl alcohol as a 30% wt aq soln with Hg sulfate and sulfuric acid (6g + 0.6g per mole of alc, respectively). On stirring and warming the mixt to 70°, a violent exothermic eruption occurred. Quartering the scale of operations to 1 g mole, and reducing the amt of acid to 0.37g/mole, gave a controllable reaction at 70° (Ref 3)
Refs: 1) Beil **2**, (234) 2) Anon, AngChem **2**, 209 (1954) 3) W. Reppe et al, Ann **596**, 38 (1955) 4) Anon, "Fire Protection Guide on Hazardous Materials", 6th Ed, Natl Fire Protection Assoc, Boston (1975), **491M**, 321 5) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 440–41 6) Merck (1976), 1012 (No 7599)

Propargyl Bromide (3-Bromo-1-propyne). $HC{\equiv}CCH_2Br$; mw 118.97; colorl to faintly brownish liq; mp 24.4°; bp 88–90°; d 1.52 g/cc; RI 1.4320 at 20°. Sol in alc, eth, benz & chlf. Flammable; flash pt 10° (closed), 18° (open); ignition temp 328°; lower flammable limit 3.0%. It can be decompd by mild shock. When heated under confinement, it decomps with expl violence and may detonate. When suitably diluted, as with 20–30% by wt of toluene, its expl properties are practically eliminated (Ref 4)

Pure propargyl bromide will decomp violently or detonate at temps as low as 220° (Ref 2). Liq propargyl bromide is easily ignited by impact from such possible sources as "water hammer" or accidental pressurization of the accelerated liq (Ref 3). Tests at the BuMines showed a mixt of chloropicrin and propargyl bromide to be shock sensitive (Ref 3)
Refs: 1) Beil **1**, {922} 2) R.D. Coffee & J.J. Wheeler, ChemEngProgrTechMan **1**, 6–9 (1968) 3) D.R. Forshay et al, FireTech **5** (2), 100–11 (1969) 4) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 441

PROPELLANTS, SOLID

I. Introduction

Solid Propellants (SP) are solid substances that can be transformed into gases (usually hot) which act as driving jets in *propulsion systems.* Propulsion systems can be classified into: *guns, jet engines* and *rockets.* In a gun the SP propels a "slug" out of the gun barrel. In both jet engines and rockets the SP provides forward thrust by the rearward ejection of fluid jets thru nozzles mounted on the jet engine or rocket. In a rocket the *propulsive system* (eg the SP) requires no contribution from the surrounding medium to produce the exhaust jet, whereas jet engines function by ingesting the surrounding medium (air or water). Thus rockets can function in vacuum (space) but jet engines cannot. It is usually understood that a *rocket motor* is that part of the propulsion system in which the proplnts are transformed into the exhaust jet, while a *rocket engine* is the entire system – rocket motor, containers, pumps, etc. For solid proplnt rockets, rocket motor and rocket engine are the same piece of apparatus, which is not the case in liq proplnt rockets (see Vol **7**, L34-R)

During the past thirty years a tremendous volume of literature has dealt with all aspects of solid proplnts. A comprehensive review of all this literature is quite beyond the scope of this Encyclopedia. Indeed an all-inclusive discussion of SP would require an entire Encyclopedia wholly devoted to solid proplnts. The impracticality of a comprehensive review is not the only reason for limiting the scope of the present article. Solid proplnt literature suffers more than usually from repetition and poor quality. Thus even in a comprehensive review, considerable selectivity of subject matte is imperative. Furthermore, as shown below, certain aspects of SP, in particular cannon proplnts, have already been treated in previous Encyclopedia volumes

Since this Encyclopedia deals primarily with explosives and explosive phenomena, the present article emphasizes the explosion hazards of SP. It also features modern concepts of proplnt ignition and combustion. Other aspects of SP such as uses, production methods, physical characteristics, etc, will be treated in less detail, but recent efforts on improving performance will be emphasized. Because previous Encyclopedia articles on SP have emphasized cannon proplnts and established practices, the present article, to avoid repetition, will emphasize rocket proplnts and modern concepts

As stated above, various aspects of SP have been presented in previous Encyclopedia volumes. In alphabetical order, they are:

Subject	Vol & Page(s)	Latest
AN & Aerojet Propellants	**1**, A349–350	1959
Ballistite (double-base formulations)	**2**, B8–9	1960
Ball Powder (mostly single base)	**2**, B11–16	1959
Black Powder	**2**, B165–179	1959
Burning of Propellants *	**2**, B346–355	1961
also Combustion of Propellants	**4**, D173–74	1968
Erosive Burning	**2**, B357	1959
Cannon Powder (Propellants)	**2**, C29–39	1961
Cast Propellants	**2**, C84–86	1962
Cellulose Nitrate (NC)	**2**, C100–125	1961
Centralites (stabilizers)	**2**, C126–140	1962
Colloidal Propellants	**3**, C398–403	1961
Cool Propellants	**3**, C511–12	1963
Composite Propellants *	**3**, C464–473	1964
Cordite	**3**, C531–541	1962
Degradation of Propellants *	**3**, D41	1959
Deflagration-to-Detonation Transition (DDT) *	**4**, D245–252	1963
Diphenylamine	**5**, D1416–26	1967
Double Base & Triple Base Propellant *	**5**, D1536–39	1965
DTA of Propellants	**5**, D1255–56	1966
EC Powders	**5**, E6	1958
Electrostatic Ignition of Smokeless Powder	**5**, E43	1972
Erosion of Gun Barrels *	**5**, E112–20	1966
FNH Propellants	**6**, F152	1946
Force Constant (thermochemical parameters of propellants)	**6**, F156–158	1965
Glycerol Trinitrate (NG)	**6**, G98–108	1972
Hygroscopicity of Propellants	**7**, H252–253	1955
Hypergolic Propellants	**7**, H254–259	1973
Ignition *	**7**, I11–16	1961
JATO	**7**, J67	1959
Moisture Determination in Propellants (under "Ethanol")	**6**, E171–76	1963

* To be updated and revised in the present article

Recent general references on SP in book or pamphlet form are:

J. Corner, "Theory of the Interior Ballistics of Guns", J. Wiley, NY (1950)

S.S. Penner, "Chemical Rocket Propulsion & Combustion Research", Gordon & Breach, NY (1962)

P.G. Sutton, "Rocket Propulsion Elements", Wiley, NY (1963)

R.L. Wilkins, "Theoretical Evaluation of Chemical Propellants", Prentice-Hall, NJ (1963)

B. Siegel & L. Schieler, "Energetics of Propellant Chemistry", Wiley, NY (1964)

A.M. Ball, "Solid Propellants", EngrDesHndbk, **AMCP 706-175** (1964)

Anon, "Ballistics Series, Interior Ballistics of Guns", EngrDesHndbk, **AMCP 706-150** (1965)

S.F. Sarner, "Propellant Chemistry", Reinhold, NY (1966)

R.F. Gould, Ed, "Advanced Propellant Chemistry" in Advances in Chemistry Series, ACS (1966)

T. Urbański, "Chemistry & Technology of Explosives", Vol **3**, Pergamon Press, NY (1967)

A.C. Eringen et al, "Mechanics & Chemistry of Solid Propellants", Pergamon Press, NY (1967)

I. Glassman & R.F. Sawyer, "The Performance of Chemical Propellants", AGARD-ograph No 129 (1970)

J.H. Bradley, "Flame and Combustion Phenomena", Science Paperbacks, London (1972)

H.W. Jones, "Propellants & Explosives" (Patent Info since 1970) Noyes Data Corp, Park Ridge, NY (1974)

S.E. Mitchell, "Selected Properties of Navy Gun Propellants", **IHSP-76-128** (1976)

The present article will consist of: a brief *History of SP* (Section II); *Representative SP and their Uses* (Section III); *Production Methods of Representative Propellants* (Section IV); *Physical Characteristics of Representative Propellants* (Section V); *Chemical Characteristics & Performance* (including modern concepts of ignition and combustion) (Section VI); *Explosion Hazards* (Section VII); and *Brief Summaries of Recent Literature on SP* (Section VIII)

II. History of Solid Propellants

The earliest solid propellant was *Black Powder*, also known as *Gun Powder*. Its history is described in detail in Vol **2**, B165–68 & Vol **7**, H117–34. Black Powder is no longer used as a propint, but it is still used in igniters for SP

The next stage in the development of SP, namely the early development of *single base smokeless powder*, followed the discovery of *Nitrocellulose* (NC). We quote Urbański (Ref 46a, p 528):

"A few years after the discovery that the treating of cellulose with nitric acid converts it into a combustible substance, the idea arose of using nitrocellulose as a propellant instead of blackpowder. Schönbein's experiments (Ref 1), repeated by Pelouze (Ref 2), showed the high energy of nitrocellulose. It was found that a charge of nitrocellulose endows a projectile with a penetrating effect similar to that of a triple charge of blackpowder

The primary difficulty in exploiting this property lay in finding a method of manufacturing nitrocellulose. It was not until large-scale manufacture of nitrocellulose was achieved by Lenk (Ref 13) that propellant charges could be used for Austrian artillery. Shortly afterwards, however, this method proved to be unsatisfactory, due to the variable results obtained and to the excessive pressure developed when firing nitrocellulose charges, which in many instances damaged or even blew up the cannon

Earlier observations that nitrocellulose burns very quickly in a confined space – much more quickly than blackpowder – were confirmed. Since it is difficult to reduce the burning rate by physical methods only e.g. by compressing the nitrocellulose to increase its density, attempts were made to slow down the rate of burning by the addition of 'phlegmatizing' substances, such as glues, waxes, fats etc

Partly successful results were obtained by Schultze (Ref 3) who prepared his powder by the following method. Wood cut into 1–2mm grains was purified by boiling in sodium hydroxide solution and bleaching with calcium hypochlorite. It was then nitrated with a mixture of nitric and sulphuric acids. The nitration product was stabilized by boiling in a sodium carbonate solution, then dried and impregnated with a solution of either potassium or barium nitrate. After drying the grains were polished in a drum with paraffin wax to form a powder of the following composition:

50% nitrocellulose & nitrated hemicelluloses
13% non-nitrated wood pulp
33% potassium and barium nitrates
4% paraffin

This powder, however was still too fast-burning for use in military rifles, but was found suitable for use in shot guns, and was a forerunner of propellants of the 'Schultze type' used in some countries (chiefly Great Britain) as sporting powders

A few years later it was discovered that nitrocellulose dissolves in organic solvents, such as acetone, ethyl acetate and in mixtures of alcohol with ether, leaving on evaporation of the solvent a highly dense, transparent film, which burns more slowly than nitrocellulose itself (Ref 5)

Some investigators tried to make use of this property. Volkmann (Ref 4) improved Schultze's powder by dipping nitrated grains of wood into a mixture of ether and alcohol and then either mixing them with blackpowder to prevent caking and coating them with a layer of this explosive or compressing the sticky grains into larger cubes. In spite of the encouraging results obtained in using this powder (the size of charges required was half of that of blackpowder) the Austrian authorities stopped manufacture on the formal grounds that the plant concerned infringed their blackpowder monopoly

A number of patents were then registered for various methods of using solvents to prepare granular powder from nitrocellulose [Spill (Ref 6), Reid (Ref 7), Wolf and Förster (Ref 8)]. None of those methods, however, found practical application, except for a short time in the work of Duttenhofer at Rottweil (Ref 14). Duttenhofer nitrated slightly carbonized cellulose, stabilized it and saturated the nitrocellulose so obtained with ethyl acetate until a gelatinized mass was formed. After being dried, the horn-like mass was broken up in a corning mill and the grains so obtained were graded. Clearly, Duttenhofer employed virtually the same production method as that used to manufacture blackpowder

Duttenhofer's powder was used for a certain time in Germany under the name of RCP (Rottweil Cellulose Pulver). Its greatest disadvantage was the irregularity of the shape of the grains which prevented it from burning as uniformly as the smokeless powder (Ref 11) invented by Vieille at about the same time

Vieille developed his powder as the result of systematic investigations. In 1879 he began a study of the burning of explosives in a manometric bomb which he invented together with Sarrau

In the course of studying the burning of blackpowder Vieille found that it can burn in parallel layers provided that its specific gravity is approximately 1.80 or more. He extended his experiments (1882–1884) to nitrocellulose, and tested its behaviour at various densities. Since it turned out that high specific gravity nitrocellulose cannot be achieved simply by pressing, Vieille made use of the recognized method of increasing its specific gravity by treatment with various solvents. He formed the dough-like mass into flakes and thin sheets which on drying showed a fairly high specific gravity (about 1.65). By experiments in the manometric bomb, Vieille demonstrated that the flakes of the new powder burn in parallel layers and that this property makes their time of burning dependent upon their smallest dimension i.e. upon their thickness. Hence by altering this the total time of burning of the flakes may be controlled, and the 'coefficient of the vivacity' (coefficient de vivacité) of the powder

$$\left[\frac{dp}{dt}\right]_{max}$$

where p is pressure produced by burning the powder, t is time of burning, may be determined in the manometric bomb. Thus powders of an adequate vivacity adjusted to a given calibre of arms may be easily standardized

Shortly afterwards (1885) Vieille's powder was introduced in France under the name of B powder (Poudre B). Vieille utilized two types of nitrocellulose for its manufacture: collodion cotton CP_2, soluble in a mixture of ether and alcohol and forming the powder dough; cotton CP_1, insoluble in a mixture of ether and alcohol, incorporated into the powder mass in the form of unchanged fibres

In Russia, Mendeleyev (Ref 12) worked out a method for the manufacture of smokeless powder from pyrocellulose, i.e. relatively high-nitrated (12.5% N) nitrocellulose soluble in a mixture of ether and alcohol. In 1892 the manu-

facture of this powder was started for naval guns. Nitrocellulose powder of this type was soon adopted for military purposes in the USA, where nitrocellulose powder became known as 'single base powder' "

Double base smokeless powder was first produced by Alfred Nobel. Again we quote Urbański (Ref 46a, p 530):

"A second type of smokeless powder, *Ballistite*, was invented by Alfred Nobel (Ref 9) in 1888. He took advantage of the ability of nitroglycerine to dissolve nitrocellulose and thus replaced a volatile, non-explosive solvent (ether and alcohol in former powders) by a non-volatile explosive solvent – nitroglycerine. The ratio of nitrocellulose to nitroglycerine was 45:55. This is a relatively small amount of nitroglycerine which dissolves nitrocellulose with difficulty. Abel and Dewar (Ref 10) however succeeded in adapting acetone for the manufacture of nitroglycerine powder. This is a solvent of both the active ingredients: nitrocellulose and nitroglycerine. The product – British *Cordite* – has not been used outside the British Commonwealth. The powders made of nitrocellulose, nitroglycerine and a mixture of ether and alcohol as a solvent achieved only temporary success. The use of any solvent was troublesome and proved a drawback in manufacture, so that nitroglycerine powder without a volatile solvent, derived from ballistite, aroused much greater interest

Work on the improvement of nitroglycerine powder without a volatile solvent was aimed at the reduction of its content of nitroglycerine. By the selection of a suitable nitrocellulose and by the addition of non-volatile solvents ('gelatinizing agents'), of the so-called 'centralite' type ('carbamite' according to English nomenclature) as in Claessen's (Ref 15) patents, a new type of nitroglycerine powder, the so-called RP-12 or RPC-12, was manufactured from 1912 onwards. This powder was used extensively during World War I since it could be produced much more quickly than nitrocellulose powder. The manufacture of this powder contributed largely to the long resistance of the Central Powers in World War I

The enormous consumption of smokeless powder during this war led to difficulties in producing a sufficient quantity of nitroglycerine. In Russia and Germany attempts were made to replace part of the nitroglycerine by aromatic nitro compounds such as DNT or 'liquid TNT' (an oily mixture of DNT and TNT with isomers of TNT). This powder had several advantages. In comparison with nitroglycerine nitro compounds give a powder with a lower temperature of explosion that produces less erosion and flash. Powders containing nitro compounds with nitroglycerine were later adopted in the USSR

Attempts to replace nitroglycerine partly or wholly by nitroglycol had little success due to the high vapour pressure of the latter which facilitates volatization and, consequently, reduces its ballistic stability (ballistic properties change as nitroglycol volatilizes). Later, diethylene glycol dinitrate was tried (nitrodiglycol, DGDN) and was shown to have great advantages over nitroglycerine. With nitroglycerine, good gelatinization of the nitrocellulose may be obtained if the ratio of nitroglycerine to nitrocellulose is not less than 60:40, whereas with nitrodiglycol this ratio may be much lower, viz. 20–45 nitrodiglycol to 80–55 nitrocellulose, since nitrodiglycol is a better solvent of nitrocellulose than nitroglycerine. This facilitates manufacture and, at the same time produces a more uniformly gelatinized mass. Various alterations may also be introduced in the composition of powder such as an increase in the content of nitrocellulose or on addition of insoluble ingredients, serving, for instance, to suppress flash

Solventless powder without nitroglycerine (G powder) has a lower heat of explosion, and consequently causes less wear on the bore

Gallwitz (Ref 16) reports the following data on the influence of the heat of explosion upon the bore wear. With a nitroglycerine powder containing no solvent and giving a heat of explosion of 950 kcal, the barrel stands up to 1700 rounds while with a similar powder giving a heat of explosion of 820 kcal, it withstands 3500 rounds. The reduction of the calorific value of the powder by 130 kcal therefore doubles the useful life of the barrel

Further reduction of the calorific value of nitroglycerine powder proved to be impossible. But by using nitrodiglycol instead of nitroglycerine, a powder was obtained with a heat of explosion of 690 kcal, which prolonged the life of the barrel considerably, i.e. to 15,000–17,000

rounds

A further development led to the invention of flashless powder. Tests carried out in various countries, included the addition of aromatic nitro compounds to nitrocellulose powders and of potassium salts to nitroglycerine powders. Nitrodiglycol powder with an addition of 2% K_2SO_4 produced a small flash. During World War II in Germany and Great Britain it was the custom to add a considerable amount of nitroguanidine to nitrodiglycol powders. In Germany this was called 'gudol' powder (German Gudol Pulver)

Other attempts to improve nitrodiglycol powders were based on the introduction of substances such as penthrite (German Nipolit Pulver) and cyclonite. In both cases a powder with a high calorific value was obtained. The manufacture of these powders never went beyond the pilot plant scale"

Triple base proplnts contain NC, NGu and a nitrate ester such as NG or DEGDN. They are claimed to produce less flash & gun barrel erosion than double base proplnts. The earliest triple base proplnt appears to be *Gudolpulver,* developed in Germany in 1937 (see Vol **5**, D1537-R), which had NC, DEGDN & NGu as its major ingredients. During WWII many triple base formulations based on NG, NC & NGu were developed and used by the US and its allies (see Vol **5**, D1536 & Vol **2**, C34–37)

Smokeless powders (single, double & triple base) although excellent as gun proplnts have some disadvantages. It is difficult and costly to produce large size smokeless proplnt grains needed in rockets. The presence of NG creates manufg & use hazards. Moreover, these proplnts can have rather poor stability and consequently require continuous stability checks. Because of these disadvantages, a different type of proplnt, primarily for rockets, began to be developed during WWII. These so-called *composite propellants* consist of a solid oxidizer dispersed in a solid fuel matrix. They may contain addnl solid fuel such as Al and/or hydrides and additional high energy ingredients such as HMX. Usually the matrix is an elastomer-type material, either polymerizable, castable, or vulcanizable. These proplnts are relatively cheap, stable, and need not contain components that are hazardous per se (eg, no NG). One of the earliest composite proplnts appears to be based on perchlorate salts dispersed in an asphalt matrix (see Vol **3**, C464-R)

Recent trends in rocket proplnt development, and most of the recent developments in SP are for rocket and not gun proplnts, were directed toward the attainment of higher energy systems (actually higher specific impulse). Unfortunately, the use of exotic components presents grave stability problems which are yet to be overcome. Some energetic plasticizers have been developed and in some applications specific impulse has been increased substantially by substituting Be for Al. Much of this subject remains classified

For further historical information the reader is referred to Vol **7**, H117–61, which has historical data on proplnts interspersed within information relevant and irrelevant to the history of expls and firearms

III. Representative Solid Propellant Types and Their Uses

A. *Smokeless*

By far the largest use of smokeless solid proplnts is in gun proplnts where they are categorized as single-, double-, and triple-base. Typical single-base proplnt formulations use NC as the principal binder and are plasticized with such compds as DNT, dibutylphthalate, and relatively small amts of DEGDN and TEGDN. Stabilizers such as 2-nitrodiphenylamine or ethyl centralite are added to retard the decompn of the NC nitrate group. These proplnts are normally extruded into small cylindrical shapes or ribbons which are chipped. Typical formulations are given in Table 1 (Ref 32a)

As stated, the major uses for these proplnts are for small arms ammo, mortar shells and artillery shells up to 280mm. They are also used as the propelling charge in naval guns

Double-base compns are primarily NC which is plasticized with NG. Additives are required to reduce sensitivity to expln, flash, and smoke production. Some typical compns are listed in Table 2 (Refs 27, 32a)

At this time the major uses of double-base smokeless compns are in Navy rocket weaponry and gun proplnts. The 2.75-inch FFAR, Sidewinder, SHRIKE, ASROC and Polaris weapon systems employ such proplnts. The major dis-

Table 1
Typical Single-Base Solid Propellants

Designation	Nominal wt % M6	M10	IMR	EC-NACO
Nitrocellulose (13.15% N)	87	98	100	91.4
Ethyl centralite	–	–	–	3.8
Basic lead carbonate	–	–	–	1.0
Total volatile (ethyl alcohol + dibutyl ether)	–	–	–	3.8
Potassium sulfate	–	1	1 (added)	–
Diphenylamine	1 (added)	1	0.7 (added)	–
Dinitrotoluene	10	–	8 (deterrent coating)	–
Dibutyl phthalate	3	–	–	–

Table 2
Common Double-Base Solid Propellants

Designation	Nominal wt % M2	M5	M8	M21	N5
Nitrocellulose (13.25% N)	77.45	81.95	52.15	53.00	50.00
Nitroglycerine	19.50	15.00	43.00	31.00	34.90
Potassium nitrate	2.15	2.15	1.25	–	–
Ethyl centralite	0.6	0.6	0.6	2.00	–
Graphite	0.3	0.3	–	–	–
Triacetin	–	–	–	11.00	–
Lead salicylate	–	–	–	2.50	–
Lead stearate	–	–	–	0.50	–
Carbon black	–	–	–	0.03	–
Diethyl phthalate	–	–	3.00	–	10.50
2-Nitrodiphenylamine	–	–	–	–	2.00
Lead salts	–	–	–	–	2.40
Candelilla wax	–	–	–	–	0.20

Table 3
Triple-Base Propellants

Designation	Nominal wt % M15	M16	M17	M31
Nitroguanidine	54.70	–	54.70	54.70
Nitrocellulose (13.15% N)	20.00	55.50 (12.6% N)	22.00	20.00
Nitroglycerin	19.00	27.50	21.50	19.00
Ethyl Centralite	6.00	4.00	1.50	–
Sodium aluminum fluoride	0.30	–	0.30	0.30
Dibutyl phthalate	–	–	–	4.50
2-Nitrodiphenylamine	–	–	–	1.50
Dinitrotoluene	–	10.50	–	–
Potassium sulfate	–	1.50	–	–
Carbon black	–	0.50	–	–
Lead stearate	–	0.50	–	–

advantage is the increased sensitivity of these compns to detonation

Triple-base proplnts use primarily NGu as a third major ingredient in addition to NC and NG. Typical compns are shown in Table 3. The major use of this type of proplnt is in gun proplnts for mortar and artillery shells

The proplnts described above are in the realm of prior art and depict those NC proplnts with low smoke potential that are used primarily as gun proplnts. Recent research and development work has been concentrated on creating both gun proplnts and rocket proplnts with reduced smoke output in order to foil countermeasures. Lavitt (Ref 76) found that the concurrent use of optimum proportions of lead stearate and sodium barbiturate in double-base proplnts resulted in a marked reduction in smoke output. This was attributed to the synergistic interaction of the two salts to produce more complete oxidation of the exhaust products. The importance of using the optimum ratio of the two catalysts is demonstrated by the higher smoke values shown in Table 4 for Propellants 105, 106 and 107, when compared to other standard NC base proplnts and a standard ammonium nitrate composite proplnt with about the same flame temp. The attenuation of a beam of light across the exhaust gases was measured for each formulation. Note that these formulations have less energy as measured by the heat of explosion (600–700cal/gm range) when compared to the standard proplnts described previously where ΔH_{ex} is in the 800–900cal/gm range

The most common high energy smokeless compns used in rockets employ HMX or RDX in double-base compns to improve the combustion efficiency. However, other rocket proplnts employing ammonium perchlorate and high-energy NF compds have yielded low smoke proplnts. One such compd, 1,2,3-tris[1,2-bis(difluoramino)-ethoxy] propane (TVOPA) has been investigated as a plasticizer in acrylate-acrylic acid copolymer binder proplnts for this use. However, its high cost led to a search for replacements. Sayles (Ref 77) described the use of butanetriol trinitrate (BTTN) as a partial or complete replacement for TVOPA in high-energy smokeless proplnts. The effect of this substitution on the

Table 4

Designation	101	102	103	104	105	106	107	MDB-7[a]	LFT-3[b]
Composition, % (nominal)									
Nitrocellulose (12.6% N)	48.3	53.3	48.3	48.3	48.6	48.2	48.1	48.6	–
Nitroglycerin	27.0	24.2	27.0	27.0	27.0	26.0	27.0	27.0	–
Triacetin	19.5	14.2	12.5	7.5	19.9	14.5	20.4	18.8	–
Ethyl Centralite	1.0	0.9	1.0	1.0	3.0	2.8	3.5	1.1	–
Lead Stearate	3.2	3.0	3.2	3.2	1.5	1.5	–	4.6	–
Sodium Barbiturate	1.0	0.6	3.0	3.0	–	1.0	1.0	–	–
Oxamide	–	3.8	5.0	10.0	–	6.0	–	–	–
Calculated Flame Temp °F	2523	2715	2646	2747	2462	2460	2450	2480	1808
Heat of Explosion (Expt), cal/g	700	726	715	727	699	698	704	705	734
Static Firing Data									
Pressure, psi	710	960	690	1138	1340	1130	910	960	650
Burning Time, sec	1.59	1.24	1.74	1.18	1.36	1.31	1.78	1.35	3.48
Mass Rate of Discharge, lb/sec	0.340	0.556	0.396	0.585	0.478	0.519	0.376	0.489	0.198
Light Attenuation, %	3.7	2.0	4.7	4.4	21.4	16.3	17.4	7.9	2.5
Specific Attenuation[c]	10.9	3.6	11.8	7.3	44.8	31.4	46.3	16.1	12.6

[a] Standard type nitrocellulose base propellant
[b] Standard type ammonium nitrate composite propellant
[c] Specific attenuation = Light attenuation divided by Mass Rate of Discharge

Table 5
Effect of Substitution of BTTN for TVOPA

Ingredient	Composition A	B	C	D
EA/AA (95:5)	4.6	4.60	5.7	4.6
TVOPA	25.7	12.85	8.0	0.0
BTTN	0.0	12.85	23.8	25.7
HMX	48.5	48.50	60.1	48.5
AP	19.2	19.20	0.0	19.2
Diepoxydicyclohexyl carboxylate	1.5	1.50	1.8	1.5
Carbon black	0.5	0.50	0.6	0.5
Total Wt %	100.0	100.0	100.0	100.0
C*	5152	5416	5220	4319
C_f	1.562	1.575	1.565	1.587
I_{sp}	250.1	265.1	253.9	262.4
CH_4	0.010	–	0.010	–
CO	25.038	26.930	30.218	20.805
CO_2	8.732	11.636	9.812	14.916
HCl	3.747	3.885	–	4.087
H_2	18.310	14.398	22.130	12.459
H_2O	9.000	15.081	10.782	25.320
N_2	20.545	12.904	22.612	22.411
NF	14.627	15.164	44.445	–

calculated performance of typical proplnts is shown in Table 5. The compns employing no ammonium perchlorate (AP) generate less smoke. RDX may be substituted for HMX in the formulation. Ethyl acrylate-acrylic acid copolymer (EA/AA) consists of from 90 to 96 parts acrylate and from 4 to about 10 parts acrylic acid. Those in Table 5 are about 95 parts ethyl acrylate and 5 parts acrylic acid. TVOPA is a difluoramino plasticizer for the EA/AA binders. Projected cost data for BTTN range from 1/4 to 1/6 that of TVOPA.

Sayles (Ref 82) also found that bis N-(trinitroethyl) nitramino ethane can be used as an oxidizer in EA/AA proplnts to produce smokeless proplnts. In these formulations it can replace HMX or HMX and AP. The results of this substitution on performance is shown in Tables 6 and 7

Most exptl smokeless proplnts based upon the high-energy NF compds have been plagued with stability and ageing problems which results in poor shelf-life. Additionally, the cost projections on some of the ingredients results in an unreasonably high cost proplnt

B. *Composite Propellants*

Composite proplnts, which are used almost entirely in rocket propulsion, normally contain a solid phase oxidizer combined with a polymeric fuel binder with a $-CH_2-CH_2-$ structure. Practically speaking AP is the only oxidizer which has achieved high volume production, although ammonium nitrate (AN) has limited special uses such as in gas generators. Other oxidizers which have been studied more or less as curiosities include hydrazinium nitrate, nitronium perchlorate, lithium perchlorate, lithium nitrate, potassium perchlorate and others. Among binders, the most used are: polyurethanes, polybutadiene/acrylonitrile/acrylic acid terpolymers and hydroxy-terminated polybutadienes

Modern polyurethane binders are derived by reacting polymeric diols with 2,4-toluene diisocyanate (TDI) and a trifunctional alcohol for cross-linking. By using glycols having molecular weights of 1000 to 4000 the shrinkage and heat of polymerization of the proplnt as it is cured can be reduced to an optimum level to give the

Table 6
Effect of Substituting BTNEEDNA for HMX in an EANF-Propellant Formulation

Ingredient	Composition A	Composition B
Ethyl acrylate-acrylic acid (95/5)	4.63	4.63
1,2,3-tris[1,2-bis(difluoroamino)-ethoxy] propane	25.68	25.68
HMX	48.56	0.0
bis[N-(trinitroethyl)nitramino] ethane	0.0	48.56
Ammonium Perchlorate	19.21	19.21
UNOX 221	1.44	1.44
Carbon Black	0.48	0.48
Theoretical Performance		
C* (fps)	5152	5265
C_f	1.562	1.578
I_{sp} (lb-sec/lb)	250.1	258.2
Exhaust Gas Composition (Mole Fractions)		
CH_4	0.00001	–
CO	0.25038	0.22347
CO_2	0.08732	0.14066
H	0.0	0.00001
HCl	0.03747	0.04165
HF	0.14627	0.16256
H_2	0.18310	0.09145
H_2O	0.09000	0.14900
NH_3	0.0001	–
N_2	0.20545	0.19120

required physical properties. The most significant variable in determining the mechanical properties of the polyurethane binder is the chemical structure of the polyol and the triol cross-linking agent. For instance, the physical properties of the 2,4-TDI/polypropylene glycol polymer are improved significantly by incorporating triethylene glycol, diethylene glycol, 2,5-hexanediol, ethylene glycol, polypropylene glycol, or polybutylene oxide in the binder formulations to cross-link the polymeric structure. Some typical polyurethane resin formulations are given in Table 8 (Ref 74). Among the curing catalysts for polyurethanes are cobaltic acetyl acetonate, lead naphthenate, cobalt naphthenate and ferric acetyl acetonate, with the latter being the most used

Bimodal oxidizers are normally used to improve fluidity for mixing and casting. These

Table 7
Effect of Substitution BTNEEDNA for HMX and AP in an EANF Propellant Formulation

Ingredient	Composition A	Composition B
		% (by wt)
Ethyl acrylate-acrylic acid (95/5)	4.63	4.63
1,2,3-tris[1,2-bis(difluoroamino-ethoxy)] propane	25.68	25.68
bis[N-(trinitroethyl)nitramino] ethane	–	67.77
UNOX 221	1.44	1.44
Carbon Black	0.48	0.48
HMX	48.56	–
Ammonium Perchlorate	19.21	–
Theoretical Performance		
C* (fps)	5152	5283
C_f	1.562	1.569
I_{sp} (lbf-sec/lbm)	250.0	258.0

consist of unground material which is in the range of 100 mesh and 30% ground oxidizer in the 10 to 30 micron size range. Two specific formulations are given below for an unaluminized JPL X500 proplnt in Table 9 (Ref 74). Uncatalyzed polyurethane proplnts have unusually low burning rates. Copper chromite and ferric acetyl acetonate are the more commonly used burning rate catalysts in polyurethane proplnts, although ferric oxide, chromic oxide, ammonium dichromate, and organic ferrocenes are also effective (Ref 40). Lithium fluoride has been used as a burning rate depressant for polyurethane proplnts (Ref 32)

Surface-active agents are introduced into polyurethane formulations to improve physical properties and to give increased fluidity during mixing. The polar residue of a suitable wetting agent adheres to the AP particles leaving the non-polar end as an effective lubricating film around the particle. Plasticizers are also added to improve physical properties such as elongation and brittle point, to improve castability, to lower the shrinkage and curing exotherm, and to reduce the interaction between resin binder and oxidizer. The variation in physical properties of JPL X500 with plasticizer and surface-active agent are shown in Table 10 (Ref 74)

Table 8
Polyurethane Resin Formulae

Components	JPL X500 (wt %)	JPL X500 (mol)	JPL X360 (wt %)	JPL X360 (mol)
Diols				
Polypropylene glycol 2025[1]	79.7	0.364	81.2	0.438
Polypropylene glycol 3000[1]	–	–	–	–
Polypropylene glycol 150[1]	–	–	–	–
Triethylene glycol	–	–	–	–
Diisocyanate				
Toluene diisocyanate[2]	15.8	1.000	14.9	1.000
Triols				
Hexane Triol[3]	4.1	0.335	3.8	0.333
Triol 230[4]	–	–	–	–
Triisopropanolamine	–	–	–	–
Curing catalyst				
Ferric acetyl acetonate	0.35	–	0.011	–
Ratio of isocyanate to alcohol	1.15	–	1.07	–
Polymer weight per mole of cross-linking agent (gm/gm mol)	3280	–	3510	–

[1] Polyether diols
[2] 2,4-toluene diisocyanate
[3] 1,2,6-hexane triol
[4] $HOCH_2CH_2OCH_2C(CH_3)(CH_2OH)CH_2CH(CH_3)CH_2OH$

Table 9
Composition of JPL X500

	Wt % of Propellant 70% Oxidizer	Wt % of Propellant 80% Oxidizer	Wt % of Binder[b]
Ammonium perchlorate			
ground[a]	21.0	24.0	–
ground[a]	49.0	56.0	–
Polypropylene glycol 2025 (PPG)	23.9	15.9	79.6
Ferric acetyl acetonate (FAA)	0.1	0.08	0.4
Tolylene diisocyanate (TDI)	4.8	3.2	16.0
1,2,6-Hexanetriol (HT)	1.2	0.8	4.0

[a] A bimodal oxidizer system is used in this propellant, consisting of 30% ground and 70% unground ammonium perchlorate
[b] Weight of plasticizer and/or surfactant used is subtracted from weight of binder in propellant

Table 10
Variation of Physical Properties of JPL X500 Propellant[a] with Addition of a Plasticizer and a Surface-Active Agent

Compound Added	Tensile Strength (psi) at			Elongation (%) at			Initial Modulus (psi) at		
	−40°F	80°F	160°F	−40°F	80°F	160°F	−40°F	80°F	160°F
None	1,355	155	130	5.3	11.2	6.6	79,000	3,840	4,000
Ionol (1%)	934	120	76	12.0	12.6	6.4	41,500	2,765	3,235
Dioctyl azelate (10%)	310	80	61	37.0	16.2	11.0	3,095	1,120	1,145
Ionol (1%) and dioctyl azelate (10%)	263	69	49	44.0	14.0	8.4	2,945	985	735

[a] Composition: ammonium perchlorate 70% and polyurethane binder 30% (includes plasticizer and/or surfactant weight)

Another class of hydrocarbon binders used in proplnts are the carboxy-terminated polybutadiene polymers which are cross-linked with either tris[1-(2-methyl)aziridinyl] phosphine oxide (MAPO) or combinations with phenyl bis[1-(2-methyl)aziridinyl] phosphine oxide (Phenyl MAPO). Phenyl MAPO is a difunctional counterpart of MAPO which makes possible chain extension of polymers with two carboxylic acid groups. A typical proplnt formulation with ballistic properties is in Table 11 (Ref 83)

Another class of composites includes those using hydroxy-terminated polybutadienes cross-linked with toluene diisocyanate as binders. The following simplified equations illustrate typical reactions involved in binder formation

Prepolymer Preparation:

$$\text{HO–polybutadiene–OH} + \text{OCN–R–NCO} \rightarrow \text{OCN–R–NH–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O–polybutadiene–O–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–NH–R–NCO}$$

Chain extension with a diol:

$$\text{OCN–polybutadiene–NCO} + \text{HO–R–OH} \rightarrow \left\{\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–NH–polybutadiene–NH–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O–R–O}\right\}_n$$

Chain extension with a diamine:

$$\text{OCN–polybutadiene–NCO} + \text{H}_2\text{N–R–NH}_2 \rightarrow \left\{\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–NH–polybutadiene–NH–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–NH–R–NH}\right\}_n$$

A composite proplnt formulated with this binder is shown in Table 12 (Ref 66a)

Other binder polymers which are used to make composites are copolymers of 1,3-buta-

Table 11
Carboxy-Terminated Polybutadiene Propellant Formulation

Ingredient	% by wt
Butarez CTL (carboxy-terminated polybutadiene polymer)	8.28
MAPO	0.31
Isodecylpolargonate	5.41
Ammonium perchlorate	64.00
Copper chromite	1.00
Aluminum powder	21.00
Burning rate (1000psi, 70°F, inch/sec)	0.53
Specific impulse (lbf-sec/lbm)	232.3

Table 12
Hydroxy-Terminated Polybutadiene Propellant Formulation

Ingredient	% by wt
Hydroxy-terminated polybutadiene	7.82
Toluene diisocyanate	0.46
Triethanolamine	0.38
Dioctyl azelate	4.48
sym-Di-beta-naphthyl-p-phenylene-diamine	0.20
Ammonium perchlorate	68.00
Powdered aluminum	18.00
Fe_2O_3	1.00

Table 13
Typical PBAA Propellant Formulation

Ingredient	% by wt
PBAA	14.30
EPON 562, epoxide derivative of glycerol	2.85
5,8,11,13,16,19-hexosa-tricosane	2.85
Ammonium perchlorate, 18 micron	12.00
Ammonium perchlorate, 200 micron	56.00
Powdered aluminum (Re 1-511)	12.00
Burning rate, in/sec at 1000psi	0.31
Burning rate exponent, n	0.34

Table 14
Typical PBAN Propellant Formulation

Ingredient	% by wt
PBAN terpolymer	10.886
Epoxy curing system	5.914
Ammonium perchlorate (unground)	44.20
Ammonium perchlorate (ground 11 μ)	24.00
Aluminum (Re 1-131)	15.00
Burning rate, inch/sec at 1000psi	0.33
Burning rate exponent, n	0.34

diene with acrylic acid (PBAA) and terpolymers of 1,3-butadiene, acrylic acid, and acrylonitrile (PBAN). Formulations using these binder materials are given in Tables 13 and 14 (Refs 32 & 63)

Without the influence of burning rate catalysts most of these hydrocarbon proplnts have similar burning rates and ballistic behavior. They may differ significantly in mechanical properties, particularly as a function of temp. Most hydrocarbon-based composites are used in larger rockets because of their ease of fabrication and high specific impulse. Polaris first and second stages, the Titan 3C booster rocket and Minuteman are all powered with composite proplnts

A relatively new class of fluorocarbon composite proplnts with relatively high specific impulse and a high density impulse have been tested as booster rockets for 5-inch projectiles.

Table 15
Extrudable Fluorocarbon Composite Propellants

Ingredient	Percent by Weight A	B	C	D
Teflon	10	5	8	8
Viton A	15	15	12	12
Ammonium perchlorate	55	65	–	–
Aluminum powder	20	–	20	5
Beryllium	–	15	–	–
Nitronium perchlorate	–	–	45	50
Triaminoguanidine	–	–	15	–
Aluminum hydride	–	–	–	25

The compns are based upon a copolymer of vinylidene fluoride and perfluoropropylene (Viton A) with polytetrafluoroethylene (Teflon) and various metals and oxidizers. A number of extrudable formulations are listed in Table 15 (Ref 57). The major advantages claimed for these proplnts are high density impulse, compatibility with highly energetic proplnt ingredients and resistance to high centrifugal forces

Modification of the burning rates, pressure exponents, and temp coefficients of burning rate of the fluorocarbon composites has been accomplished with copper, lead, tin, sodium, ammonium and potassium fluoborates; sodium, potassium, lithium, lead, copper and calcium fluorides; potassium and ammonium dichromate; lead and zinc stearate; cesium carbonate; potassium and ammonium sulfate; copper chromite; oxides of magnesium, copper and manganese; boron; zinc dust; and carbon black (Ref 75)

C. *High Energy Solid Propellants*

To achieve higher energy in solid proplnts the most notable advances were achieved with the addition of aluminum and beryllium to both double-base and composite proplnts. Energy in this case is commonly equated to high specific impulse. Later developments added aluminum hydride and beryllium hydride to this list. In Table 16, the specific impulse performance of proplnts using AP with various metals and hydrides is compared to those systems without these additives (Ref 43)

There are stability problems with most of the metal additives other than aluminum, although

Table 16
Effect of Metal Additives on Specific Impulse of Ammonium Perchlorate Propellants

Fuel	wt % fuel	wt % additive	I_{sp} (lbf-sec/lbm)	Chamber Temp, °K	Density g/cc
$-CH_2-$	15	0	246.5	2950	1.66
Double-base	40	0	250.7	3051	1.73
$-CH_2-$	15	Al (19%)	264.1	3179	1.74
Double-base	45	Al (20%)	263.5	3760	1.80
$-CH_2-$	15	AlH_3 (34%)	274.2	2546	1.53
Double-base	40	AlH_3 (28%)	285.2	3417	1.61
$-CH_2-$	15	Be (12%)	285.6	3172	1.66
Double-base	40	Be (16.8%)	279.3	4071	1.72
$-CH_2-$	20	BeH_2 (25%)	304.0	2644	1.14
Double-base	50	BeH_2 (20%)	313.8	3154	1.28

this is not as serious a problem with beryllium as with the two hydrides AlH_3 and BeH_2. All three induce gassing in most formulations with resulting porosity and higher than normal burning rates. The other disadvantage, for most military uses, is the lower density achieved with hydride formulations. For the most part, the higher velocity, and therefore longer ranges, are achieved with the higher density impulse proplnts. The applicable equation is

$$BV = g_o I_{sp} \ln(1/1-MF)$$

where MR = 1/1–MF, MR = mass ratio; MF = mass fraction, g_o = gravity constant, I_{sp} = specific impulse, lbf-sec/lbm, and BV = boost velocity, ft/sec. The mass fraction is defined as the ratio of the proplnt mass to the total mass of the rocket. Thus the effect of high proplnt density is to increase the mass ratio and therefore maximize the boost velocity. Since the reduction of metal parts and payload weights pays diminishing returns, the other alternative is to increase the specific impulse of the proplnt in order to achieve higher performance. A large effort has been exerted toward this end thru research into more energetic oxidizers and binders

Hydrazinium diperchlorate (HP_2) is one of the higher energetic oxidizers considered for use in composite solid proplnts with hydrocarbon binders. Its other advantages include high density, high burning rate, and moderate projected cost. Its shortcomings include relatively poor stability to vibrational and thermal shock when formulated into the usual polymeric fuel binders. Because of its poor shock sensitivity, batch size and motor size are limited to exptl research quantities. Stabilization of HP_2 has been effected by adding from 0.1 to 10% by weight of ethylenediamine tetraacetic acid (EDTA) to HP_2 in aq or non-aq solns prior to the final crystn which precedes the final drying step (Ref 55). In general, many chelating agents have been found to be effective in stabilization of HP_2. Wall (Ref 58) was able to incorporate HP_2 into composite formulations using such stabilizers as N,N′-diphenyl-p-phenylenediamine, N,N′-ditolyl-p-phenylenediamine, N,N′-dixylyl-p-phenylenediamine and many others containing sulfur and nitrogen usually bound in a heterocyclic ring and with weakly basic characteristics. Proplnt compns with better stability, physical properties, ballistic performance and lower cost were formulated as follows:

Ingredient	Parts by weight
Stabilizer	0.5 – 4.0
HP_2	60 – 80
Ammonium perchlorate	0 – 20
Carboxy-terminated polybutadiene binder	15 – 25
Aluminum or beryllium powder	10 – 20

Hydroxylammonium perchlorate is another high energy oxidizer with stability, high impulse and high density claimed to be an improvement over AP (Ref 59). Several preferred proplnt compns incorporating this oxidizer are listed in Table 17

Table 17
Composite Propellants Containing Hydroxylammonium Perchlorate

Ingredient	Percent by Weight A	B	C
Hydroxylammonium perchlorate	64.00	64.00	65.00
Aluminum powder	18.00	18.00	20.00
Hydroxy-terminated copolymer of butadiene and styrene	15.40	–	–
Epoxy, ERL-2795	2.60	–	–
Hydroxy-terminated polybutadiene	–	15.08	–
Epoxide 201	–	2.92	–
Castor oil	–	–	12.03
Toluene diisocyanate	–	–	2.97
Delivered I_{sp}, lbf-sec/lbm at 1000psi	246	254	–
Burning rate, inch/sec at 1000psi	0.60	0.30	0.82
Burning rate exponent, n	0.49	0.25	0.5
Density, lb/inch^3	–	0.067	–

Table 18

Composition and Properties	Example 1	2	3	4
Ammonium perchlorate	21.5	30	23.5	27.0
Aluminum, atomized	21.5	20	21.5	23.0
Nitrocellulose (12.6% N)	16.2	17.1	19.0	14.3
PETRIN	39.9	27.0	35	35
Dibutyl phthalate	–	5	–	–
Ethyl centralite	0.9	0.9	1.0	0.7
Burning rate, 70°F 1000psi, inch/sec	0.45	0.37	0.45	0.45
Pressure exponent	0.6	0.5	0.5	0.5
Heat of Explosion, cal/g	1675	1521	1675	1741
Taliani, mmHg/min	0.5	0.5	0.5	0.4
Impact sensitivity, 50% point, cm	15	14	16	–

NC-based composite proplnts have also been formulated with high energy ingredients, although in many cases the NG is replaced with other expl plasticizers. Reinhart (Ref 62) has developed a series of plastisol-NC proplnts using pentaerythritol trinitrate (Petrin) and/or trimethylolethane trinitrate (TMETN) as plasticizers. Table 18 gives examples of these formulations and their ballistic properties. Other high energy additives such as HMX and TNEOC (trinitroethyl-orthocarbonate) were also used with this binder as indicated in Table 19. Measured specific impulse at 1000psi ranged from a low of 227 to a high of 274 lbf-sec/lbm for these variants

Beryllium hydride has been used by Butts (Ref 70) in combination with a specific nitronitrate ester plasticizer for NC selected from the group consisting of nitroisobutanetriol trinitrate (NIBTN), 2,2-dinitropropanediol dinitrate (DNPDN) and nitroethylnitrate (TNEN). Coplasticizers which are used include diethyleneglycol dinitrate (DEGDN) or ethyleneglycol dinitrate (EGDN). Formulations with BeH_2 are in Table 20. The formulation in Example 2 has a theoretical I_{sp} of 301 lbf-sec/lbm and a non-equilibrium flame temp of 2600°K

Table 19

Composition and properties	Example 1	2	3	4	5
Binder type [a]	G	G	G	H	H
HMX, 100 avg percent	–	37	22	20	30
TNEOC, percent	32	–	–	–	–
Ammonium perchlorate, percent	–	–	12	–	–
Aluminum, atomized, percent	18	13	16	20	20
Burning rate, 70°F and 1000psi, inch/sec	0.35	0.15	0.22	0.34	0.3
Pressure exponent	1.0	0.9	0.6	0.7	0.8
Heat of explosion, cal/g	1,057	908	1,079	1,433	1,490
Taliani, MM Hg/min	1.4	0.3	0.5	0.3	0.3
Impact sensitivity, 50% point, cm	–	33[b]	–	25[b]	–

[a] See the following table:

	G	H
Binder formulations, weight percent:		
Nitrocellulose (12.6% N)	38	28.5
Petrin	39	70
Dibutyl phthalate	20	–
Adiponitrile	1	–
Ethyl centralite	2	1.5

[b] Uncured

Table 20

Example 1	
Plastic Binder	9–14%
Co-Plasticizer	3–15%
Oxidizer	0–35%
Beryllium Hydride Fuel	15–24%
Nitro-Nitrate Ester Plasticizer	10–40%
Example 2	
Nitrocellulose	10.8%
Diethyleneglycol dinitrate	3.8%
Ammonium Perchlorate	35.2%
Beryllium Hydride	15.0%
Nitroisobutanetriol Trinitrate (NIBTN)	35.2%
Example 3	
Nitrocellulose	10.0%
Diethyleneglycol dinitrate	5.1%
Ammonium Perchlorate	34.9%
Beryllium Hydride	16.2%
2,2-dinitropropanediol dinitrate	33.8%
Example 4	
Nitrocellulose	10.5%
Ethyleneglycol dinitrate	4.4%
Potassium perchlorate	31.1%
Beryllium Hydride	17.7%
Nitroethylnitrate (TNEN)	36.3%

Table 21

Run No	Propellant Composition weight per cent NC[1]	TMETN[2]	AlH_3	HNF[3]	Results Comb Temp °K	Specific Impulse I_{sp}(sec)
1	12.5	37.5	30	20	3296	287.8
2	12.5	37.5	27	23	3466	293.3
3	11.25	33.75	31	24	3325	289.9
4	12.5	37.5	24	26	3520	291.1
5	11.25	33.75	28	27	3496	294.6
6	11.25	33.75	25	30	3560	292.7
7	10	30	30	30	3485	294.7
8	8.75	26.25	33	32	3381	291.5
9	10	30	27	33	3582	295.1
10	8.75	26.25	30	35	3550	296.7
11	10	30	24	36	3609	292.9
12	8.75	26.25	27	38	3630	295.8

[1] nitrocellulose
[2] trimethylolethane trinitrate
[3] hydrazinium nitroformate

Klunsch (Ref 72) has incorporated hydrazinium nitroformate and aluminum hydride in plastisol NC formulations which cure at room temp without undesirable gas formation. A number of such formulations and calculated ballistic results are given in Table 21. Although these are attractive proplnts from the standpoint of potential energy, their impact sensitivity was not described. Similar plastisol binder propellants in Table 18 were sensitive enough to impact to warrant extreme caution in processing into rockets.

Flynn (Ref 73) continued the trend of using the rather inert plastisol NC binder to synthesize the proplnts containing aluminum hydride and nitronium perchlorate shown in Table 22. In this case, the stability of nitronium perchlorate, in terms of gassing and friction sensitivity is enhanced by surface-coating it with from 7 to 8 percent of a polymeric dichlorostyrene. For optimum physical stability during formulation, curing, and storage, substantially all traces of moisture and acids must be removed from all ingredients. Furthermore, these operations should be carried out in an inert atm of nitrogen or argon. This well illustrates the extremes in technology which are required to safely handle many of these proposed high-energy ingredients

Table 22

Run No	Propellant Composition weight per cent NC[1]	TMETN[2]	AlH_3	NP[3]	Results Comb Temp °K	Specific Impulse I_{sp} (sec)
1	11.25	33.75	34	21	3696	295.3
2	11.25	33.75	31	24	3834	296.6
3	11.25	33.75	28	27	3920	294.9
4	8.75	26.25	38	27	3778	296.4
5	8.75	26.25	35	30	3921	298.2
6	8.75	26.25	32	33	4017	297.0

[1] Nitrocellulose
[2] Trimethylolethane trinitrate
[3] Nitronium perchlorate

Experimentally, Flynn (Ref 73a) has tested plastisol NC composite proplnts containing beryllium and triaminoguanidinium hydrazinium diazide in a closed bomb and measured the high specific impulses indicated in Table 23

Other formulations containing the ingredients aluminum and hydrazine nitroformate resulted in high calculated impulses as the data in Table 24 show

Table 23

Run No	Propellant Composition Nitrosol′	Al	Be (% by weight)	AP[3]	THA[4]	ΔH (cal/g)	Combustion Results I_{sp} (obs) (sec)	I_{sp} (theo) (sec)	Eff (%)
1	40[1]	19	–	17	24	1387	247	274.8	89.8
2	40[1]	16	–	26	18	1543 ±3	246	272.6	90.6
3	35[1]	16	–	26	23	1500 ±2	243	273.9	88.7
4	40[2]	–	13	23	24	1838 ±12	281	293.8	95.7
5	40	–	9	27	24	1693 ±10	270	286.5	94.4

[1] 25 parts by weight plasticized grade nitrocellulose, 55 parts by weight trimethylolethane trinitrate, 15 parts by weight diethyleneglycol dinitrate, 5 parts by weight toluene diisocyanate
[2] 25 parts by weight plastisol grade nitrocellulose, 60 parts by weight trimethylolethane trinitrate and 15 parts by weight triethylene glycol dinitrate
[3] ammonium perchlorate
[4] triaminoguanidinium hydrazine diazide

Table 24

Run No	Propellant Composition NC[1]	TMETN[2]	Al	Be	THA[3]	AP[4]	HNF[5]	Results Comb Temp (°K)	Specific Impulse I_{sp} (sec)
				wt percent					
1	7.5	27.5	17.9	–	29.2	17.9	–	3407	275.6
2	5.0	25.0	15.0	–	31.5	23.5	–	3379	274.5
3	7.5	27.5	18.0	–	32.5	14.5	–	3236	272.3
4	5.0	25.0	18.0	–	35.0	17.0	–	3243	273.2
5	5.0	25.0	21.0	–	31.5	17.5	–	3263	270.3
6	10.0	30.0	23.0	–	18.0	19.0	–	3617	272.0
7	10.0	30.0	18.0	–	12.0	30.0	–	3745	271.4
8	5.0	25.0	19.0	–	21.0	30.0	–	3677	274.7
9	10.0	30.0	21.0	–	12.0	–	27.0	3789	278.2
10	10.0	30.0	19.0	–	18.0	–	23.0	3628	278.5
11	10.0	30.0	17.0	–	24.0	–	19.0	3455	277.6
12	10.0	30.0	–	8.0	27.0	25.0	–	3262	284.9
13	10.0	30.0	–	9.0	21.0	30.0	–	3406	285.5
14	10.0	30.0	–	13.0	24.0	23.0	–	3497	293.8
15	7.5	27.5	–	16.0	22.8	26.2	–	3424	289.7
16	10.0	30.0	–	10.0	18.0	–	32.0	3509	294.8
17	10.0	30.0	–	12.0	18.0	–	30.0	3609	297.3
18	10.0	30.0	–	13.0	12.0	–	35.0	3744	295.8

[1] Nitrocellulose
[2] Trimethylolethane trinitrate
[3] Triaminoguanidinium hydrazinium diazide
[4] Ammonium perchlorate
[5] Hydrazine Nitroformate

This review of the state-of-the-art in high-energy propInt technology is not intended to be all-inclusive, but it is intended to give typical examples of the compounds under consideration and the problems in sensitivity and stability which have been encountered

D. *Configurations*

Missions flown by solid propInt rockets are predetermined or programmed by the design of the burning surface. Normally the propInt is case-bonded to the motor case or otherwise inhibited so that it burns only on the internal surface. The simplified approach is to assume that the burning surface recedes in burning parallel layers in a direction perpendicular to the surface itself. For rocket motors where combustion pressures do not normally exceed 2000psia, the propInt burning rate may be given as a function of the chamber press by the following empirical equation:

$$r = aP_c^n$$

where r = burning rate (inch/sec), P_c = chamber press (psi), n = burning rate exponent, and a = a constant. Thus the propInt mass flow rate (neglecting erosion) becomes

$$\dot{m} = A_s \rho a P_c^n$$

where $\dot{m}$ = propInt mass flow rate (lb/sec), A_s = burning surface area (sq inches), ρ = propInt density (lb/cu inch). For stable operation, the mass flow rate must equal the mass discharge rate at the nozzle which is

$$\dot{m} = C_D P_c A_t$$

where C_D = nozzle discharge coefficient and A_t = nozzle throat area (sq inch); and therefore the equilibrium chamber press by this simplified analysis will be

$$P_c = \left[\frac{A_s \rho a}{C_D A_t}\right]^{1/1-n}$$

Since the thrust (F) is given by

$$F = C_F P_c A_t = C_F \left[\frac{A_s \rho a}{C_D A_t}\right]^{1/1-n} A_t$$

where C_F = thrust coefficient, the design of the internal propInt grain configurations determines the thrust level required for the mission. Some typical star grain configurations give the thrust versus time curves shown in Figure 1 (Ref 28)

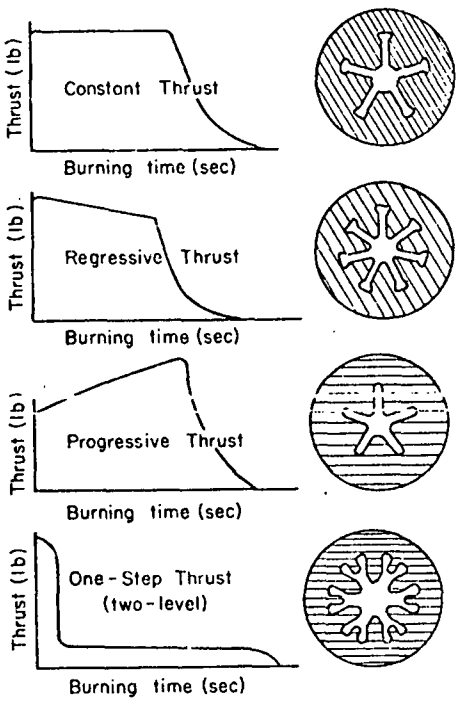


Fig 1 Grain Configurations and Thrust-Time Records

Erosion of Gun Barrels

One of the earliest uses of SP, and a use that continues to be important even at present, was in propelling projectiles out of gun barrels. The heat and combustion products of the propelling SP charge can have a deleterious effect on the bore of a gun barrel. This breaking down and wearing away of bore metal is called *erosion.* Gun barrel erosion has been discussed at some length in Vol **5**, E112–20 and D1536

Since the publication of these articles no major breakthroughs in erosion, or rather erosion prevention, have been made. However, several patents claiming methods and means of minimizing gun barrel erosion have appeared recently. These are abstracted below:

Additives for reduction of gun wear. M. Roth, USP 3282215 (1966) & CA **66**, 30648 (1967). An additive is added to cartridges and shells to reduce erosion in gun barrels. The additive may be $CaSO_4$, $CaCO_3$, TiO_2 or combinations dispersed in amounts of 10–90 weight % in a paraffin wax, which is impregnated into rayon yarn containing a melamine resin and is then wrapped around the proplnt. Other additives include ZnO, ZnS and Sb_2O_3; and Mg, Sr, and Ba sulfates, carbonates, and oxides

Gunpowder erosion reducer. J.P. Picard, FrP 1526983 (1968) & CA **71**, 31968 (1969). Hot gas erosion in the barrel of a firearm is reduced to about 0.8% of its usual value by incorporation into or on the surface of the proplnt of 1–5% 3–60 micron, cheap, plentiful inorganic materials cuh as SiO_2 and MgO separately, or preferable, in a wt % ratio of 45–65/20–55, or of talc. with the proplnt, by coating the proplnt grains, or by application of a sheet of the additive dispersed in a carrier such as synthetic fibers, foamed polyurethane, or paraffin or microcrystalline wax (mp 50–120°) placed between proplnt charge and projectile. Mode of application is diagrammatically detailed. Thus, in firing tests of a 105mm rifle using M2 proplnt, the loss of erosion with each firing averaged 24.1mgs. When rayon fabric (95–120g/m^2) coated with a layer ~1.6mm thick of a mixt of 55% paraffin and 45% SiO_2, a 65:35 SiO_2–MgO mixt, or Calif, NY, or Montana talc was placed ahead of the proplnt, the loss dropped to 0.2mg/firing

Gun barrel wear reduction additives. D.E. Jacobson & S.Y. Ek, USP 3403625 (1968) & CA **70**, 13144 (1969). Wear due to the erosion of a metal surface, such as the inside of a gun barrel, thru contact with hot rapidly flowing gases is reduced to one-tenth or less of its normal value without substantial change in firing characteristics by incorporating into a proplnt charge powdery inorganic material at about or in front of the position of the said charge prior to the firing thereof, which becomes suspended in the hot gases emanating from the charge upon firing and coats the barrel with an erosion-resistant layer. The powdery inorganic material, such as sulfides or oxides of Ti, Ta, W, V, Zn or Nb is admixed with approx an equal weight of a carbonaceous material such as paraffin, ozokerite, China-Lack paint, NC, or lubricating grease, the molten mixt applied to the inner surface of a rayon, silk, or nylon wrap in an amount equal to 0.05–30% (preferably about 3%) of the weight of the proplnt charge, and the treated fabric wrapped around the charge. Preferably, the inorganic additive mixt is largely at the forward portion of the charge. Details of application are described with the aid of 12 figs. Thus, wraps having a layer about 50mm long and 0.5mm thick of a 50:50 mixt of paraffin and WO_3, Nb_2O_5, TiO_2, or Ta_2O_5, a 60:40 paraffin-ZnO,

or a 67:33 paraffin-Zn mixt in conjunction with the charge of a 37mm cannon resulted in reduction in barrel wear to less than 5% of its value in the absence of the additive

Gun barrel wear reduction additives. D.E. Jacobson & S.Y. Ek, USP 3404626 (1968) & CA **70**, 13145 (1969). ZrO_2, HfO_2, $ZrOCl_2 \cdot 8H_2O$, or $K_2TiF_6.H_2O$ is substituted for the oxides or sulfides described in USP 3403625 above

S. Ek & D. Jacobson, SwedP 212983 (1968) & CA **70**, 69755 (1969). ZnO is claimed as an additive in reducing gun barrel erosion

A variant of gun barrel erosion, namely rocket nozzle erosion, is discussed in the following abstract:

Role of carbon gas reactions in the erosion of rocket nozzles. G.A. Heath & R.W. Thackray, AGARD Conf Proc, **52**, 28 (1970) & CA **73**, 100602 (1970). While graphites had excellent physical and mechanical properties in uncooled rocket nozzles, they underwent corrosion from chemical reactions with gaseous combustion products. The reactivity of the nozzle surface rose progressively with the temp during rocket operation. Up to 1600°K, the erosion agreed with that predicted by a chemical rate-control mechanism. Above 1600°K, the predicted values were too high because of boundary layer effects which hindered transfer of reactants from the free stream to the surface. Highly anisotropic pyrolytic graphite, which had the lowest reactivity to oxidizing gases and the highest resistance to erosion in nozzles, may be used to advantage in practical designs

IV. Production Methods of Representative Propellants

A. *Technology*

NC-base proplnts are categorized as single-base, double-base, or triple-base proplnts. The manufacturing processing steps for the proplnts are distinct from those employed for making the final rocket motors. However, when the final product is a gun proplnt, it normally goes thru only the initial manufacturing step. Smokeless powder for shells and casting powder for rocket motors may be made either by a solvent or solventless extrusion process (Ref 33). In the solvent process, NC fibers in water- or alcohol-wet form are masticated with alcohol-ether and/or acetone in a heavy-duty mixer such as the sigma-blade Baker-Perkins. When the mix is homogeneous, stabilizers, burning rate additives, and plasticizers are blended in. If the formulation is double-base or triple-base, the additional ingredients are also added. The mixture is then pressed into blocks and extruded into long strands, usually with hollow cylindrical forms with perforations required to give the desired burning rates. The strands are cut to the desired length and dried to drive off the solvents. After drying, they are cut to the final specified length

Another processing method has been termed the solventless process. In this method, a premix is made from NC fibers plus liquid NG and minor ingredients dispersed in water. The paste is centrifuged and air-dried. The remaining ingredients are tumble-blended and then calender-rolled into sheets called "carpet rolls". These are then extruded into finished pellets or cylinders

Gun proplnts do not require physical processing to prepare them for the loading operation, whereas most double-base proplnts used in rocket motors require further processing to shape them into the larger "grain" sizes used in this application (see Fig 1)

The "carpet rolls" used for extruding double-base proplnt grains for rocket motors are about 8 ft x 2 ft and 0.06 inch thick, which are then slit into widths of about 5 inches. These are rolled into cylinders of length and diameter as to fit conveniently into the barrel of a 12 to 18-inch batch extrusion press. The die of this press forms both the external dimension and internal shape of the grain. Most double-base formulations are classified as hazardous, so the extrusion process is carried out remotely behind barricades designed to suppress detonation or direct it and any resulting projectiles upward. After extrusion, the proplnt grains are inhibited by wrapping or extruding a coating of cellulose acetate or ethyl cellulose on the outside periphery to prevent burning.

In the casting process for double-base proplnt grains which are larger than conveniently extruded, the double-base granules from the solvent processing described previously, or "casting powder", becomes the starting material. The casting solvent containing the NC plasti-

cizer, usually NG, desensitizing agents and other liquid ingredients, is then introduced into the mold. Upon curing at about 140°F the solvent causes the individual grains to coalesce and form a single proplnt grain within the mold (Ref 33)

Composite proplnts are normally mixed in heavy-duty sigma-blade mixers or vertical mixers which impart the necessary work to the mixt required to ensure a homogeneous dispersion of binder and oxidizer. Several continuous mixing plants have also been constructed utilizing the Baker-Perkins continuous extrusion machine to achieve the required dispersion of liquids and solids. The batch machines are favored for those plants where production runs are short and proplnt formulation changes are frequent. The continuous processes are favored for high-volume production runs of the same formulation. Elaborate continuous feeding mechanisms are required to maintain formulations within specification ranges. For the most part, the production volume rarely justifies the capital expenditure required for continuous mixing processes, and today the volume of proplnts which are mixed by continuous processes is small

Batch mixing of composite proplnts begins with the preparation of a premix containing all ingredients except the AP and curing agent. This reasonably low viscosity premix can be prepared in rather large batches which are sampled for quality control of ingredient proportions. The proper weight of heated premix is then charged to the mixer which is operated remotely as the oxidizer is charged and the proplnt is heated to temps in the range of 150–60°F. Oxidizer preparation consists of drying to low moisture, grinding a portion to a size in the range of 10–12 microns and blending. Upon completion of oxidizer addition, the curing agent is added. The mix cycle is adjusted to give a homogeneous proplnt with uniform ballistic properties and a suitable casting viscosity. After mixing is completed, the change-can mixing bowl is transported to the casting area where the proplnt is cast under vacuum into motor cases lined with inhibitor for curing. Typical curing cycles for polyurethanes are in the range of 5 days at 140°F. For carboxy-terminated polybutadiene binders, curing times of 3 days at 165°F are common. Upon completion of curing, the mandrel which forms the burning perforation is stripped from the rocket motor and finish trimming or inhibiting, if required, is performed

In composite proplnt processing, the mixing process has always been the highest risk area and numerous mixers have been damaged or destroyed by fires and explns. When the industry came into being, the horizontal bread-dough mixers predominated and the bearings were submerged in proplnt where friction could cause ignition. The final solution to this problem was the introduction of the vertical batch mixers with overhead bearings and change-can mixing bowls to achieve higher productivity. As solid rocket sizes increased, mixers in the 150-gallon and 300-gallon sizes were introduced. A second generation mixer with a capacity of 500 gallons (10,000 lb capacity) is in operation at United Technology Center where it produces proplnt for large booster rockets each containing several hundred thousand pounds of composite proplnt. This large vertical mixer is single-shafted using a single helix for an impeller (Ref 41)

Another continuous mixing procedure being employed for the more sensitive double-base proplnts utilizes an inert and insoluble carrier to convey the proplnt ingredients thru the mixer (Ref 23). First the oxidizer and other solid ingredients, including metal powders, are each dispersed in a suitable carrier. These streams are brought together in a small jet mixer which minimizes the total volume of proplnt. Upon leaving the mixer, the carrier is largely separated from the proplnt by gravity. The remaining mixt is vacuum cast which removes the remaining carrier

B. *Cost Trade-Offs*

All rocket motor costs per unit, and therefore rocket proplnt costs, are most sensitive to the number of units being produced and to the number of different formulations mixed in a given time interval, by the same equipment, so that a direct comparson based only on processes or proplnt types are meaningless. There are also inherent difficulties in comparing NC base proplnts with composite proplnts. The former are made in government plants (some of which are operated by private industry) for the most part and so accounting for indirect costs (taxes, depreciation, insurance, and return on investment) cannot be compared to the situation

Table 25
Mixer Production Cost Comparison for Composite Propellants *

	COST/LB			
	1 million lbs/month		3 million lbs/month	
	Direct	With materials**	Direct	With materials**
Continuous mix – direct cast	$0.28	$0.79	$0.18	$0.68
Continuous mix – transport to cast	0.29	0.81	0.20	0.72
300-gallon vertical batch	0.33	0.84	0.28	0.79
150-gallon vertical batch	0.46	1.00	1.22	2.86
Continuous mix – transport to cast (processing 3 dissimilar formulations per week)	0.32	0.90	0.21	0.76

* 1964 data
** material cost @ $0.40 per lb

where private industry owns the plants making composite proplnts. Another factor making comparison impossible is the fact that most double-base proplnts go into the smaller rockets, whereas composites are best suited to the larger rockets and space boosters

It is possible to make a somewhat meaningful comparison of mixer costs for composite proplnts made in large volume production in the various large mixers. McGehee (Ref 42) did so using 1964 prices and the data are summarized in Table 25. He concluded that continuous mixing produced composite proplnts at less cost/lb than any of the known vertical mixers at the time (when processing a single formulation at rates of 1 million pounds per month and up). However, when three dissimilar formulations per week were required, the total proplnt production cost per pound became cheaper for the 300-gallon vertical mixer. At 2 million pounds per month the costs were roughly equal. The major reasons for this are that the proplnt losses become significant and maintenance costs increase for the continuous mixer on turnarounds. Since most contractors produce a variety of formulations, most proplnt is made in large vertical mixers

V. Physical Characteristics of Representative Propellants

A. *Mechanical Properties*

NC content is a major compositional variable affecting the physical properties of tensile strength, elongation, and modulus of elasticity of cast double-base proplnts. Steinberger (Ref 21) has reported the data shown in Figs 2, 3 & 4 for temps ranging from –60° to 120°F

McAbee (Ref 31) measured the tensile properties of two cast double-base rocket proplnts (OGK and ARP) and two extruded materials (T-16 and X-8) at 25° over a range of loading times from 0.005 to 2500 seconds. The effects of temp were also investigated at 0.1 inch/inch/min (conventional static test rate) and at high rates of loading over a range of –60° to 80°. Typical curves showing the stress-strain behavior of X-8 and OGK over the temp range are given in Figs 5 & 6 for the nominal strain rate of 0.1 inch/inch/min. Variable loading rates produce the type of stress-strain behavior indicated in Fig 7 for X-8 at 25°

Since these double-base proplnts consist essentially of a single phase which bears the total load in any application of force, their mechanical property behavior is significantly different from composite proplnts. In the latter formulations, the hydrocarbon binder comprises only about 14% of the composite structure, the remainder being solid particles. Under stress, the binder of these proplnts bears a proportionately higher load than that in the single phase double-base proplnts. At small strain levels, these proplnts behave in a linear viscoelastic manner where the solids reinforce the binder. As strain increases, the bond between the oxidizer and binder breaks down

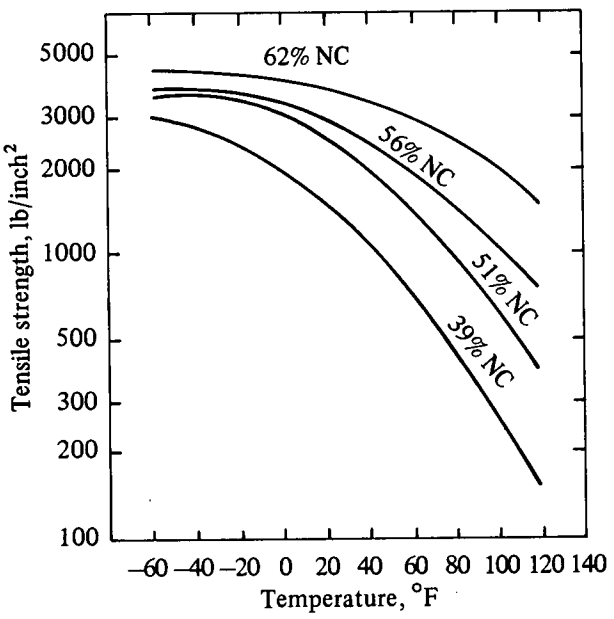


Fig 2 Tensile strength of cast double-base powder as a function of nitrocellulose content

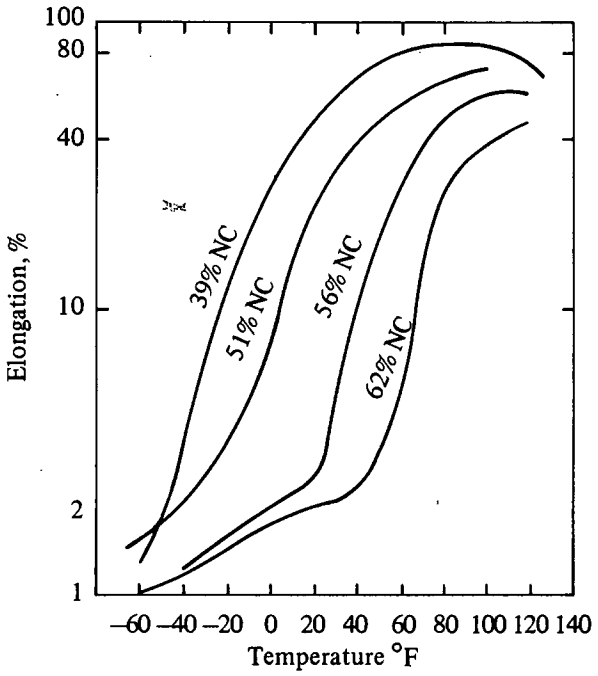


Fig 3 Elongation of cast double-base powder as a function of nitrocellulose content

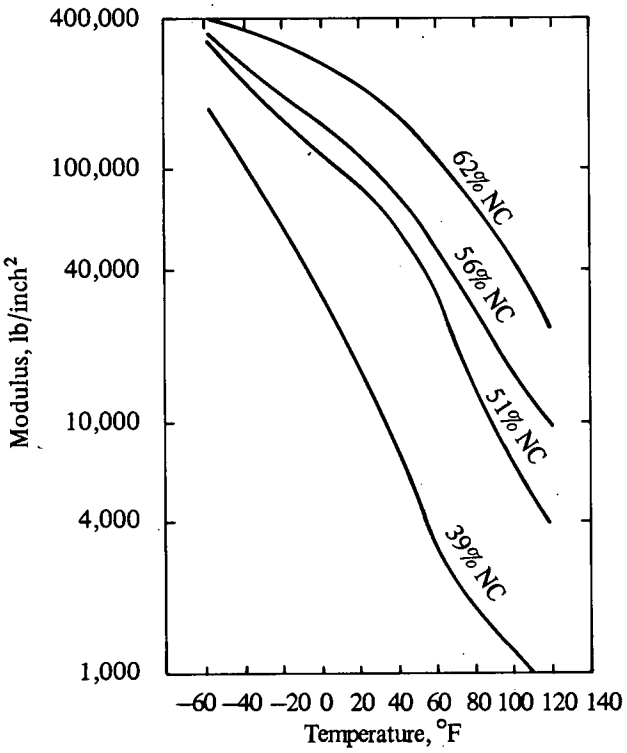


Fig 4 Modulus of elasticity of cast double-base powder as a function of nitrocellulose content

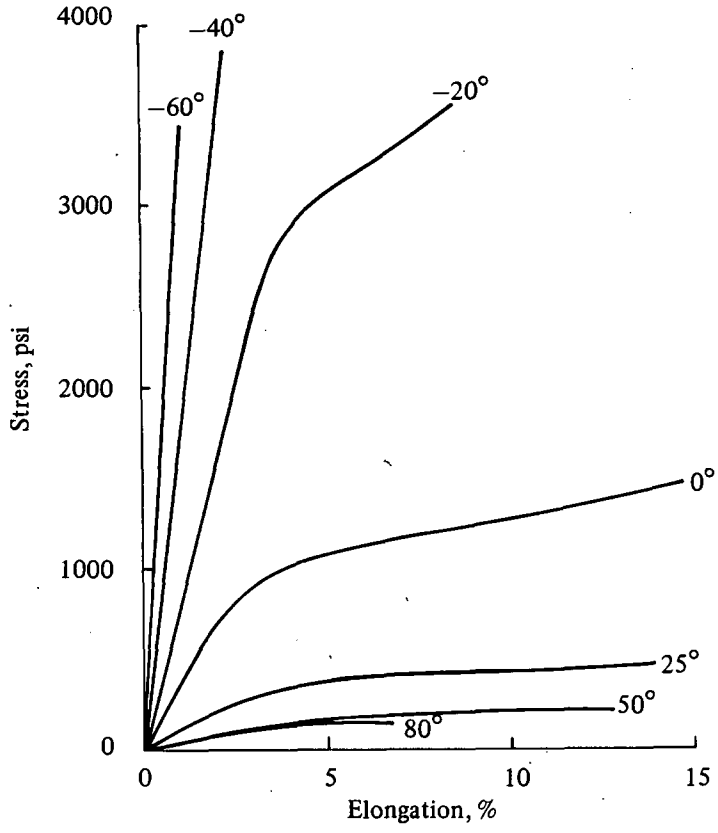


Fig 5 Effect of temperature on the stress-strain behavior of X-8 at 0.1 inch/inch/min

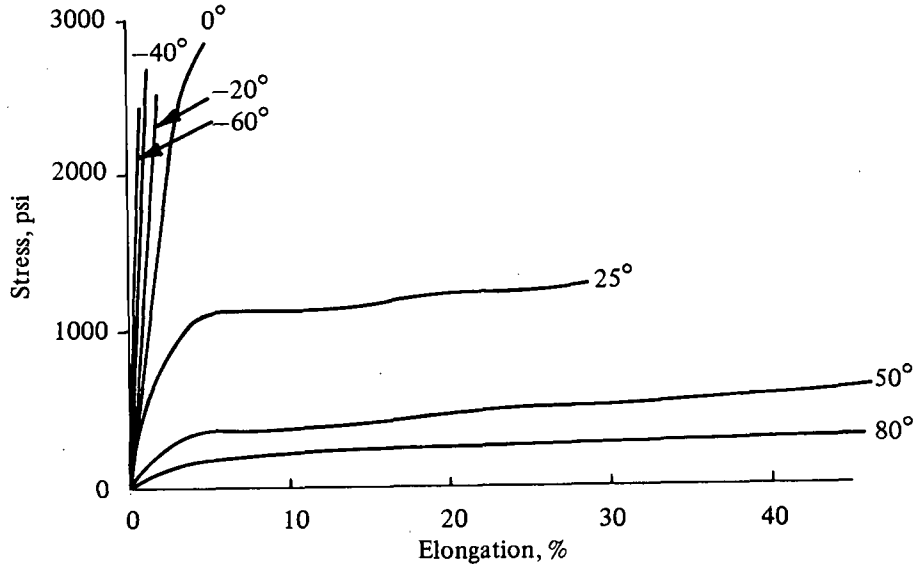


Fig 6 Effect of temperature on the stress-strain behavior of OGK at 0.1 inch/inch/min

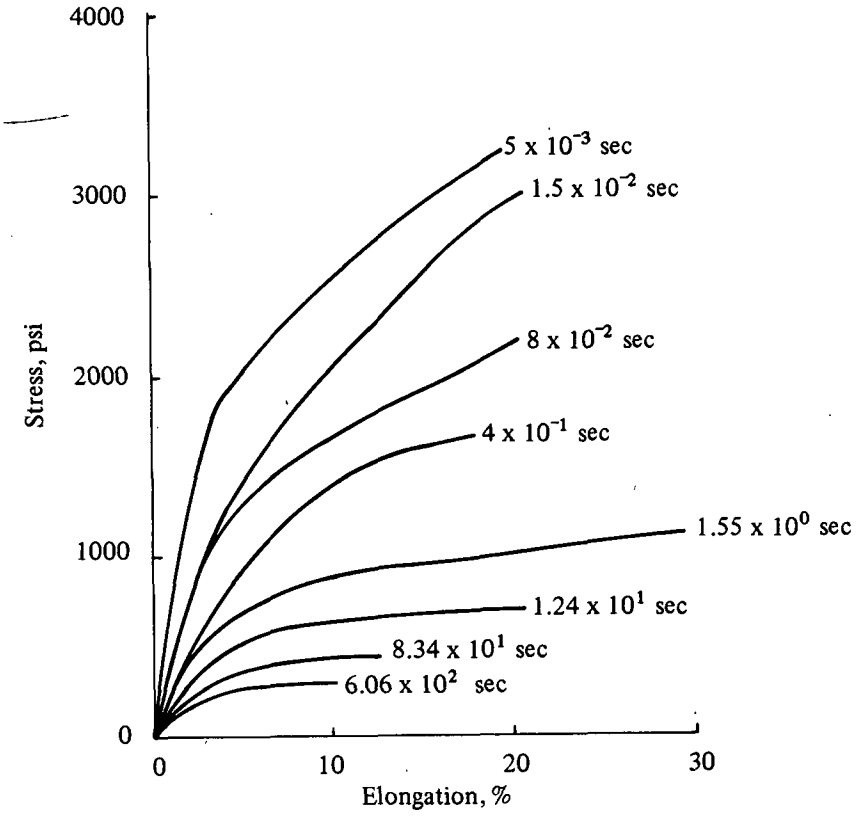


Fig 7 Effect of rate on the stress-strain behavior of X-8 at 25°

Reliable data in the literature for the stress versus strain properties of composite proplnts are exceedingly difficult to find. Since the binder chemical properties and curing additions are susceptible in many cases to hydrolytic degradation, the exact formulations under test should be specified. Additionally, the binder to oxidizer adhesion properties are dependent upon particle size distribution used in the proplnt. This should be specified and in almost all literature sources unearthed, it remained unknown. As some of these data show, the manner of conducting the test and control of such ambient conditions as relative humidity also influences the result. Consequently, the data presented herein should be used only to estimate the effects that certain binder types and sample processing conditions can produce on the me-mechanical properties reported

Some typical stress-strain curves for a carboxy-terminated polybutadiene proplnt (CTPB) containing 86% solids are given in Figure 8, and for a PBAA propellant (see Table 13) containing 83% solids in Figure 9 (Ref 52). The authors concluded that the CTPB proplnts studied were highly susceptible to humidity degradation

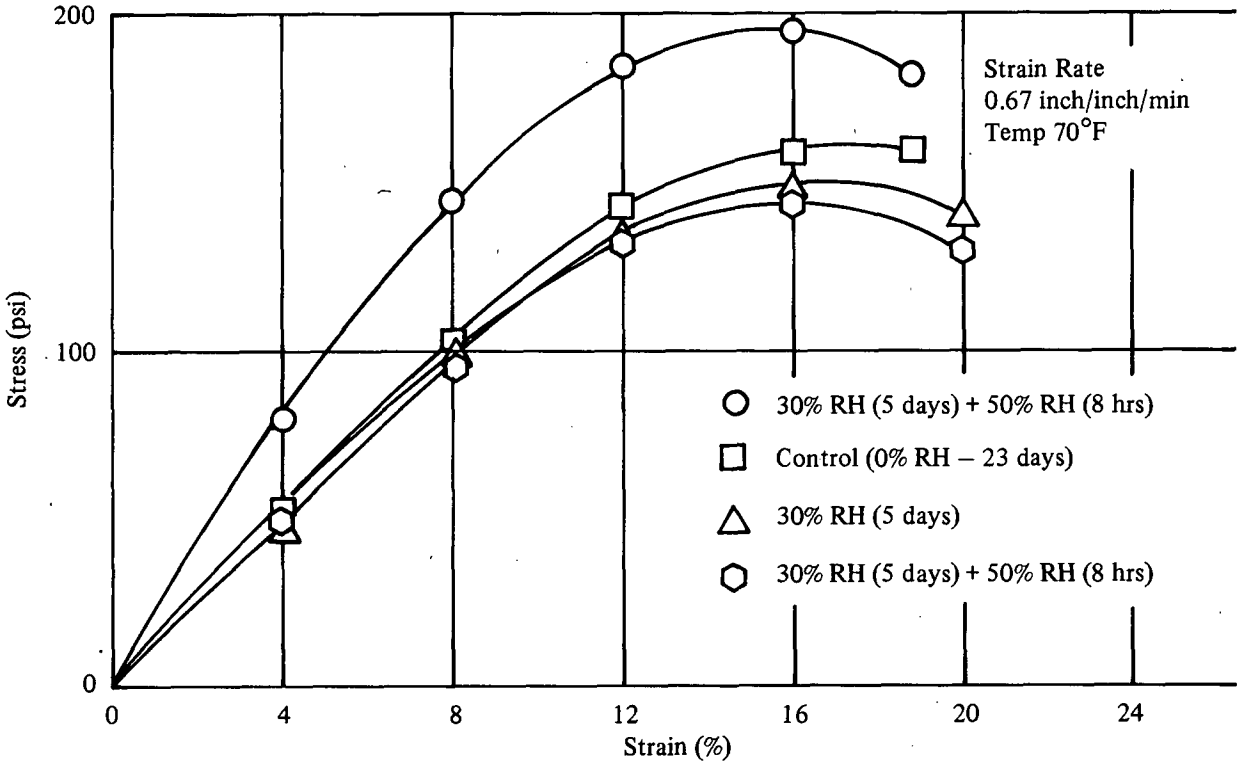


Fig 8 Effect of Storage Condition Upon the Mechanical Properties of CTPB#2 Propellant

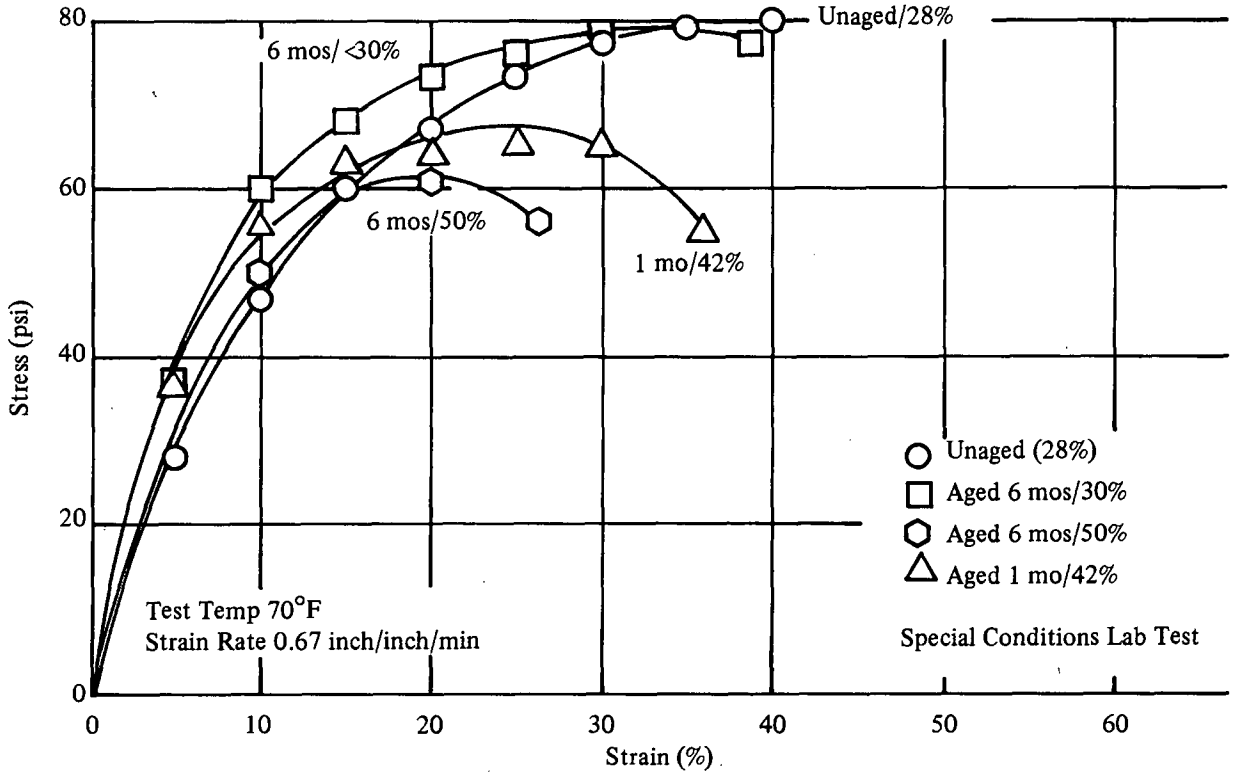


Fig 9 Effect of Aging (70°) and Average Humidity During Processing/Testing Upon the Mechanical Properties of PBAA (83% Solids) Propellant

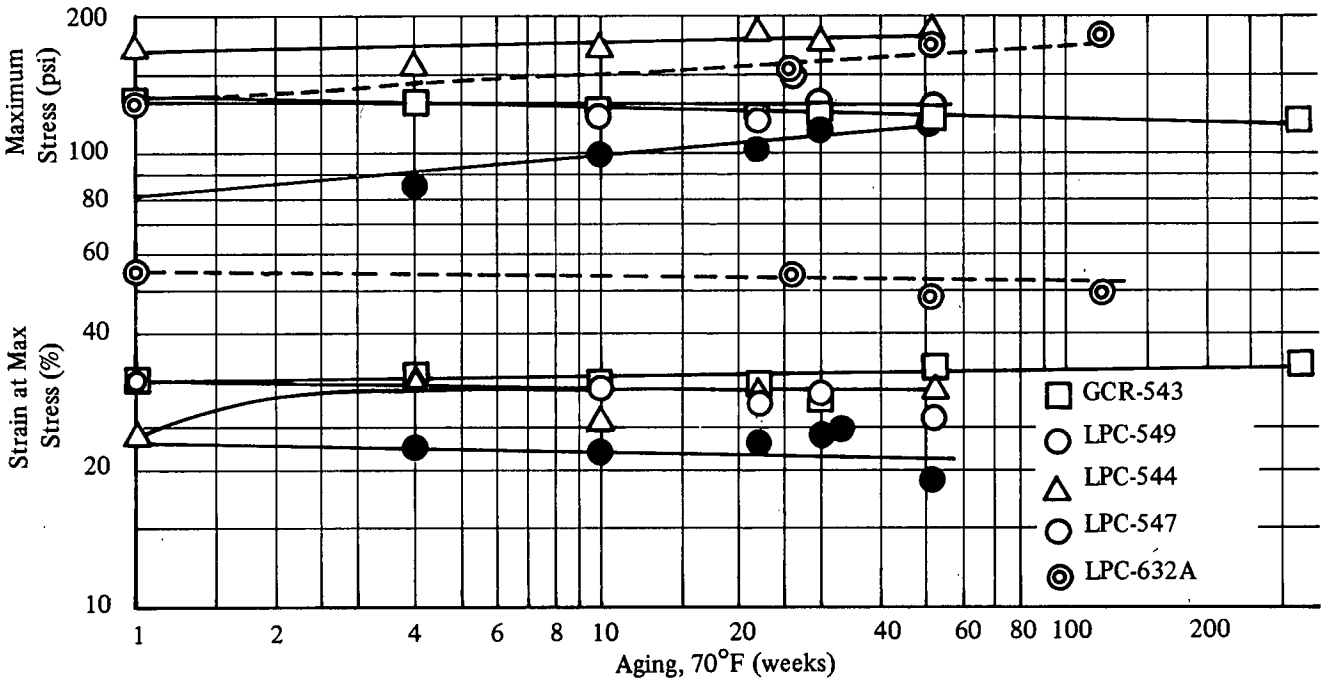


Fig 10 Ambient Temperature Aging of Polybutadiene Propellants

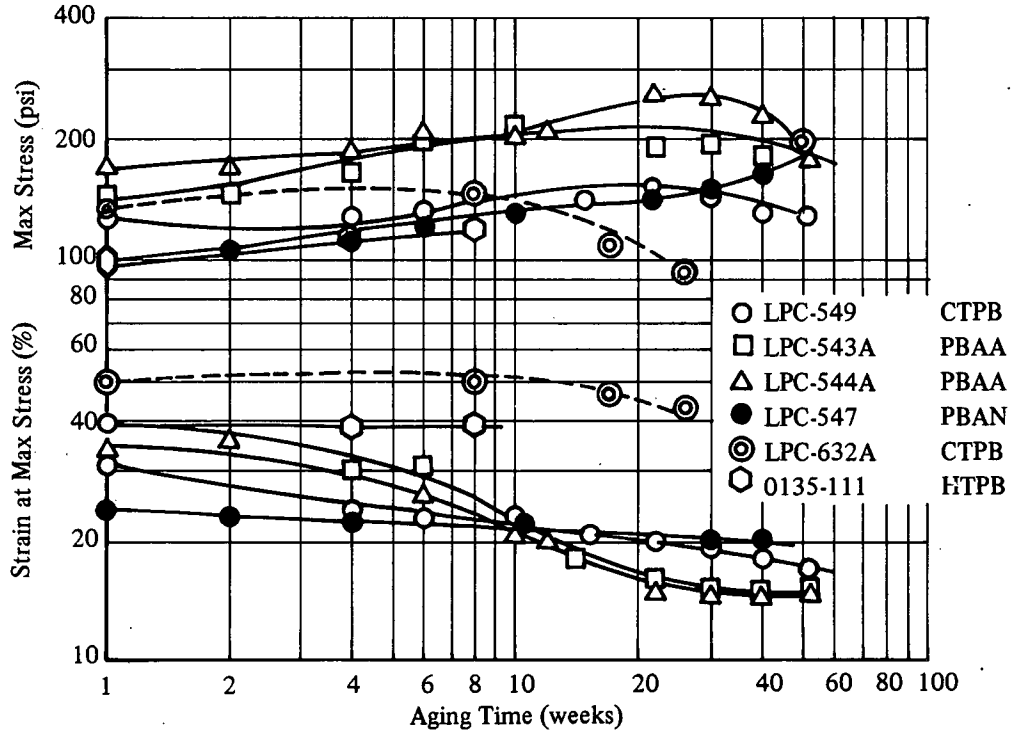


Fig 11 160°F Aging of Polybutadiene Propellants

The influence of ambient aging at 70°F and accelerated aging at 160°F on the stress-strain behavior of carboxy-terminated polybutadiene, polybutadiene-acrylic acid, polybutadiene-acrylic acid-acrylonitrile, and hydroxy-terminated polybutadiene composite proplnts is shown in Figures 10 and 11. The elastomers and curative agents for these formulations are listed below

Formulation	Elastomer	Curative
GCR-543	PBAA	MAPO/PMAPO
LPC-544A*	PBAA	MAPO/PMAPO
LPC-547	PBAN	EPON 828
LPC-549	CTPB	MAPO/PMAPO
LPC-632A	CTPB	HX-868
0135-111	HTPB	TDI

*Contains ferrocene

Whether any of the formulation variables change the mechanical properties significantly upon aging cannot be answered due to the lack of definition of chemical composition parameters as discussed previously

For the reader interested in more elaborate treatments of the influence of mechanical properties upon rocket motor service life, the meeting papers of the Interagency Chemical Rocket Propulsion Group, Mechanical Behavior Working Group, as published by the Chemical Propulsion Information Agency are recommended

Under increasing strain the proplnt volume increases from the voids created around the unbonded solid particles. Nonlinearities in Young's modulus and Poisson's ratio then occur. Francis (Ref 50) shows this effect for a carboxy-terminated polybutadiene composite propellant with 14% binder as in Figure 12. He concludes that nonlinearities in low-temperature properties reduce the predicted stress and strain values upon cooling a solid motor, and therefore a structural analysis that neglects these effects will be conservative. However, when the predictions are extended to a pressurized fiberglas motor case, the nonlinearities in properties produce greater strains than those predicted with linear analysis

Prediction of the service life of the solid proplnt third-stage Minuteman motor has been made by Chappell (Ref 48). This motor has a fiberglas case and a cast double-base grain. The motor parameters on which the structural

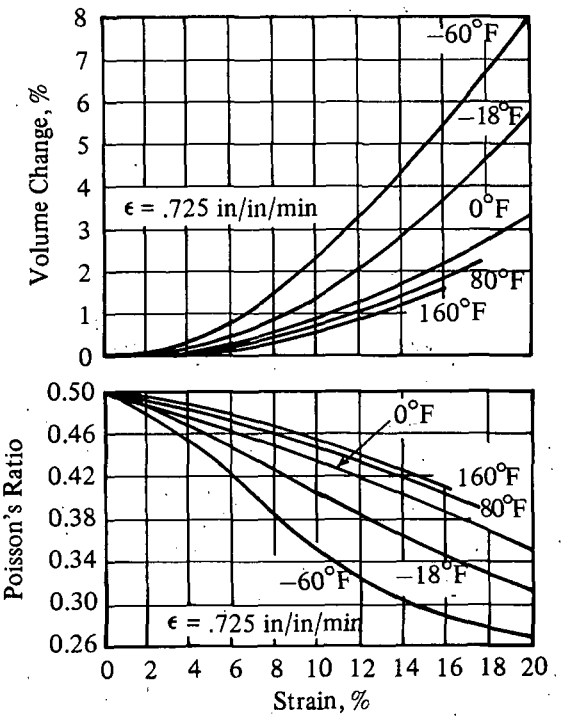


Fig 12 Volume change and Poisson's ratio vs strain for various temperatures

safety margin depends are: (1) motor geometry, (2) case thickness (elastic tensile modulus and Poisson's ratio), (3) proplnt stiffness (tensile relaxation modulus and bulk modulus), (4) proplnt strength (strain at maximum stress versus strain rate), and (5) ignition pressure transient. Both stress relaxation modulus and strain at maximum stress were determined from samples from aged (7 years) operational motors that were sectioned and sampled for that purpose. These data are presented in Figures 13 and 14. The service life (10 years) was estimated by using a cumulative damage approach similar to Mina's rule for fatigue in metals (Ref 37)

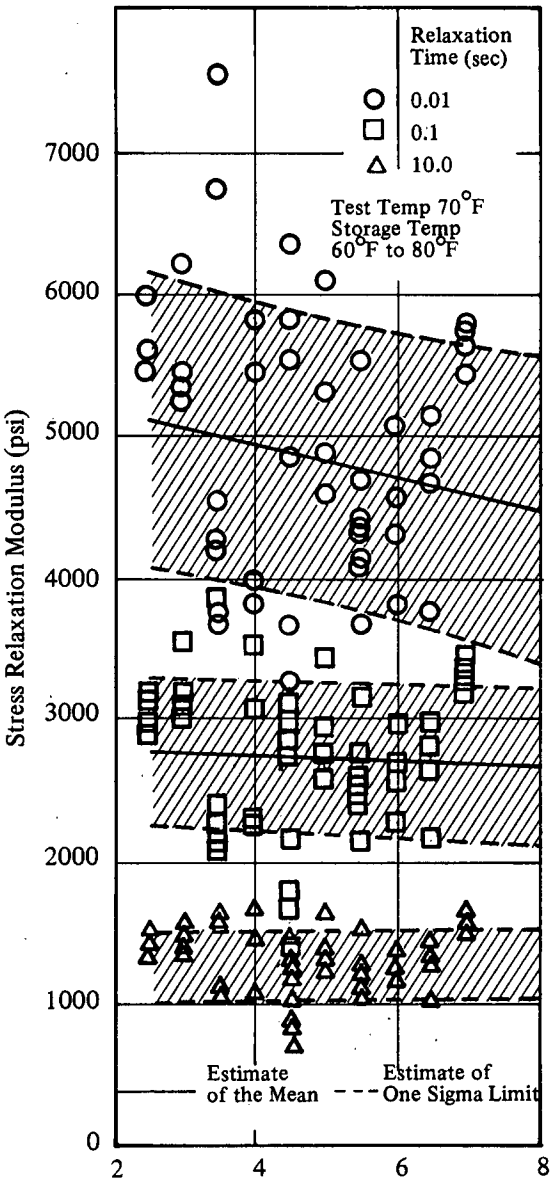


Fig 13 Stress relaxation modulus vs propellant age for times of 0.01, 0.1, and 10 sec

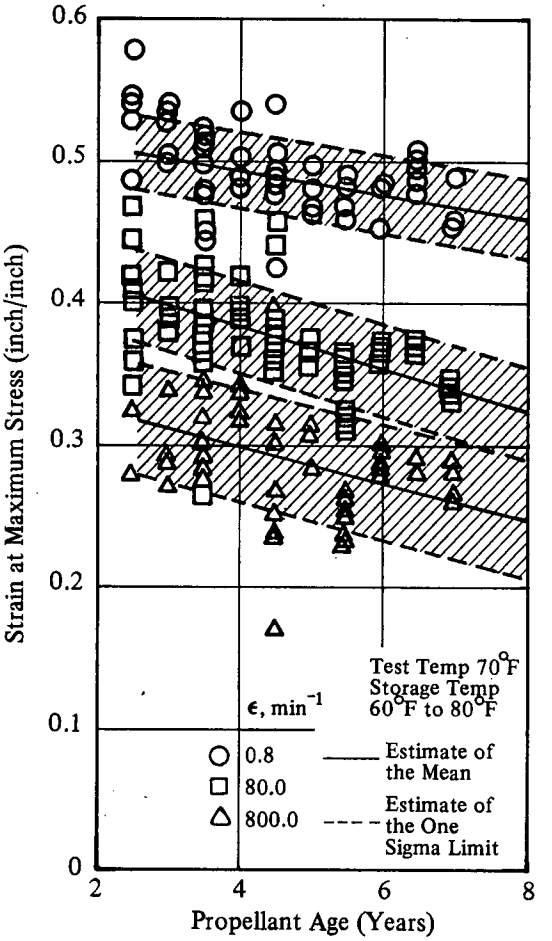


Fig 14 Effect of age on failure strain for various strain rates

B. *Chemical Factors Contributing to Aging*

Many proplnt systems have built-in defects which contribute to degradation of the polymer system and reduce service life. The polyurethane binder systems react adversely to water. As a result, the ingredients must be dried thoroughly before processing. The following reaction illustrates the sequence that occurs between a monofunctional isocyanate and water:

$$R{-}N{=}C{=}O + HOH \rightarrow RNH{-}\underset{\underset{O}{\|}}{C}{-}OH$$

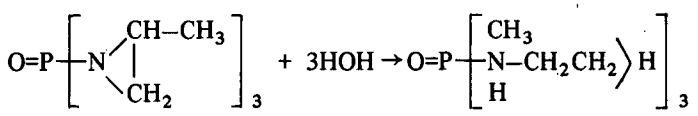
$$RNH{-}\underset{\underset{O}{\|}}{C}{-}OH \rightarrow RNH_2 + CO_2$$

$$RNH_2 + R{-}N{=}C{=}O \rightarrow R{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}R$$

In this way one mole of water reacts with two moles of isocyanate. For a urethane prepolymer with an equivalent weight of about 300, it only takes 9 grams of water to effectively consume the prepolymer. This can lead not only to degraded physical properties, but it also forms gas bubbles in the proplnt which lead to voids and higher than predicted burning rates. This sensitivity to water content also exists with hydroxy-terminated polybutadiene polymers cured with

isocyanates. In contrast, carboxy-terminated polybutadiene polymers are relatively insensitive to water content when cured with epoxies

Some binder systems have used MAPO as the only curing system for carboxy-terminated polybutadiene polymers. Again a problem in long term stability of physical properties is sometimes encountered since MAPO is hydrolytically unstable. The following reaction is possible:



and a slow degradation of physical properties with time may occur. Again, drying of all propInt ingredients is of importance

The composite propInts are not the only ones subject to degradation processes which affect shelf-life, although they are relative newcomers to propInt history. In NC-based propInts, NC decomposes slowly to release NO_2 which reacts catalytically to hasten the degradation in physical and ballistic properties. To slow the process, stabilizing agents such as diphenylamine or 2-nitrodiphenylamine are added to react with the NO_2. The first reaction product is diphenylnitrosoamine, followed by ring nitration. When the stabilizer is used up, for all purposes the shelf-life of the propInt is ended

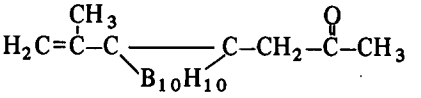
VI. Chemical Characteristics and Performance

A. *Burning Rate*

For the conventional treatment of both double-base and composite propInt burning rates, the reader is referred to Refs 22, 33 & 51. This article will review recent papers and patent literature which disclose new advances in the state-of-the-art. In the past, the burning rates of double-base propInts have been modified by using such lead salts as lead salicylate, lead acetylsalicylate, lead azide, lead stearate, lead oxide, lead 2-ethyl hexoate, and others. There are several objectives in using these salts. One is to produce a plateau or mesa effect where the burning rate of the plateau propellant remains relatively constant over a stated pressure range and the burning rate of the mesa propellant decreases with pressure over stated ranges. Lantz (Ref 81) recently found that thorium salts such as the malonate, malate, tartrate, cyclopentane carboxylate, stearate, salicylate, resorcylate, succinate, pimelate, adipate, and mixts thereof impart mesa and plateau characteristics in double-base propInts. Examples of propInt compns employing this ballistic modifier are shown in Table 26, and representative burning rate curves from $-40°$ to $160°F$ are shown in Figure 15

Although the specific impulse of double-base propInts can be substantially increased by incorporating aluminum and AP in conventional formulations, they become highly temp sensitive with relatively high pressure exponents (n). PropInts with exponents much above 0.5 are subject to undesirably high fluctuations in performance induced by small changes in combustion pressure. Shaver (Ref 64) found that decreases in temp sensitivity and pressure exponents of such formulations can be achieved by using fine particle aluminum along with variations in the particle size of the AP used. It was also found that an organic lead salt could be used with these formulations to increase the burning rate, a catalytic phenomenon not encountered with the conventional aluminized double-base propInt. The effects of the stated compositional changes on temp and pressure sensitivites are shown in Tables 27 and 28

Recent technology advances in both offensive and defensive missiles have generated a requirement for high burning rate propInts to achieve high acceleration rates and reduced time to target. In double-base propInts, high burning rates have been achieved with derivatives of carborane and biradical burning rate catalysts. Hill (Ref 68) described the use of 1,1-isopropenyl-1,2-prop-(2-one)-yl-carborane (IPCA),



in aluminized double-base formulations plasticized with TEGDN. His data in Table 29 compare burning rates for 12% IPCA to a control without this ballistic modifier. Most carborane derivatives are not compatible with NC; so this compound is an exception. Further increases in burning rate may be achieved by using ultrafine AP. The rate at 2000psi for the composition containing IPCA shown in Table 29 is increased to 6.5 inches/sec by substituting 2.5 micron particle size AP for the 8 and 15 micron blend shown

Table 26
Additional Examples

Example No	2	3	4	5	6	7	8
	Composition is expressed in % by weight						
Nitrocellulose (12.6% N)	40.0	44.5	53.2	58.0	50.8	59.6	50.0
Nitroglycerine	20.6	14.7	26.9	27.0	19.2	10.7	22.6
Crystalline	HMX	RDX	HMX	HMX	HMX		RDX
Filler	9.4	7.1	4.3	5.2	5.0	–	5.2
Plasticizers	triacetin	diethylene-glycol dinitrate	trimethylol-ethane trinitrate	triacetin	triacetin	diethylene-glycol dinitrate	triacetin
	15.0	13.6	4.1	9.8	9.8	10.7	18.0
	sucrose octaacetate	diethyl-phthalate	dioctyl-phthalate	sucrose octaacetate	sucrose octaacetate	triacetin	
	10.0	14.8	6.7	10.2	10.2	12.0	
Stabilizer	ethyl centralite	ethyl centralite	ethyl centralite	ethyl centralite	ethyl centralite	2-nitro diphenylamine	diphenyl-amine
	1.0	1.0	1.0	1.0	1.0	2.0	1.0
	N-methyl p-nitroaniline	N-methyl p-nitroaniline	N-methyl p-nitroaniline	N-methyl p-nitroaniline	N-methyl p-nitroaniline	–	–
	1.0	1.0	1.0	1.0	1.0	–	–
Thorium containing	malonate	malate	tartrate	salicylate	succinate	adipate	cyclopentane carboxylate
Ballistic Modifier	3.0	3.3	2.8	3.0	3.0	3.0	3.2
Carbon Black (added)	0.02	0.03	0.03	0.04	0.03	0.03	0.03

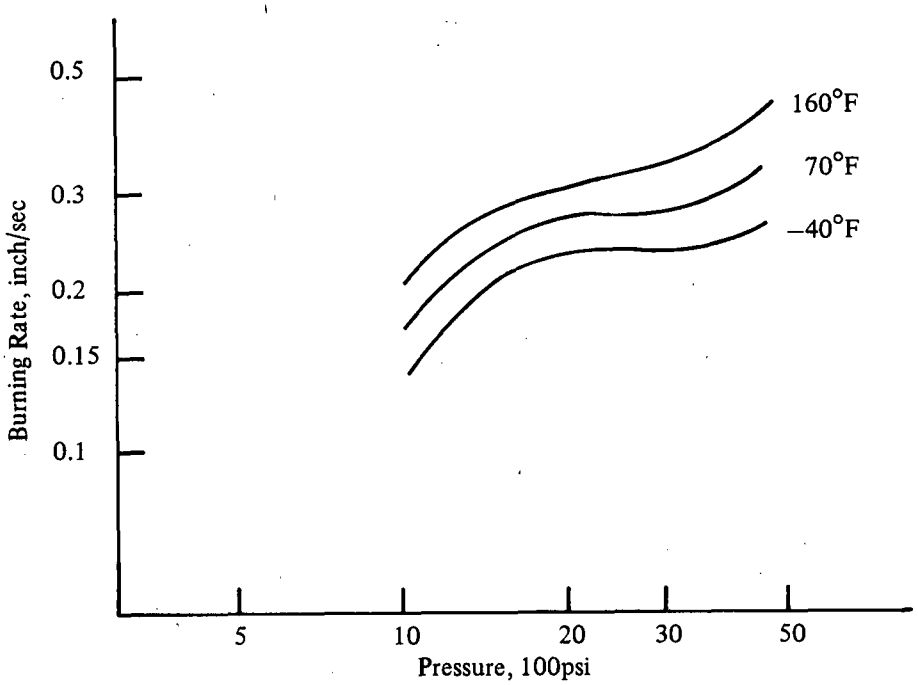
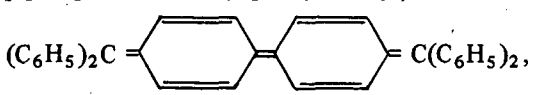
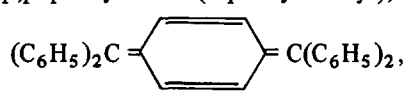


Fig 15

Sales (Ref 80) used the biradical compounds, p,p′-biphenylene-bis(diphenylmethyl),



and p,p′-phenylene-bis(diphenylmethyl),



as high burning rate catalysts for crosslinkable double-base proplnts. The burning rates of proplnt compns with this biradical catalyst are compared in Table 30 to a conventional double-base with lead peroxide as a burning rate catalyst. Not only do these compds promote burning rates, but they also function as inhibitors for resonance burning and combustion instability. It is not known whether these will function as catalysts for aluminized double-base formulations as most of the lead salts do not when aluminum is introduced

In contrast to the difficult problem of accelerating the burning rates of double-base proplnts, the options open to the composite proplnt formulator are many. These may be grouped under the categories of carborane derivatives, carborane plus NF derivatives, metal staples, fine particle ammonium perchlorate, ferrocene derivatives, free radical and biradical compds. As demands for higher burning rates are pressed, it should be remembered that at the higher burning rates the combustion control problems and rocket motor design problems become greater. The transition point between deflagration and detonation becomes more blurred. There is also a decided trend to inherit physical and chemical stability problems along with the enhanced burning rates

The burning rates of standard aluminized hydrocarbon binder composite proplnts may be increased significantly not only with ferrocene derivatives but also with compatible carborane-type burning rate additives. However, most ferrocene derivatives are volatile solids or liquids which have a tendency to evaporate from the proplnt during storage, thereby degrading ballistic performance. Rudy (Ref 71) minimized this problem by the use of polynuclear ferrocene

Table 27

Formulation	BR in/sec at 70°F	n[1]	σ_p[3] %/°F	π_{k_n}[2] %/°F
A	0.44	0.62	0.21	0.56
B	0.32	0.64	0.19	0.53
C	0.46	0.47	0.13	0.25
D	0.38	0.48	0.10	0.19

[1] The value of the pressure exponent was the same at each of the three test temps, −20°F, 70°F and 165°F

[2] $\pi_{k_n} = \sigma_p/(1-n)$

[3] Temp coefficient of burning rate at constant pressure, $\sigma_p = (\partial \ln BR/\partial T)_p$

Sample A	Particle Size	Parts by Weight
NH_4ClO_4	$D_{\overline{w}}$ 25 microns	13.39
	$D_{\overline{w}}$ 200 microns	13.39
Al	$D_{\overline{w}}$ 18 microns	23.22
Sample B		
NH_4ClO_4	$D_{\overline{w}}$ 200 microns	26.78
Al	$D_{\overline{w}}$ 18 microns	23.22
Sample C		
NH_4ClO_4	D_w 200 microns	26.78
Al	D_w 1 micron	23.22
Sample D		
NH_4ClO_4	$D_{\overline{w}}$ 200 microns	26.78
Al	$D_{\overline{w}}$ 300 A	10.00
	$D_{\overline{w}}$ 18 microns	13.22

Ingredient	Parts by Weight
NC, $D_{\overline{w}}$ 15 microns	21.50
2-Nitrodiphenylamine (2NDPA - stabilizer)	1.00
NG/dibutyl phthalate, 3:1	25.02
Dibutyl sebacate	2.48
Ammonium perchlorate	26.78
Aluminum	23.22

Table 28

Formulation	BR in/sec at 70°F	n	σ_p %/°F	π_{k_n} %/°F
E	0.43	0.52	0.21	0.44
F	0.52	0.37	0.13	0.21
G	0.46	0.43		

Propellant grains were prepared according to the oxidizer grind of Example 1, as follows:

Sample E

Same as Sample A, Example 1, plus 2.00 parts by weight of lead salicylate

Sample F

Same as Sample C, Example 1, plus 2.00 parts by weight of lead salicylate

Sample G

Same as Sample D, Example 1, plus 2.00 parts by weight of lead salicylate

Table 29
Burning Rates of Double-base Propellants (IPCA Modifier)

	Control, percent	IPCA, percent
Component:		
Nitrocellulose	12.0	12.0
TEGDN	35.0	20.0
Aluminum	2.0	2.0
Ammonium perchlorate:		
8 micron	40.0	40.0
15 micron	8.0	8.0
Adiponitrile		3.0
IPCA		12.0
Resorcinol	1.0	1.0
Burning rate (inches/sec)		
2,000psi	2.00	4.00
1,000psi	1.30	2.50
500psi	0.83	1.60

Table 30
A Comparison of Crosslinkable Double-Base Propellants With and Without Burning Rate Catalyst

Ingredients/Burning Rate	Propellant Compositions Percent by Weight and Burning Rates		
	A	B	C
Casting Powder* (binder)	11.25	11.25	11.25
Triethylene Glycol Dinitrate (TEGDN)	28.75	28.75	28.75
Butanetriol Trinitrate (BTTN)	15.5	15.5	15.5
Cyclotetramethylenetetranitramine (HMX)	40.0	40.0	36.0
Lead Peroxide	4.0	–	4.0
p,p′-Biphenylene-bis(diphenylmethyl)	–	4.0	4.0
Resorcinol	0.5	0.5	0.5
Toluene Diisocyanate (added)	1.0	1.0	1.0
Burning Rate (ips at 1000psi)	0.35	0.72	0.85

*Casting powder formulation:		
	10.1	parts nitrocellulose
	.95	parts nitroglycerine
	.20	parts 2-nitrodiphenylamine
TOTAL	11.25	parts Casting powder

derivatives which have low vapor pressures and do not tend to evaporate or migrate from the proplnt. The compds are prepd by reacting a hydrocarbyl-substituted ferrocene such as n-butyl ferrocene with an aliphatic aldehyde such as methylal in diethyl ether. The following general structural formula appears to represent the products which are mixts of compds of varying molecular weight and isomerism:

$$(RR'R''C_{10}H_6Fe)\text{–}\overset{R'''}{\underset{|}{C}}H$$

$$\left[(RR'R''C_{10}H_5Fe)\text{–}\overset{R'''}{\underset{|}{C}}H\right]_{\rho}(RR'R''C_{10}H_6Fe)$$

The crude product from the above reaction mixt was fractionated into a distilled product (bp 200°/0.3 Torr) with an average molecular weight of 514 and a residue with an average molecular weight of 940. These were evaluated as catalysts and compared to prior art ferrocenes in a standard carboxy-terminated polybutadiene formula cured with MAPO. The results are shown in Table 31

Table 31

Ingredient	Concentration % Weight
Carboxy-terminated polybutadiene Thiokol HC-434	11.35
Tris[1-(2-methyl) aziridinyl] phosphine oxide (MAPO)	0.65
Dioctyl adipate + combustion catalyst	5.00
Ammonium perchlorate	83.00

Catalyst		Burning Rate in/sec
Type	Concn, %w	at 1000psia
None	–	0.36
Crude	1.0	0.75
Distillate	1.0	0.68
Distillate	3.0	0.96
Residue	1.0	0.77
Residue	3.0	0.90
Ferrocene	1.0	0.62
Ferrocene	3.0	0.82
n-Butylferrocene	1.0	0.68
n-Butylferrocene	3.0	0.82
Dimethylferrocene	1.0	0.56
Dimethylferrocene	3.0	0.86

Table 32

	Composition		
	A	B	C
Ingredient, wt percent:			
Ammonium perchlorate	68.0	68.0	68.0
Aluminum	14.0	14.0	14.0
Carboxyl-terminated polybutadiene prepolymer	10.5	10.5	10.5
n-Butylferrocene	7.0	7.0	3.5
Tris(methylaziridinyl)-phosphine oxide	0.2	0.2	0.2
Tris(oxiranyl)-para-aminophenol	0.2		
Iron linoleate	0.05	0.05	0.05
Lecithin	0.05	0.05	0.05
1,2,bis(2,3-epoxypropyl) carborane		0.2	0.2
1-(2,3-epoxypropyl) carborane			3.5
Burning rate (1000psi) inches/sec	1.2	1.6	1.9

Table 33

	Per Cent by weight		
Composition	A	B	C
Butarez CTL (Carboxy-terminated polybutadiene polymer)	8.28	8.28	8.28
MAPO[1]	0.31	0.31	0.31
IDP[2]	5.41	5.41	5.41
Ammonium perchlorate	64.00	64.00	64.00
Copper Chromite	1.00	1.00	1.00
Aluminum powder	21.00	19.00	17.00
Aluminum staple[3]	–	2.00	4.00
Burning rate (1000psi, 70°F)	.53	.71	1.00
Specific impulse (lb-sec/lb)	232.30	229.20	233.40

[1] tris[1-(2-methyl) aziridinyl] phosphine oxide
[2] isodecylpelargonate
[3] size of staple .125″ x .0025″ x .0005″

Sayles (Ref 67) combined n-butylferrocene with 1-(2,3-epoxyaliphatic) carboranes of at least 3 carbonations in the aliphatic chain to function both as burning rate catalysts and cross-linking agents for carboxylated polybutadiene and acrylate binders. The use of 1,2-bis(2,3-epoxypropyl) carborane and 1-(2,3-epoxypropyl) carborane boosted the burning rate of a butylferrocene proplnt from 1.2 to 1.9 inches/sec as the data in Table 32 indicates

The use of ultra-fine AP to increase the burning rates of double-base proplnts has been described previously. This technology has also been used with hydrocarbon binders, but dispersion and high viscosity have presented mixing problems. Fine AP can be conveniently dispersed by slurrying first with a surfactant and an organic liq such as 1,1,2-trichloro-1,2,2-trifluoroethane or normal hexane in a process described by Alley (Ref 58a). Sodium sulfonate

Table 34
A Comparison of a Carboxyl-Terminated Polybutadiene-Based Propellant (CTPB) Using N-Butylferrocene as Burning Rate Catalyst With a CTPB–Based Propellant Using Biradical Burning Rate Catalyst

Propellant Ingredients/Burning Rate	Propellant Percent by Weight/Burning Rate	
	Composition A	Composition B
Ammonium Perchlorate	66	66
Aluminum	14	14
Normal-Butylferrocene	7	–
p,p′-Biphenylene-bis(diphenylmethyl)	–	7
Carboxyl-terminated Polybutadiene Prepolymer	12.5	12.5
Tris[1-(2-methyl)aziridinyl] phosphine oxide	0.5	0.5
Tris(oxiranyl)-para-aminophenol (added)	0.1	0.1
Iron Linoleate (added)	0.1	0.1
Burning Rate (ips at 1000psi)	1.8	2.4

Table 35

Burning Rate Data on Butadiene-CMA Copolymers in Propellant Formulations

Copolymer No	Boron Content (% of propellant)	Burning Rate (in/sec) 800–824psi	1600–1615psi
Standard	0	0.501	0.797
6	0.20	0.529	0.816
7	0.42	0.542	0.858
8	0.78	0.558	0.910
9	0.81	0.660	1.033

Butadiene/CMA copolymer binder – 10.0 wt %
Isodecyl Pelargonate plasticizer – 10.0
Aluminum Powder – 10.0
Ammonium Perchlorate (56μ) – 70.0

Physical Property Data on Butadiene-CMA Copolymers

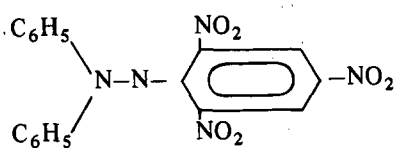
No	Molecular Weight	Weight % OH Calc'd*/Found		% B in Polymer Calc'd**/Found	
6	3200	1.06	1.36	2.32	2.00
7	3300	1.03	1.31	4.69	4.20
8	3600	0.94	1.0	4.02	7.8
9	2600	1.31	1.04	10.07	8.1

* Calculated OH content is based on observed molecular weight, with the assumption that each molecule contains two hydroxyl groups
** Based on monomer charge

in mineral oil was found to be a satisfactory surfactant at the 0.1 to 0.5 weight percent level. After the AP is dispersed, the binder is mixed in and the organic liq removed by evaporation

The burning rates of carboxy-terminated polybutadiene composite proplnts have been approximately doubled by using metal staples made from aluminum and other metals such as silver or copper according to Madden (Ref 83) and Lawrence (Ref 66). Data for a carboxy-terminated polybutadiene are given in Table 33 (Ref 83). The embedded staples are effective regardless of the specific compn of the proplnt, although the actual increase in ballistic performance and burning rate will vary to some extent according to the specific proplnt compn. Increased staple content along with burning rate catalysts have given burning rates at 1000psi up to 3.9 inches/sec (Ref 66)

The biradical catalysts described previously for double-base proplnts (Ref 80) are also effective for hydrocarbon proplnts. Table 34 shows how p,p'-biphenylene-bis(diphenylmethyl) compares to n-butyl ferrocene as a catalyst in a carboxy-terminated polybutadiene. These catalysts are claimed to overcome all of the processing difficulties, chemical stability and volatility disadvantages attributed to catalysts based on ferrocene and carborane derivatives. Another somewhat similar functioning catalyst, the free radical compd, 2,2-diphenylpicrylhydrazyl,



is far less effective as a burning rate catalyst (Ref 54)

Another approach to high burning rate proplnts has been to incorporate an energetic compd based on a carborane derivative into the polymer. Both copolymers and terpolymers have been prepared based upon carboranylmethacrylate (CMA). Typically, butadiene is reacted with carboranylmethacrylate to give a copolymer with a molecular weight of 3500, a hydroxy end group content of 0.6 and boron equal to 13.5 weight percent. Baldwin (Ref 65) formulated the polymers described in Table 35 into composite proplnts which gave a 30% increase in burning rate over the standard proplnt without the copolymer

Baldwin (Ref 65) also synthesized a copolymer from acrylic acid and carboranylmethyl acrylate which was used to make the proplnts in Table 36. Composition A has the burning rates shown in the table for the AP particle sizes indicated. Composition B had an average AP particle size of 15 microns and a burning

Table 36
Particle Size of Ammonium Perchlorate and Burning Rate at 2000psi

Particle Size (Normal)	Burning Rate, in/sec
75 micron	2.0
45 micron	2.2
35 micron	2.4
15 micron	3.0
5 micron	3.6

Composition A

Component	Wt %
Ammonium Perchlorate	55.0
Aluminum (powder)	5.0
Carboranylmethyl acrylate/ Acrylic Acid (95/5) prepolymer	22.06
Triethyleneglycol dinitrate	14.70
Dicyclo diepoxy carboxylate (UNOX 221)	3.09
Ferric acetylacetonate (curing agent, catalyst)	0.15

Composition B

Component	Wt %
Ammonium Perchlorate (5 μ)	42.0
Ammonium Perchlorate (45 μ)	14.0
Aluminum (powder)	5.0
Carboranylmethyl acrylate/ Acrylic acid (95/5) prepolymer	16.3
Triethyleneglycol dinitrate	10.8
Butanetriol trinitrate* (contains in addition 2 parts of dicyclo diepoxy carboxylate per 100 parts of proplnt)	10.9

*Also known as 1,2,4-trinitrobutane

Dicyclo diepoxy carboxylate is a curing agent. A dicyclo diepoxy carboxylate curing agent is sold under Union Carbide Corporation's trademark UNOX 221

rate of 3.65 inches/sec at 2000psi. No data were given for the pressure exponents which in many carborane derivative proplnts are well above 0.5

Terpolymers of butadiene, carboranylmethacrylate (CMA) and acrylic acid have been used to formulate proplnts with high burning rates by Huskins (Ref 78). The compns of these proplnts are given in Table 37. Burning rates at 1000psi ranged from 0.25 inch/sec for the standard, to 0.4 inch/sec for 25% CMA in the terpolymer and to 3.5 inches/sec for 75% CMA in the terpolymer. It was found that burning rate was proportional to CMA content. These terpolymers were also combined with polybutadiene-acrylic acid copolymer and carboxy-terminated polybutadiene polymers with similar increases in burning rates

A final class of high burning rate proplnts combines the high density and high impulse difluoramino compds in their binders with the carborane derivatives. Jones (Ref 79) described the preparation of TVOPA (1,2,3-tris[1,2-bis-(difluoramino)ethoxy] propane, IPCA (1-iso-propenyl-carboranyl-acetone) and NFPA (2,3-bis(difluoramino) propyl acrylate) and proplnts

Table 37

Compn	Ingredients	Percent by Weight
A	Terpolymer (25% CMA)	19.7
	AP	64.0
	Aluminum powder fuel	16.0
	Lecithin	0.3
		100.0
B	Terpolymer (50% CMA)	19.7
	AP	64.0
	Aluminum powder fuel	16.0
	Lecithin	0.3
		100.0
C	Terpolymer (75% CMA)	19.7
	AP	64.0
	Aluminum powder fuel	16.0
	Lecithin	0.3
		100.0
D (standard)	Carboxy-terminated poly-butadiene	19.7
	AP	64.0
	Aluminum powder fuel	16.0
	Lecithin	0.3
		100.0

Table 38
Burning Rates, Densities, and Specific Impulses for Ethyl Acrylate Propellants Containing TVOPA Modifier

Component	Control Propellant Composition F	Modified Propellants Composition G	Composition H
EA	2.67	2.67	3.4
AA	0.20	0.20	0.2
TVOPA	None	4.89	18.3
IPCA	21.48	16.59	3.1
AP (8 micron)	75.65	75.65	70.0
Al	—	—	5.0
Additive: UNOX 221 (dicyclo diepoxy carboxylate curing agent)	0.5	0.5	0.5
Density (lbm/in^3)	0.0594	0.0607	0.0653
I°sps (lbf-sec/lbm) [a]	256.9	254.0	263.7
Burning Rate (in/sec)			
20,000psia	24.2	23.2	
15,000psia	20.0	18.9	
10,000psia	14.9	13.8	13.0
8,000psia	12.8	11.5	11.3

[a] Calculated impulse, 1000psia chamber pressure, standard condition

Table 39
Burning Rates, Densities, and Specific Impulse for NF Propellant Containing CMA Modifier

Component	Control Propellant Composition A	Modified Propellant Composition B
NFPA	12.5	9.2
CMA	None	3.3
AA	0.5	0.5
TVOPA	26.0	26.0
AP	46.0	46.0
Al	15.0	15.0
Additive: UNOX 221 (dicyclodiepoxy carboxylate curing agent)	1.5	1.5
Density (lb/in^3)	0.0662	0.0652
I_{sps} (lb/sec/lbm) [a]	268.8	266.0
Burning Rate (in/sec)		55 micron oxidizer
20,000psia	12.8	21.0
15,000psia	10.0	16.2
10,000psia	7.0	11.1
5,000psia	3.8	5.9
Burning Rate (in/sec)		8 micron oxidizer
20,000psia	14.2	28.5
15,000psia	11.5	19.9
10,000psia	8.5	14.2
5,000psia	5.0	9.2

[a] Calculated impulse, 1000psia chamber pressure, standard conditions

containing these ingredients. His data for typical formulations are given in Tables 38 and 39. EA refers to ethyl acrylate and AA to acrylic acid. There are a number of problems with such proplnts. The pressure exponent, n, of 0.88 signifies extreme problems in achieving stable burning in practical rocket motors. Other disadvantages include marginal safety characteristics of sensitivity to shock, chemical stability in contact with AP, and the high cost of raw materials

B. *Ignition theories*

Price (Ref 39) compares the three principal quantitative models of ignition and concludes that there are serious deficiencies in the existing models, so much so that no one theory appears adequate to represent the complexity of ignition of composite solid proplnts. In the gas-phase model (Refs 22 & 36) the hot oxidizing environmental gas and fuel vapors from the proplnt mix and react to provide a self-sustaining heat source. The heterogeneous ignition theory (Ref 30) assumes that the sole source of heat is a heterogeneous surface reaction between powerful oxidizing gases given off by the decompn of AP and fuel binder constituents. The hypergolic ignition theory (Refs 26 & 29) evolved from the study of the ignitability of binders and proplnts by ClF_3 and F_2. In the limiting case where the solid oxidizer is the sole source of oxidizing species, the theory becomes the same as the heterogeneous ignition theory. The ignition theories for NC base proplnts differ from composite proplnts because of the inclusion of oxygen in the reactive sequences envisioned. Summerfield proposes a gas-phase ignition mechanism for double-base proplnts with the oxygen content of the igniting gas having an active role in ignition (Ref 25). The importance

of runaway reactions in the solid phase has also been emphasized (Ref 56). Hicks (Ref 18) proposed the solid phase thermal theory of ignition which led to a transient surface heating analysis with exothermic chemical heating in the solid with an exponential dependency of rate on temp. This model was compatible with the known exothermic decompn of proplnts of the NC-NG type. Upon introduction of composite proplnts, the need for a different mechanism became apparent

The varied and conflicting ignition theories can be reconciled if one appreciates the fact that more than one possible mechanism of ignition probably exists and the varying experiments designed to prove the theories accentuate the particular mechanism discussed. Generally the experimentalists have developed data which strongly supports the heterogeneous ignition theory for composites containing AP. The initial low-temp step is the proton transfer which results in the formation of absorbed NH_3 and $HClO_4$. Further decompn of $HClO_4$ yields ClO_3 and ClO_4 followed by the rapid decompn of the unstable chlorine oxides to yield O atoms and ClO radicals, which oxidize NH_3 and react heterogeneously with solid fuel. The experiments of Fishman (Ref 46) disclosed a surface exotherm preceding ignition at high heat fluxes which is clearly associated with surface reactions, the heterogeneous decompn of $HClO_4$ and subsequent oxidation of the fuel. In support of this theory, the experiments of Pearson (Refs 38 & 44) showed that ignition occurred when either oxygen at about 400° or perchloric acid at 200–300° contacted solid proplnt fuels. With NH_3, ignition was achieved only on copper chromate catalyst via a heterogeneous reaction

C. *Specific Impulse*

As developed from the equation for conservation of momentum (Ref 27), the thrust, F, on a rocket motor is

$$F = (\tfrac{1}{2}+\tfrac{1}{2}\cos\alpha)\,(\dot{w}V_e/g) + (P_e - P_o)A_e$$

where α = half of the divergence angle of the nozzle, $\dot{w}$ = weight rate of proplnt flow, g = acceleration of gravity, V_e = exit flow velocity, P_e = nozzle exit pressure, P_o = external atm pressure, and A_e = cross section at nozzle exit plane. An effective exhaust velocity is defined by

$$C = (\tfrac{1}{2}+\tfrac{1}{2}\cos\alpha)V_e + \frac{(P_e - P_o)A_e}{\dot{w}/g}$$

and the thrust becomes,

$$F = \dot{w}C/g$$

Maximum thrust is attained when $P_e = P_o$ and α is made small, then

$$C = V_e \quad \text{and} \quad F = \dot{w}C/g = \dot{w}V_e/g$$

The specific impulse is the thrust per unit weight rate of flow and so,

$$I_{sp} = F / \dot{w} = C/g$$

Experimentally thrust is measured by standard procedures (Ref 53) which put rigid specifications on motor sizes, test equipment and data reduction. Prior to obtaining exptl proof of performance by expensive test procedures, most prudent investigators will make theoretical calcns of the specific impulse as a measure of proplnt performance since this parameter is basically a property of proplnt compn. A theoretical value for I_{sp} is calcd by consideration of the thermochemistry of the chemical reaction in the rocket combustion chamber and in the expansion process. The basic development of the mathematical equations used in this type of calcn is given in Ref 27. The calcn is sufficiently complicated in the case of multi-component systems so that the use of digital computers is required to reduce the time required for the estimation. Such programs and services are available to government agencies and contractors for nominal fees (Refs 49 & 60). Tables 40–48 list physical and thermochemical properties required for performance calcns for the most common fuels and oxidizers used in solid proplnts (Ref 43)

The influence of $\{CH_2\}_X$ binder content on the theoretical specific impulse of AP composite containing 8, 12 and 16% aluminum reaches a max at binder contents between 10 and 15% as shown in Fig 16, while the max level of acceptable physical properties occurs at the 10–16% level. Most operational proplnts accept a sacrifice in energy and operate at the 14–16% binder level since this normally determines service life. Differences in hydrocarbon binders as typified by polyurethane, polybutadiene-acrylic acid copolymer, polybutadiene-acrylic acid-acrylonitrile terpolymer and carboxy-terminated

Table 40
Properties of Metals

	Li	Be	B	Mg	Al	Zr
Molecular weight	6.94	9.013	10.82	24.32	26.98	91.22
Melting point, °C	180.5	1283	2027	650	659	1855
Boiling point, °C	1347	2484	3677	1108	2467	4474
Density*, g/cc	.534	1.85	2.30	1.74	2.70	6.49
Specific heat*, cal/g-°C	.848	.436	.261	.244	.216	.067
Heat of fusion, kcal/mole	.717	2.80	4.60	2.14	2.55	4.89
Heat of vaporization, kcal/mole	35.16	71.14	121.3	30.56	70.7	136.4

*At ambient temp and press

Table 41
Properties of Solid Binary Hydrides

	LiH	BeH_2	MgH_2	AlH_3	$B_{10}H_{14}$	ZrH_2
Molecular weight	7.948	11.029	26.336	30.004	122.312	93.236
Melting point, °C	686	–	–	–	98.78	–
Decomposition temp, °C	972	240**	280	>100	–	500
Density*, g/cc	.780	(.7)	1.42	(1.5)	.94	5.67
Specific heat*, cal/g-°C	.842	–	.321	–	.426	–
Heat of formation, kcal/mole	−21.63	−1	−18.2	−3	−6.9	−42.4
Heat of fusion, kcal/mole	7.0	–	–	–	5.25	–

* At ambient temp and press
** See text
( ) Denotes estimated values

Table 42
Properties of Some Complex Hydrides

	$LiAlH_4$	$LiBH_4$	$Be(BH_4)_2$	$Mg(AlH_4)_2$	$Al(BH_4)_2$
Molecular weight	37.952	21.792	38.717	86.344	71.536
Melting point, °C	–	280d.	–	–	−64.5
Boiling point, °C	–	–	91.3 (sub)	–	44.5
Decompn temp, °C	137	280	123	140	–
Density*, g/cc	.917	.66	.604	1.046	.538
Specific heat*, cal/g-°C	.545	.907	–	–	(.65)
Heat of formation*, kcal/mole	−28.0	−45.522	−25.8	−36.5	−74.7

*At ambient temp and press
( )Denotes extrapolated data

Table 43
Properties of Nonmetallic Nitrates

	NH_4NO_3	$N_2H_5NO_3$	N_2H_6-$(NO_3)_2$	NH_3OH-NO_3	$C(NH_2)_3$-NO_3	$C(N_2H_3)_3$-NO_3	N_2H_5C-$(NO_2)_3$
Oxygen, wt %	59.96	50.49	61.12	66.63	39.31	28.72	52.43
ΔH_f, kcal/mole	−87.27	−59	−111	−86.3	−93.0	−11.21	−17.2
ΔH_f, kcal/atom oxygen	−29.1	−19.7	−18.5	−21.6	−31.0	−3.7	−2.9
Density, g/cc	1.725	1.685	–	–	1.20	–	1.86
Melting point, °C	169.6	70.71	104	48	214	206-216	123d.
Decompn temp, °C	210	>180	80	<100	–	–	–
Molecular weight	80.048	95.064	157.080	96.048	122.091	167.139	183.091

Table 44
Properties of Metallic Nitrates

	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$Be(NO_3)_2$	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$
Oxygen, wt %	69.62	56.47	47.47	24.63	72.16	64.72	58.50	45.36	36.73
ΔH_f, kcal/mole	−115.279	−111.54	−117.76	−118.11	−188.3(aq)	−188.72	−224.00	−233.25	−237.06
ΔH_f, kcal/atom oxygen	−38.4	−37.2	−39.3	−39.4	−31.4(aq)	−31.5	−37.3	−38.9	−39.5
Density, g/cc	2.38	2.261	2.109	3.685	1.557	2.026*	2.504	2.986	3.24
Melting point, °C	253	310	333	414	60	129.5*	561	645	592
Decomposition temp, °C	474	380	400	584	–	–	–	–	–
Molecular weight	68.948	85.005	101.108	194.918	133.029	148.336	164.096	211.646	261.376
ΔH_{fusion}, kcal/mole	6.1	3.8	2.8	3.25	–	–	5.1	–	6
Heat capacity, cal/mole-°C	–	22.24	23.01	–	–	33.94	35.69	38.3	36.1

*Data for the dihydrate

Table 45
Properties of Nitroexplosives

	RDX	HMX	TNT
Formula	$(CH_2NNO_2)_3$	$(CH_2NNO_2)_4$	$(C_6H_2CH_3(NO_2)_3)$
Melting point, °C	203.5	276–7	80.6
Molecular weight	222.129	296.172	227.141
ΔH_f* (c), kcal/mole	+14.69	+17.92	–8.6
ΔH_{fusion}, kcal/mole	–	–	5.09
Density*, g/cc	1.818	1.903	1.654
Impact sensitivity	34	(same as RDX)	100
Bullet impact sensitivity	0	(same as RDX)	100
Explosion temp, °C	260	337	240
Activation energy, kcal/mole	47.5	52.7	34.4

*At 25°C

Table 46
Properties of Glycol Nitrate Esters

	NG	TMETN	DEGDN	TEGDN	Petrin	BDDN
Empirical formula	$C_3H_5N_3O_9$	$C_5H_9N_3O_9$	$C_4H_8N_2O_7$	$C_6H_{12}N_2O_8$	$C_5H_9N_3O_{10}$	$C_4H_8N_2O_7$
Molecular weight	227.097	255.152	196.124	240.178	271.151	180.124
Freezing pt, °C	13 [e]	2 [a]	2 [f]	–19 [b]	–28 [c]	–6 to +11
ΔH_f[d] kcal/mole	–90.75	–97.8	–103.52	–181.6	–134	–
Density[d], g/cc	1.60	1.47	1.39	1.33	1.54	1.33
Impact sensitivity						
BuMines, cm (2kg)	4	47	100	100	–	–
PicArsn, inches (1 lb)	–	20	9	43	5–10	24

[a] Supercools to –60°C
[b] Commercial product contains DEGDN impurity and freezes at –57°C
[c] Commercial product freezes at 0–15°C
[d] At 25°C
[e] Stable form–labile form freezes at 2°C
[f] Stable form–labile form freezes at –11°C

Table 47
Properties of Alkali and Alkaline Earth Perchlorates

	$LiClO_4$	$NaClO_4$	$KClO_4$	$CsClO_4$	$Mg(ClO_4)_2$	$Ca(ClO_4)_2$	$Sr(ClO_4)_2$	$Ba(ClO_4)_2$
Weight % oxygen	60.1	52.2	46.1	27.5	57.4	53.5	44.6	38.0
Molecular weight	106.397	122.454	138.553	232.367	223.234	238.994	286.554	336.274
Melting point, °C	247	482d.	525	250d.	251d.	270d.	–	505
Transition temp, °C	–	313	299.5	224	–	–	–	284.360
Decomposition temp, °C	430	482	530	250	251	270	–	–
Density*, g/cc	2.428	2.536	2.530	3.327 (4°C)	2.21 (18°C)	2.651	–	3.2
ΔH_f*, kcal/mole	–91.0	–91.48	–102.8	–103.86	–140.6	(–178)	(–184)	–192.8
ΔH_f*, kcal/atom oxygen	–22.8	–22.9	–25.7	–26.0	–17.8	–22	–23	–24.1
ΔH_{fusion}, kcal/mole	(7)	–	–	–	–	–	–	–
$\Delta H_{transition}$, kcal/mole	–	(3.34)	3.29	–	–	–	–	–
Heat capacity*, cal/mole-°C	(25.1)	(26.6)	26.865	25.71	–	–	–	–

* At 25°C
( )denotes estimated data

Table 48
Properties of Nonmetallic Perchlorates

	NH_4ClO_4	$CN_3H_6ClO_4$	$CN_6H_9ClO_4$	$N_2H_5ClO_4$	$N_2H_6(ClO_4)_2$	NH_3OHClO_4	$NOClO_4$	NO_2ClO_4
Weight % oxygen	54.5	40.0	31.2	48.3	54.9	59.9	61.8	66.0
Molecular weight	117.497	159.540	204.588	132.513	232.978	133.497	129.465	145.465
Melting point, °C	–	240	132	137	–	81	–	–
Transition temp, °C	240	180	–	–	–	–	–	–
Decomposition temp, °C	270	350	–	145	170	180	100	120
Density*, g/cc	1.95	1.75	1.56	1.939	2.2	(2)	2.169	2.22
ΔH_f*, kcal/mole	–70.73	–74.10	–23.8	–42.5	–70.1	–66.5	–41.8	+8.88
ΔH_f*, kcal/atom oxygen	–17.7	–18.5	–6.0	–10.6	–8.8	–13.3	–8.4	+1.5
$\Delta H_{transition}$, kcal/mole	2.3	–	–	–	–	–	–	–
Heat Capacity*, cal/mole-°C	30.61	–	–	–	–	–	–	–

* At 25°C
( )denotes estimated data

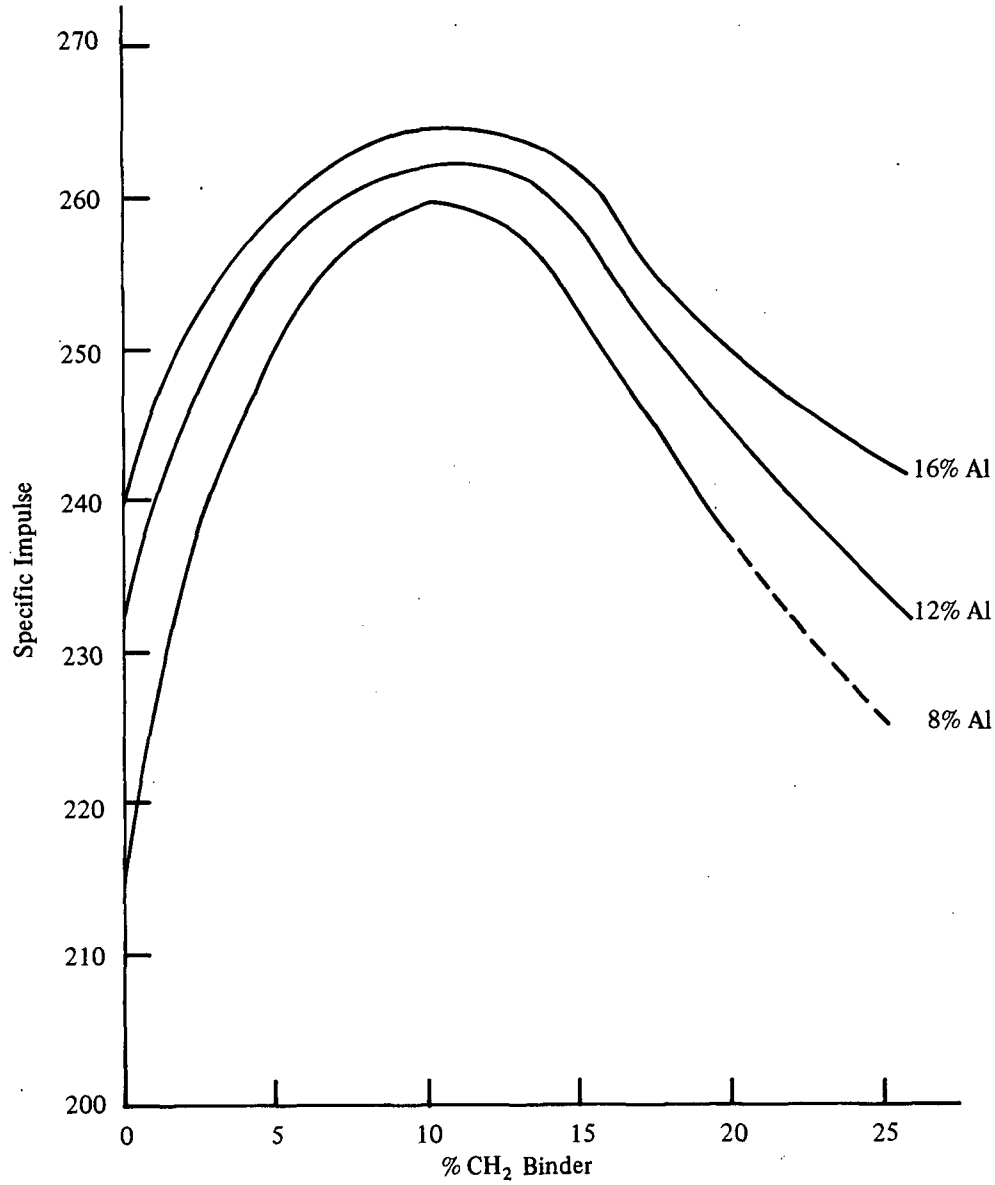


Fig 16 I_{sp} vs % Binder at 3 Al Levels for $\{CH_2\}_X$ -Al-AP Propellants

polybutadiene polymers influence specific impulse very little (Ref 35). Hence most binder development has been directed at improving physical properties. However some work has been directed at increasing the energy content in order to operate at the level required to maximize both physical properties and specific impulse. Two approaches have been directed at this. One is to reduce solids loading by incorporating oxygen in the polymer structure; the other is to incorporate the high heat of formation of the acetylenic group into the polymer structure (Ref 34)

The influence of metal type on the specific impulse of proplnts has been described previously in this article (Table 16). The max theoretical specific impulse and density impulses (I_{sp} x ρ) for the oxidizers AN, AP and hydrazinium nitrate with 15 weight percent $\{CH_2\}$ binder have been calculated for various fuels (Ref 24). These data are in Tables 49–51. The I_{sp} performance of nitronium perchlorate, lithium perchlorate and potassium perchlorate and metallized fuels with $\{CH_2\}$ binder are given in Table 52 (Ref 43)

Table 49
Polyethylene ($-CH_2-$) as Binder, Ammonium Nitrate (NH_4NO_3) as Oxidizer
15 wt % CH_2

maximum specific impulse (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	Max I_{sp} (sec)	ρ I_{sp} (lb sec/in^3)
none	85	1508	1.53	202	11.12
Li	65	2162	1.09	247	9.747
Be	69	2823	1.54	288	16.03
Mg	57	2536	1.53	249	13.72
B	61	2638	1.61	251	14.63
Al	61	2593	1.65	256	15.25
LiH	53	1694	1.16	234	9.814
BeH_2	45	2823	–	333	–
MgH_2	45	2281	1.43	254	13.12
$B_{10}H_{14}$	57	2311	1.26	270	12.32
AlH_3	53	2423	1.52	282	15.55

maximum density impulse (ρ I_{sp}) (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	I_{sp} (sec)	Max ρ I_{sp} (lb sec/in^3)
Li	85	1508	1.53	202	11.12
Be	69	2823	1.54	288	16.03
Mg	57	2536	1.53	249	13.72
B	61	2638	1.61	251	14.63
Al	57	2633	1.67	254	15.39
LiH	85	1508	1.53	202	11.12
MgH_2	45	2281	1.43	254	13.12
$B_{10}H_{14}$	61	2279	1.30	263	12.32
AlH_3	53	2423	1.52	282	15.55

Table 50
Polyethylene ($-CH_2-$) as Binder, Ammonium Perchlorate (NH_4ClO_4) as Oxidizer
15 wt % CH_2

maximum specific impulse (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	Max I_{sp} (sec)	ρ I_{sp} (lb sec/in^3)
none	85	2638	1.68	240	14.51
Li	67	2628	1.19	258	11.07
Be	70	3239	1.66	284	17.07
Mg	60	2926	1.63	258	15.20
B	71	2740	1.71	256	15.77
Al	65	3184	1.76	265	16.81
LiH	60	1865	1.29	241	11.23
BeH_2	53	2882	–	326	–
MgH_2	50	2363	1.52	256	14.03
$B_{10}H_{14}$	67	2476	1.44	266	13.82
AlH_3	63	2892	1.63	280	16.50
$LiAlH_4$	53	2307	1.26	271	12.49

maximum density impulse (ρ I_{sp}) (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	I_{sp} (sec)	Max ρ I_{sp} (lb sec/in^3)
Li	85	2638	1.68	240	14.51
Mg	63	2929	1.64	258	15.23
B	71	2740	1.71	256	15.77
Al	65	3184	1.76	265	16.81
Be	70	3239	1.66	284	17.07
LiH	85	2638	1.68	240	14.51
MgH_2	85	2638	1.68	240	14.51
$B_{10}H_{14}$	85	2638	1.68	240	14.51
AlH_3	63	2892	1.63	280	16.50

Table 51
Polyethylene ($-CH_2-$) as Binder, Hydrazinium Nitrate ($N_2H_5NO_3$) as Oxidizer
15 wt % CH_2

maximum specific impulse (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	Max I_{sp} (sec)	ρ I_{sp} (lb sec/in^3)
none	85	1654	1.50	217	11.73
Li	69	2166	1.15	254	10.53
Be	69	2823	1.52	289	15.85
Mg	57	2380	1.51	255	13.89
B	61	2831	1.59	260	14.95
Al	61	2581	1.63	262	15.44
LiH	57	1711	1.19	240	10.30
BeH_2	45	2809	–	334	–
MgH_2	49	2272	1.42	258	13.29
$B_{10}H_{14}$	57	2436	1.25	277	12.50
AlH_3	53	2409	1.51	284	15.46

maximum density impulse (ρ I_{sp}) (1000 → 14.7psia)

Fuel	Wt % Oxidizer	Tc, °K	ρ (g/cc)	I_{sp} (sec)	Max ρ I_{sp} (lb sec/in^3)
Li	85	1654	1.50	217	11.73
Be	69	2823	1.52	289	15.85
Mg	57	2380	1.51	255	13.89
B	61	2831	1.59	260	14.95
Al	61	2587	1.63	262	15.44
LiH	85	1654	1.50	217	11.73
MgH_2	49	2272	1.42	258	13.29
$B_{10}H_{14}$	69	2112	1.35	258	12.56
AlH_3	53	2409	1.51	284	15.46

Table 52
Performance Characteristics of Metallized Solid Propellants

Binder (Wt %)	Additive (Wt %)	Oxidizer	I_{sp} (sec)	Chamber Temp (°K)	Density (g/cc)
CH_2 (20)	Al (15)	NO_2ClO_4	281.5	3894	1.76
CH_2 (15)	Al (20)	$LiClO_4$	251.0	3726	1.97
CH_2 (14)	Al (16)	$KClO_4$	228.9	3492	2.04
CH_2 (15)	AlH_3 (25)	NO_2ClO_4	293.3	3783	1.66
CH_2 (15)	AlH_3 (25)	$LiClO_4$	269.0	3119	1.72
CH_2 (17.5)	$LiAlH_4$ (20)	NO_2ClO_4	292.4	3507	1.45
CH_2 (15)	$LiAlH_4$ (20)	$LiClO_4$	237.4	2639	1.54
CH_2 (25)	Be (8)	NO_2ClO_4	291.2	3270	1.61
CH_2 (15)	Be (17.5)	$LiClO_4$	264.9	3453	1.86
CH_2 (17.5)	BeH_2 (17.5)	NO_2ClO_4	313.8	3208	1.34
CH_2 (20)	BeH_2 (27)	$LiClO_4$	300.8	2732	1.21

D. *Combustion Instability*

The phenomenon of unstable combustion results from a self-amplifying interaction between combustion processes and the acoustic oscillations of the gas within the rocket motor. The unexpected appearance of combustion instability in any rocket generally terminates its mission thru motor case rupture from overpressure, disruption of guidance systems by severe vibration, or thrust malalignment. Both axial mode and transverse mode instabilities are observed (Ref 45). In the case of the transverse mode the characteristic wave time is usually that required to travel radially around the proplnt cavity; whereas the characteristic time for the axial mode is the time for the wave to travel from end to end in the combustion chamber. Double-base proplnts predominantly are prone to transverse wave instabilities and infrequently to those in the axial mode, while composite proplnts appear to go unstable mostly in the axial mode. In the case of transverse instability chamber pressures have been known to double; whereas in axial mode instabilities artificially induced by pulsing the chamber pressure at 1000psi, the pressure excursion may reach 300–400psi. A review of recent theoretical combustion modeling for combustion instability has been made by Price (Ref 47)

Experimentally it has been shown that the threshold pressure at which combustion instability can be induced artificially in composite proplnts by pulsing is a function of the burning rate of the proplnt (in a motor size of 5-inch diameter and 40-inch length) (Ref 45). This relationship is shown in Figs 17 and 18 for both aluminized and non-aluminized composite proplnts. It was also found that potassium perchlorate, lithium perchlorate and AN proplnts were resistant to this induced instability. Since AP composites were the only proplnts, other than double-base, which were driven unstable, the rate controlling reactions and response function are those related to AP decompn and perhaps the diffusion flame between oxidizer and binder

It can be concluded that if axial combustion instability is observed it can be eliminated by simple ballistic design changes such as proplnt burning rate characteristics, motor operating pressure decrease, or a reduction in grain length

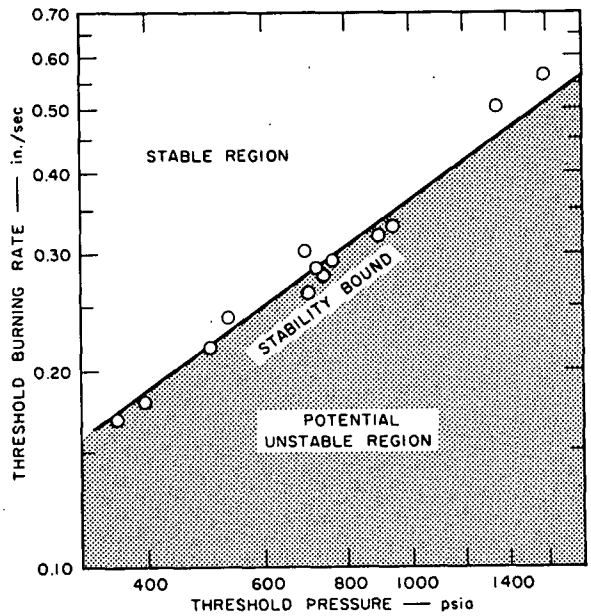


Fig 17 Correlation of threshold pressure with propellant burning rate (5- x 40-inch rocket motor)

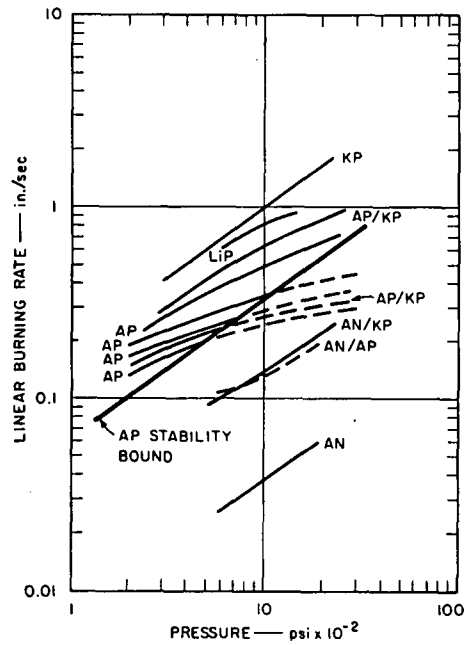


Fig 18 Influence of burning rate and composition of finite-amplitude traveling wave instability; solid line stable regime, dotted line unstable regime for 5- x 40-inch motor

to diameter ratio. In some cases a change in proplnt compn has also been found to suppress combustion instabilities. Lead salts have been used to suppress unstable burning in double-base formulations for years. Sayles (Ref 61) has found that double-base compns can be stabilized by adding about 1% weight of polybenzimidazole fibers such as polyphenoxycarboxyphenylbenzimidazole. Other effective additives which have been claimed for polyurethane, nitropolyurethane, polyesteracrylate and rubber-base composite proplnts are finely divided oxides of aluminum, zirconium, silicon, thorium, titanium or lanthanum (Ref 69)

VII. Explosion Hazards

Explosion is a generic term that encompasses *detonation* as well as other phenomena such as LVD (low velocity detonation), accelerating deflagrations, thermal explns, etc. In describing the expln hazards of SP we will confine ourselves to SP detonations and to deflagration-to-detonation transitions (DDT). We do this because we know of no LVD phenomena in SP, and thermal explns are no different from thermal explns in high explosives (HE) and have been described previously (Vol **7**, H39-R, H170–73 and K12-L; and Vol **4**, D619-L)

Table 53
Detonation Characteristics of Solid Propellants

Propellant	Density (g/cc)	Diameter (cm)	Critical Diameter (cm)	Detonation Velocity (km/sec)	Detonation Pressure (kbar)	Ref
NB 40/60 NG/NC	1.0	8–10	∿3(a)	5.45	90–93	46b
	1.3	6	–	6.40 (b)	–	46b
	1.63	–	0.8–1.0	7.60	–	46b
NC rifle powder	0.79	2.6–3.0 (c)	–	3.80	–	46a
	0.93	2.6–3.0 (c)	–	5.30	–	46a
NC cannon powder	1.45	2.6–3.0 (c)	–	7.01	–	46a
Uncolloided NC powder	0.5–0.55	0.8	–	2.3–2.4	–	17
	0.72	0.8	–	2.7	–	17
	0.82	0.8	–	2.9	–	17
NC/NG Ballistite	1.53	0.8	–	7.4–7.6	–	46a
AP/Al/PBAN (d)						
with 9.2% RDX	–	–	6.9	–	–	36b
with 7.1% RDX	–	–	13.2	–	–	36b
with 4.75% RDX	–	–	28.2	–	–	36b
90/10 AP/Wax	0.93	7.62	> 0.65 (e)	4.07	–	69a
	1.20	7.62	> 0.65 (e)	4.54	–	69a
	1.52	–	∿5	–	–	69a
80/20 AP/Wax	0.91	7.62	> 0.65 (e)	4.48	–	69a
	1.10	–	> 0.95 (f)	4.79	–	69a
	1.40	–	∿5	–	–	69a

(a) 0.43mm–diameter spheres
(b) Disks
(c) Confined in iron pipes of this diameter
(d) PBAN = polybutadiene-acrylonitrile copolymer
(e) But ≤ 0.95cm
(f) But ≤ 1.27cm

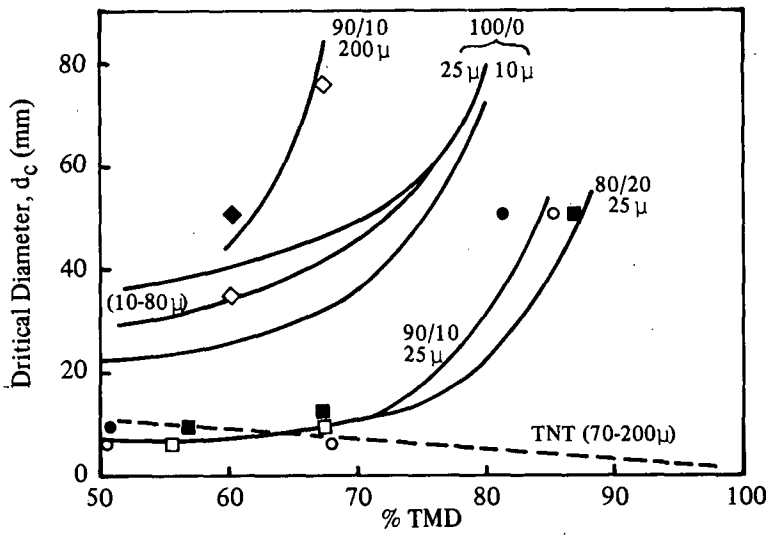


Fig 19 Detonability curves for waxed and unwaxed ammonium perchlorate and for TNT. Detonation shown by solid symbols; failure, by open ones. Circles, 90/10, 25-μ AP/wax; diamonds, 90/10, 200-μ AP/wax, squares, 80/20, 25-μ AP/wax. Reference curves: 10-μ and 25-μ AP; 10–80-μ AP; 70–200-μ TNT (Ref 69a)

Solid proplnts appropriately initiated have many of the detonation characteristics of HE. This is illustrated in Table 53, where it will be noted that the detonation velocity of SP increases with density and charge diameter similarly to that observed with HE. However, there are differences. In general, critical diameters (diameters below which no stable detonation propagates) are larger for SP than for HE. Furthermore, critical diameters for composites *increase* with increasing charge density (See Fig 19), whereas for most HE (and apparently for double-base proplnts – see Table 53) critical diameters *decrease* with increasing charge density. For well-compacted composites critical diameters tend to become very large. For some composite proplnts the detonation velocity-density curve has a max even at infinite diameter (See Fig 20). This has also been observed for some aluminized HE, but not for single-component HE or HE mixts such as Comp B, Pentolite etc

Detonation in SP is initiated by *shock* or by *DDT* (deflagration to detonation transition). Let us first examine shock initiation, ie, initiation by in-contact or close-by detonation of HE or other proplnt, or by high-velocity impact by a bullet, flying plate, or fragment

For a quantitative determination of the shock required to initiate a SP one needs the *Hugoniot* for that particular proplnt (see Vol 7, H179–83 and I56). Hugoniot relations for several SP are given in Table 54. These data, transposed into the P-u form of the Hugoniot, can be used to obtain incident shock pressures in SP regardless of whether the shock originates in a nearby detonation (eg, in a "gap test"0 or in a high velocity impact (eg, impact by a flying plate)

Threshold shock pressures to initiate detonation in several SP are shown in Table 55. In general, unless the SP contains solid HE ingredients such as HMX or RDX, the threshold pressures are considerably greater than for solid HE at a comparable degree of compaction. Even so, the pseudo-composites of AP/wax must be considered to be rather shock-sensitive provided their degree of compaction does not exceed about 90% of their theoretical max density (TMD). Figure 21 shows that up to about 90% TMD the shock sensitivity of an 80/20 AP/wax composite is very similar to that of TNT

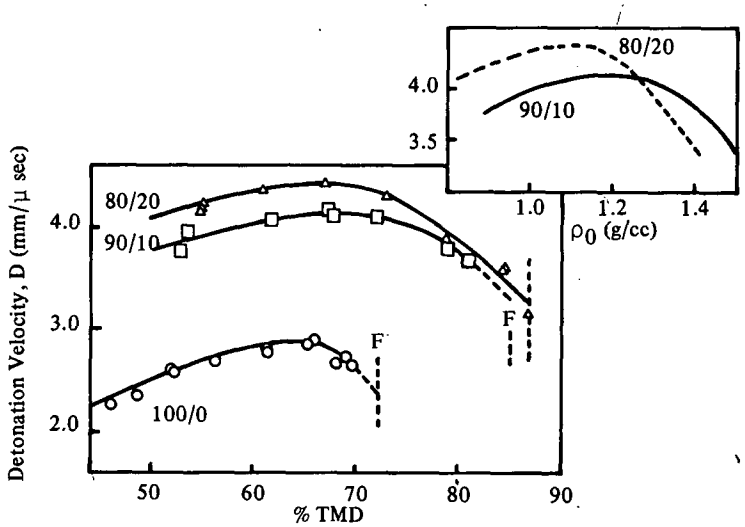


Fig 20 Effect of wax on detonation velocity of ammonium perchlorate (25-μ AP and constant diameter of 5.08cm) (Ref 69a)

Table 54
Hugoniot Equations for Several Solid Propellants

Propellant	Density (g/cc)	Hugoniot	Ref
EJC, NG/NC/AP/Al/HMX/plastic	1.80	U = 1.724 + 2.55u	40a
FFP AP/Al/binder	1.76	U = 1.327 + 2.43u	40a
PBAN-170 – 27.7/15/16.8/0.5 AP/Al/PBAN-Terpolymer/Fe_2O_3	1.69	U = 2.29 + 1.67u	47a
NB Ballistite			
60/40 NC/NG	1.63	U = 1.70 + 1.85u	52a
60/40 NC/NG	1.00	U = 0.58 + 1.68u	52a

Table 55
Shock Sensitivity of Several Unconfined Propellants

Propellant	Diameter (cm)	Density (g/cc)	Threshold Pressure (kbar)	Detonation Velocity (m/sec)	Ref
EJC (a)	2.54	1.80	≤62 (b)	7800	39a
FFP (a)	2.54	1.76	>80 (b)	Burned	39a
PBAN-170 (a)	5.08	1.69	>120 (c)	Burned	47a
90/10 25μ AP/wax	5.08	1.60	40–46 (c) (d)	Detonated	69a
90/10 25μ AP/wax	5.08	1.52	20 (c) (d)	Detonated	69a
80/20 200μ AP/wax	5.08	1.50	22 (c) (d)	Detonated	69a
AP/Al/PBAN with 9.2% RDX	30.2	–	20 (c)	Detonated	36b
Same with 7.4% RDX	38	–	19 (c)	Detonated	36b
Same with 4.75% RDX	40.8	–	15 (c)	Detonated	36b
Powder N (compn not given)	2–3	1.58	86 (b)	Detonated	25a

(a) See Table 54
(b) Plane-wave donor
(c) NOL gap test geometry
(d) 50% point; pressure in Lucite attenuator at Lucite-sample interface

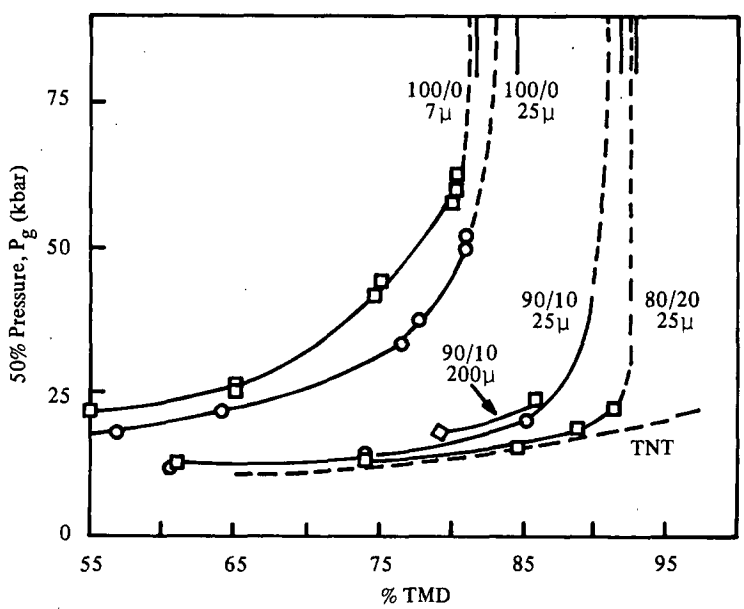


Fig 21 Shock sensitivity curves for waxed and unwaxed ammonium perchlorate and for TNT. Vertical lines at top of graph mark lowest percentage of TMD at which a sub-detonation reaction was observed (Ref 69a)

Let us now examine DDT. The latest and also the most penetrating studies of DDT were with HE rather than SP. However, there is every expectation that DDT in HE and SP are similar, with only minor differences

Modern studies (Refs 20, 49a, 49b, 55a, 69a & 69b) have stressed the importance of a *convective flame front* in establishing DDT in granular explosives. A convective flame front is an ignition wave which is propagated by the passage of hot combustion gases thru the pores of the charge. The hot gases are forced into the pores because of confinement at the igniter end of the container. However, penetration of the gases into the charge does not result immediately in the formation of a convective flame front. The gases heat the pore walls and are consequently cooled themselves. It is the *continuous* flow of gases which raises the temp of the pore walls until ignition in the pores occurs and produces what is now the head of the convective front

Bernecker & Price (B & P) (Ref 69a) present strong evidence for the convective flame front–

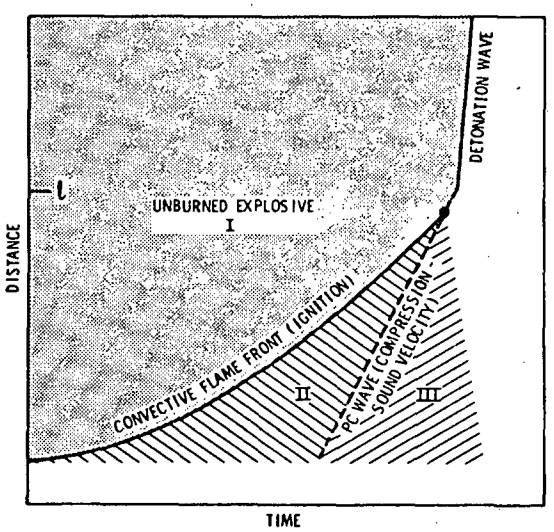


Fig 22 Proposed DDT mechanism for 91/9 RDX/wax granular charge. Regions: I. Undisturbed granular bed at initial compaction. II. Explosive burning to give linear increase of pressure with time; compaction occurs in most porous charges. III. Accelerated burning and pressure buildup to form precursor shock (Ref 69a)

DDT mechanism sketched in Fig 22 and summarized as follows:

"Granular charges of 91/9 RDX/wax have exhibited a transition from deflagration to detonation in compactions of 67 to 95% TMD (theoretical maximum density). Processes observed in such transitions are local ignition by an igniter mix, general ignition by a convective flame front, compaction of the more porous burning beds, formation of a post-convective (compressive) wave which marks the beginning of accelerated pressure buildups, subsequent coalescence of compressive waves into a shock, and finally a shock to detonation transition." The compressive phenomena leading to shock formation cannot be detected optically and have not been reported in earlier literature (eg, in Refs 20, 49a & 49b)

In a later publication (Ref 69b) B & P expand their model of DDT to explain the observed variation of predetonation run-up distance with degree of compaction and particle size in terms of charge column permeability. They characterize permeability by B_0 (in cm^2), the permeability coefficient of the Darcy equation. For TMD $\leq$ 70–80%, log B_0 is a linear function of TMD for granular PETN and TNT. B & P define a B_0^{crit} as the value of B_0 below which the log B_0 vs TMD curve is no longer linear, ie, the point beyond which the permeability of the column begins to decrease rapidly with increasing TMD. Then they proceed to discuss DDT in terms of B_0 and B_0^{crit} in the following manner:

"*Case A: Impermeable Charges*

1. *100% TMD and Cast Charges.* At crystal density (100% TMD) there is no porosity and, of course, the charge is impermeable; the latter is also true for cast charges. Hence, the ability of the expl to undergo DDT will be determined by the criteria outlined in Refs 19 & 36a. To summarize briefly, (a) there must be a sufficiently rapid pressure rise in the ignition region caused by the generation of high product gas pressures, and (b) the unburned expl beyond the ignition region must be sufficiently sensitive to be initiated by a shock wave equal in amplitude to the high pressures generated near the igniter. Consequently, the distance to the onset of detonation, ℓ, decreases as d^2p/dt^2 increases

The first criterion, (a), which pertains to the burning area of the charge could be more mean-

ingfully described in terms of an energy per unit volume concept. We define ψ_S as the energy per unit volume in the solid phase and ψ_G as the energy per unit volume in the gas phase. Thus, the first criterion could be reworded, for our discussion, to require that $d\psi_G/dt$ increase rapidly enough to effect DDT for cast materials. The energy per unit volume in the gas phase will be determined by (1) the energy available in the expl (proportional to ψ_S; this depends upon the chemical composition and compaction); (2) the rate at which this energy is released (proportional to $-d\psi_S/dt$; this depends upon the linear burning rate); and (3) the rate at which energy is lost from the ignition region (this depends upon losses to the walls, hot gases flowing out of the burning region due to permeability, either natural as in porous charges or accidental as in poorly prepared charges having air cavities or cracks)

2. *Charges with* $B_0 \ll B_0^{crit}$. The introduction of porosity into a charge does not mean that the charge will be permeable. The pores may or may not be interconnected. If the pores are not connected, permeability is very low and essentially negligible. The criteria for DDT in this subsection will be the same as discussed for Case A(1). We would expect ℓ to be smaller than in Case A(1) because the porosity will slightly enhance dp/dt and because the critical shock initiation pressure for detonation, P_i, would be slightly lower. If the expl does not undergo DDT at 100% TMD or as a cast material, it probably will not undergo DDT at these densities either. This will probably be the case for very highly waxed RDX

Case B: Charge Densities where $B_0 \leq B_0^{crit}$

As the porosity increases, the fraction of pores which are interconnected increases rapidly. However, the permeability of the charge will be small. The formation of an ignition front in the pores of the expl (convective burning) can now occur and will depend upon the permeability of the charge, the adiabatic flame temp of the expl, the ignition characteristics of the expl and the ability of the confinement to allow a critical "driving" pressure to be set up. The onset of convective burning indicates that non-negligible amounts of energy can be transported by gas flow beyond the ignition region. However, for these densities (where $B_0 < B_0^{crit}$) only very small quantities of gas can flow out of the ignition area over a time period as long as 100 μsec. Even so $d\psi_G/dt$ in the igniter region should be larger for Case B than for Case A because a larger surface area for additional burning has been introduced by the interconnected pores. Thus, ℓ should decrease in the order: Case A(1) – Case A(2) – Case B

The mechanism for DDT in this case is very similar to that in cast expls, the chief difference is the proposed ignition by a convective flame front

Case C. Charge Densities where $B_0 > B_0^{crit}$

As more porosity is introduced into the charge, the gas flow can no longer be described as choked. Enough pores are connected to permit flow which may be described as steady state. The increased permeability for this case leads to smaller values of dp/dt (ie, $d\psi_G/dt$) and ψ_S. The time required to produce a rapid increase in dp/dt is longer than in Cases A and B since more expl must be burned to compensate for the energy flow (in the gas phase) out of the burning area

The point (distance from the igniter/explosive interface, x) at which this rapid increase in dp/dt occurs may be farther from x = 0 (at a point farther away from the igniter interface and *in* the pores of the granular bed) than in cases above. Within the density range of Case C, dp/dt should increase with increasing porosity because of increasing permeability and smaller values of ψ_S, as mentioned above. The position of onset of detonation should henceforth increase with increasing porosity. Our exptl results have indicated that a buildup to DDT begins only after the pressure in the ignition region begins to accelerate (ie, is capable of sending out strong compressive waves)

The DDT mechanism for this case is similar but not identical to that of Case B. A convective flame front propagates ahead of the compressive waves which are necessary to form a precursor shock front. In modeling DDT the convective front (and its consequences) must be included because of its influence on dp/dt in the ignition region

Case D: Very Permeable Charges; $B_0 \gg B_0^{crit}$

For the very permeable charges ($B_0 \gg B_0^{crit}$), ℓ increases with increasing porosity in accord with the discussion in Case C. However, the

energy losses from the burning region near the igniter can be large enough to prevent the attainment of a sufficiently large $d\psi_G/dt$ (or dp/dt) to effect transition. Hence, the burning area is now a large region beyond the igniter area. For expls like RDX this will be the case for charges with very large porosities and it will occur at lower porosities for less energetic expls, such as 91/9 RDX/wax. Thus, in Case D the chemical compn and the linear (conductive) burning rate (as reflected in ψ_S and $d\psi_S/dt$, respectively) become increasingly important. For the more energy deficient expls, such as ammonium picrate, pressure increases at these densities can be quite slow and nonaccelerating. The absence of an increasing dp/dt does not mean the absence of a high pressure. Pressure may increase linearly to several kilobars but in the absence of a rapidly rising dp/dt no strong compressive waves emanate from the burning region

When an increasing dp/dt does not occur, the pressure and pressure gradient generated in the burning region are sufficient to initiate movement of the porous bed after a period of one to two hundred microseconds. Consequently, collapse of the porous structure occurs immediately beyond the edge of the burning bed (nearest the igniter). This collapse process increases the available energy per unit volume in the compacted material (ie, ψ_S) and here an increasing $d\psi_G/dt$ can be attained if it could be attained at higher densities (ie, Case C). If an increasing $d\psi_G/dt$ was not observed at higher densities, it may still result after pore collapse because the temp of the collapsed bed will be higher than that of the initially higher density cases

The DDT mechanism for Case D is identical to that proposed for Case C. However, the model for DDT in Case D will differ from that of Case C because of compaction of the porous bed

If from the above discussion the variation of ℓ is traced from case to case, it is seen that a minimum in the ℓ-compaction plane is a natural consequence of the effects of charge permeability and the proposed driving force for DDT"

The above model for DDT is based on exptl observation with granular and cast HE. However, as already mentioned, DDT in SP and HE should have many similarities. This contention is supported by the observations of Roth (Ref 17) and Wachtel (Ref 29a). Roth's smear camera pictures of an uncolloided single base smokeless powder at low compaction are very similar to the smear records of PETN, RDX, HMX and Tetryl obtained by Griffiths & Groocock (Ref 20), or RDX records obtained by Calzia (Ref 52b). Wachtel showed that closed bomb burning behavior of Comb B & TNT is similar to that of a double-base proplnt with a solid oxidizer, or a high energy double-base proplnt, or a composite double-base proplnt made by Rohm & Haas

Wachtel (Ref 29a) also points out the tendency of composite proplnts to undergo brittle fracture when stress is applied to them at high strain rates. This tendency is accentuated by low ambient temps, and it is known that cannon and rocket proplnts have a greater tendency to detonate at low ambient temps than at normal temps. Along similar lines, Frolov et al (Ref 55a) hypothesize that the chance of detonating SP increases if burning of the SP tends to produce collisional flow (jets) which enhances convective burning. Collisional flow is more likely to occur in non-uniform systems. Thus homogeneity of dispersion of the solid material in the binder may be an important safeguard against DDT in composite proplnts

VIII. Brief Summaries of Recent Literature on Solid Propellants

The following are somewhat subjective selections from the vast amount of *recent* published material on solid proplnts. These short abstracts are grouped under the headings of: *ignition, combustion, reactivity, detonability & safety, analytical procedures & data,* and *miscellaneous.* In each grouping the abstracts are arranged chronologically

Ignition:

Mantoro Uetake & Hiroshi Sata, Kogyo-KayakuKyokaishi **24**(2), 67–72 (1963), and CA **60**, 11835 (1964): Proplnts (I) fail to ignite when the elec resistance in the discharge circuit is too high. There is an optimum resistance value to ignite I. When the spark voltage is high, the range of resistance of I is wider. The energy to ignite I is larger than that for gas. The min measured energy is 10 millijoules for the ignition of I. The min electrostatic voltage for ignition is about 800V, and at smaller voltages

I do not ignite. The form of the electrode affects the probability of ignition of I. Double-base proplnts are more liable to ignite by electrostatic spark than single-base proplnts. Graphite-coated I are very difficult to ignite. The ignition probabilities depend upon the particle sizes of I and the smaller the particle size, the higher the probability becomes and vice versa. The mechanism of ignition is considered as follows: I are decompd by the elec spark and produce ignitable gases, the gas ignites, and then the gas flame ignites the solid proplnt. Consequently, crit time and spark are required for I to produce inflammable gas which follows burning of the proplnt

H. Wise, S.H. Inami & L. McCulley, Combust-Flame **11**(6), 483–88 (1967) & CA **68**, 61006 (1968): The contribution of exothermic, condensed-phase reactions to ignition and deflagration of proplnts is examined. Measurements of the rates of heat release, thermal diffusivity, burning rate and ignition are combined to demonstrate the role of reactions in proplnts made up of powd AP and catalysts. By means of a theoretical analysis, it is found that for the proplnts under study a thermal runaway in the condensed phase can account for the ignition phenomena observed. Also, at low steady-state deflagration rates the contribution of the solid-phase reactions can be demonstrated. Some of the proplnts quenched during deflagration showed the existence of a subsurface layer, which is located in a zone at which the temp reached the level characteristic of the crystal transition of AP

J. Pantoflicek and Frantisek Lebr, Combust-Flame **11**(6), 464–70 (1967) & CA **68**, 61107 (1968): A method for measuring the ignition energy of proplnts using hot wires at high heat fluxes is described and the influence of pressure, proplnt temp and ignition time is detd. Several expts showed good reproducibility of results using the equipment proposed. The difference between ignition at high and low heat fluxes is discussed. A method for correcting ignition energy with respect to the wire diam is proposed

M. Barrere, RechAerosp **No 123**, 15–28 (1968) & CA **70**, 69707 (1969): Static and dynamic methods for studying the ignition of solid-proplnt rockets are described. The principal parameters affecting the ignition are the level of energy required for inflammation, the nature of the gas surrounding the sample, the gas pressure, the gas velocity near the surface, the temp of the proplnt, its nature, and the effect of catalysts. The nature of the oxidizer, geometry of the grain, internal ballistics of the igniting app, and the mechanism of ignition of the proplnt block were studied and an analysis made of the pressure rise during ignition. Study of ignition of the proplnt includes a study of the evolution of gas in the central canal, heat transfer to the wall, flame propagation, etc

C.H. Waldman & M. Summerfield, AIAA J **7**(7), 1359 (1969) & CA **71**, 126689 (1969): In the theoretical prediction of the ignition delay when a condensed fuel is brought in contact with a hot reactive gas, a math model based on the assumption that the initiating exothermic reaction is a heterogeneous one on the fuel surface is compared with a model based on the assumption that the initiating reaction takes place in the thin vapor boundary level after vaporization. Curves based on both assumptions give similar predictions. Both predict that the total pressure is approx inversely proportional to the partial pressure of the oxygen in the test gas, and that the ignition delay is shortened when the total pressure is increased by a nonoxidizing neutral gas

R.S. Brown et al, AdvanChemEng **7**, 1–69 (1968) & CA **72**, 11368 (1970): The topics reviewed include: types of solid proplnts, solid-proplnt rocket motors, ignition, steady-state combustion, and combustion instability and termination

L.J. Shannon, AIAA J **8**(2), 346–53 (1970) & CA **72**, 113370 (1970): Ignition characteristics of representative composite solid proplnts were studied by using an arc-imaging furnace to provide a radiant-energy source. The variation of proplnt ignitability with formulation changes was small, provided the binder and oxidizer were fixed. The min initial pressure for which ignition occurs is predominantly detd by the thermal decompn characteristics of the binder component in AP-based proplnts. It is proposed that a key step required to achieve ignition is establishment of a crit gas-phase reaction rate threshold adjacent to the proplnt surface

R.K. Kumar & C.E. Hermance, AIAA J **9**(8), 1615–20 (1971) & CA **75**, 89711 (1971): In

previous theoretical studies of gas-phase ignition of homogeneous solid proplnts under shock-tube conditions, the ignition criteria have been related to some specific character of the temp distribution in the gas phase. Correspondence of the exptl criteria involving detection of light emission was uncertain. A new theoretical criterion has been developed, relating the light energy received by a photocell to the transient gas-phase distribution of reaction products and temp. Light emission and ignition characteristics found by using this criterion agree quite closely with exptl results. Investigation of ignition behavior for different relative reactivities of the ambient gaseous oxidizer indicate progressively less effect of the ambient gaseous oxidizer mole fraction on the ignition delay as the relative reactivity of the evolved oxidizer increases

W.H. Andersen, CombustSciTechnol **5**(1), 43–46 (1972) & CA **76**, 115652 (1972): A kinetic analysis of the published surface-ignition behavior of M2 double-base proplnts is made by using a recently developed approx analytical model that assumes ignition to result from an adiabatic, 1st-order surface reaction. Values of the kinetic parameters obtained in the analysis are the same as those obtained by using the results of numerical soln of the more rigorous ignition equations given in the literature. This agreement provides further support for the general validity of the analytical model. The manner of analyzing exptl data with the analytical model is described in detail

A. Linan & A. Crespo, USNatTechInformServ, **AD Rep No 751303** (1972) & CA **78**, 99963 (1973): An asymptotic analysis within limits of large activation energies is presented for ignition of a solid proplnt undergoing an exothermic heterogeneous Arrhenius reaction with a gaseous oxidizer. The analysis was conducted for hypergolic or shock-tube ignition conditions and also for ignition under a radiant flux with in-depth absorption of the radiation. The analysis shows that the thermal runaway follows a much longer inert heating stage. A closed-form expression relates the ignition characteristics. An analytical expression was also found for ignition time under hypergolic or shock-tube ignition conditions

P. Larue & L. Nadaud, RechAerosp **6**, 297–311 (1972) & CA **78**, 161664 (1973): Visualization of combustion by color photog and pressure measurements were used to determine the time necessary to reach self-sustaining combustion and the pressure rise in the combustion chamber after ignition of the grains. The first phase consists of establishment of contact between hot gases from the igniter and the proplnt surface, heating, and chemical reaction by pyrolysis without flames, followed by visible radiation. The igniter flow rate is related to the pressure buildup and the min flow rate below which ignition will not take place is defined. The lower the ignition flow rate, the longer the ignition time and the faster the pressure buildup after ignition. The max duration of self-sustaining combustion is also defined

N.P. Suh, J.P. Picard & C. Lenchitz, USNatTechInformServ, **AD 756880** (1972) & CA **79**, 116696 (1973): The mechanisms of ignition and deflagration of NC-based proplnts are described. The proplnt behaves like an inert solid during the preignition heating stage. The solid-phase reaction becomes important during steady-state deflagration at low pressures, especially in single-based proplnts because of their slow gas-phase reactions. During both the ignition and deflagration, the heat transported from the gas-phase reaction zones to the solid surface sustains the decompn of the solid phase. The modes of heat transfer between the gas-phase zones and the solid-phase reactions are discussed, including the contribution of thermomechanical effects

V.F. Mikheev & Yu.V. Levashov, FizGorneiyaVzryva **4**, 506–10 (1973) & CA **80**, 28968 (1974): The effects of heat flux on burning proplnts were investigated. In three series of expts, crit time of interruption of light flux during ignition, the crit heating time during stationary burning, and the crit amplitudes of the emission of a constant-burning proplnts were determined. A nitroglycerine proplnt (I) and the same proplnt with soot (I + soot) were used. The heat emission intensity (from a graphite furnace at ∿2000°) was ∿9cal/(cm^2-sec). The samples were cylinders 20mm in diam and 20mm high. In the first series of expts, they were exposed to light flux of a given intensity (q_0) until ignition, τ_v, and for a short time ($\Delta\tau_i$) after ignition. At the end of time $\tau = \tau_v + \Delta\tau_i$, the light was interrupted and the action of the burning proplnt (burning or ex-

tinction) was plotted vs q_0. At q_0 = 1cal/(cm^2-sec), the proplnt continued to burn steadily. With increasing q_0, the critical time of interruption decreased. In the second series of expts, the samples were ignited by a glowing spiral and after3–5sec (when stationary burning was established) the proplnt was exposed to a light flux of known intensity for various times ($\Delta\tau_b$). The $\Delta\tau_b$ vs q_0 curves separated the region of stable burning from the extinction region. The lower limits of q_0 for steady burning were about 1 and about 2cal/(cm^2-sec) for I + soot and I respectively. In the third series, the samples were ignited by a glowing spiral and burned on being exposed to light of a given intensity. After 4–10secs (when stationary burning was established), the light flux was interrupted and the reaction of the burning proplnt to the interruption of light was recorded. For the I + soot, critical values of q_0 were 1 and 1.5cal/(cm^2-sec) at initial temps of 20 and 100° respectively. For I the critical value of q_0 = 2cal/(cm^2-sec)

Combustion:

W.G. Brownlee, AIAA, Los Angeles, Calif, Paper No **63-228** & CA **61**, 6849 (1964): Information is obtained concerning the effects of varying the operating pressure level, grain cross section, motor diameter and length, and associated area ratios. Various Al powders are substituted for a portion of the proplnt oxidizer, and LiF is added in one instance. Use of a new pulse technique for the injection of flow disturbance at the head end of the motors permits command triggering of instability. The time average (unstable) chamber pressure is strongly dependent on the restriction ratio. Use of an exptl stability parameter in design prediction depends on a knowledge of scaling factors. A 2-inch diameter motor is more unstable than an 8-inch motor, while limited results from 8- and 17-inch motors are in general agreement. The addition of Al powder to the proplnt does not suppress axial instability. All proplnts tested, including one with 19% Al, could support instability at sufficiently high values of restriction ratio. The results indicate that the crit pressure level is higher for faster-burning proplnts. The stable burning rate of one aluminized proplnt is reduced by incorporating 1.8 parts of LiF. This modification reduces the crit pressure level drastically and leads to a proplnt that is capable of extremely violent instability at practicable restriction-ratio levels. The results and techniques described were applied to the design and testing of a motor for the Black Brant vehicle

J. Powling & W.A.W. Smith, 10th Symp-Combust, 1373–80 (1964) & CA **63**, 17782 (1965): Burning surface temps have been measured for fuel-weak AP-paraformaldehyde mixts at pressures up to 300psia by using an IR emission technique. Temp measurements up to 60psia were reasonably reproducible, and the values were compatible with the existence, at the surface, of an equilibrium between solid AP and the gaseous decompn products NH_3 and $HClO_4$. Results above 60psia were rather erratic, and exptl failure to eliminate the variations led to a reappraisal of the optical method for measuring surface temps. The temp gradients within the solid became too steep at these pressures even for this method, which can see as little as 2μ of surface depth

A.F. Belyaev et al, NauchnTekhnProblGoreniya i Vzryva (1965), (1), 25–30 & CA **63**, 17784 (1965): The burning rates of various mixts of solid oxidizers and fuels were measured at less than 1 atm. Four stoichiometric mixts (AP + TNT, $KClO_4$ + TNT, AP + bitumen, and AP + paraformaldehyde) and systems containing 80% AP and 20% mixts of polystyrene with polyesters were investigated. The particle size of the compns was 10–20μ. The density of mixts was about 98% of the theoretically possible density. Relations between burning rate (u) and pressure (p) are presented in diagrams. For all the mixts tested, the relation between u and p satisfied the equation u = bp. When the particle size of the oxidizer was 250μ, the equation was $u \sim p^{0.7}$. The discussion of the burning mechanism leads to the conclusion, however, that the relation between u and p cannot always be characterized by a simplified linear equation

F.L. Schuyler & T.P. Torda, AIAA J **4** (12), 2171–7 (1966) & CA **66**, 30631 (1967): Steady-state combustion of solid double-base and monoproplnt rockets was investigated analytically. The nonlinear differential equations describing the motion of a laminar 2-dimensional, compressible, chemically reacting viscous fluid are intimately coupled with the 1-dimensional

heat-conduction equation of a burning solid proplnt, and the 1-dimensional, compressible, inviscid flow of combustion products thru the central core of the proplnt grain. Application of numerical methods and use of realistic rocket conditions as input showed that calcd proplnt burning rates and wall temps fall within the range of previously obtained exptl values. In addition a study of the effect of various parameters on the combustion process showed that: (1) the chem reaction rate and heat of combustion have the greatest effect on the heat flux to the proplnt; (2) the axial gas velocity has the greatest effect on the proplnt surface shear stress; (3) the activation energy in the pyrolysis-rate expression together with the chem reaction rate have the greatest effect on the proplnt burning rate; and (4) the gas-phase sp heat at const pressure, the frequency factor in the pyrolysis rate expression, and the proplnt heat of decompn have only a secondary influence on the combustion process

R.P. Baumann & J.P. Picard, USDepComm, **AD 467333** (1965) & CA **66**, 87211 (1967). A project designed to gain an understanding of the mechanism of action of ballistic modifiers in NC-based proplnts was carried out. A study was undertaken to investigate the feasibility of using mass spectrometry to follow the reactions occurring on the decomposing surface of solid proplnt grains. A special low-pressure arc-image strand burner was designed and fabricated for monitoring on the New York University Mass Spectrometer. The spectrometer is a 60° sector fast-scan machine allowing 1000 sweeps/sec with an accuracy on simple mixts with interfering peaks between 0.05 and 1.0%. The equipment worked extremely well; should be suitable for studying a wide range of solid proplnts. A number of unstable species and free radicals were found, especially NO_3•, CH_3CO•, and CHO•. These species were not only detected during and after "burning", but also were detected prior to any visual indications of decompn. Preliminary data indicate that Pb catalysts increase the rate of oxidn-redn reactions between CH_3CO• and NO_3•

S.S. Novikov et al, DoklAkadNauk SSSR **174** (5), 1129–31 (1967) & CA **67**, 83549 (1967): The combustion of nonrandom and random mixts of Plexiglas and powered $KClO_4$ was studied at 1–60 atm. The nonrandom mixts were prepared by milling slots in a Plexiglas block and packing the slots with $KClO_4$. The thickness of the Plexiglas barrier between the layers of $KClO_4$ was 0.35–0.5mm. The random mixts were prepared from Plexiglas particles 0.4mm in diam and had the same overall fuel/oxidizer ratio as the nonrandom mixts. At 1 atm, only the random mixts could be ignited, but they burned unstably. Above 5 atms, both mixts burned stably. At about 5 atm, the random mixts burned at only half the rate of the nonrandom mixts; but, with increasing pressure, their burning rates increased. However, the rate did not remain constant. It was concluded that in random mixts there is a sharp increase in contact between fuel and oxidizer in the layer adjacent to the burning surface, which leads to increased heat liberation and a corresponding increase in burning rate. However, since the heat and mass transfer into the gas phase are nonuniform, this must lead to a decrease in burning rate and to nonsteady-state conditions

A.F. Belyaev & N.N. Bakhman, FizGoreniya-Vzryva **4**, 3 (1966) & CA **67**, 101542 (1967): Review over about 8 years of mostly Russian literature. Physical meaning of combustion phenomena is emphasized. Deals mostly with heterogenous systems

H. Krier et al, AIAA J **6** (2), 278–85 (1968) & CA **68**, 61103 (1968): Nonsteady burning of solid proplnts is being investigated both theoretically and exptly with attention to combustion instability, transient burning during motor ignition, and extinction by depressurization. The theory is based on a one-dimensional model of the combustion zone consisting of a thin gaseous flame and a solid heat-up zone. The nonsteady gaseous flame behavior is deduced from experimental steady-burning characteristics; the response of the solid phase is described by the time-dependent Fourier equation. Solutions were obtained for dynamic burning rate, flame temp, and burnt gas entropy under different pressure variations; two methods were employed. First, the equations were linearized and solved by standard techniques. Then, to observe nonlinear effects, solutions were obtained by digital computer for prescribed pressure variations. One significant result is that a proplnt with a large heat evolution at the surface is intrinsically

unstable under dynamic conditions even though the gas entropy amplitude and phase depend critically on the frequency of pressure oscillation and that either near-isentropic or near-isothermal oscillations may be observable. Expts with an oscillating combustion chamber and with a special combustor equipped for sudden pressurization tend to support the latter conclusion

J.B. Anderson & R.E. Reichenbach, AIAA J **6** (2), 272–77 (1968) & CA **68**, 61104 (1968): The average burning rates of composite solid rocket proplnts were measured in acceleration fields up to 2000 times the standard acceleration of gravity. The acceleration vector was perpendicular to and into the burning surface. Proplnt strands were burned in a combustion bomb mounted on a centrifuge, and surge tanks were employed to insure essentially constant pressure burning at 500, 1000 and 1500psia. The burning rates of both aluminized and nonaluminized composite proplnts depended on acceleration. The effect of acceleration on burning rate depended on the burning rate of the proplnt without acceleration, Al mass loading, and Al mass median particle size. The relative burning rate increase was greater for slow burning proplnts than for faster burning proplnts. The exptl results are compared to the analytical models proposed by Crowe for aluminized proplnts and by Glick for nonaluminized proplnts. The results indicate that these models do not adequately predict the observed relative burning rate increase with acceleration, and hence that more complex modeling will be required to explain the observed acceleration effect

S.K. Sinha & W.D. Patwardhan, Explosivstoffe **16** (10), 223–25 (1968) & CA **70**, 49144 (1969): The mechanism causing the plateau effect in the combustion of proplnts with admixt of Pb compds (ie, the independence of pressure of the combustion rate in a certain range) is discussed. This effect is caused by the transport of free Pb alkyl radicals from the foam zone to the fizz zone, which decomp there, causing a more efficient combustion, and increase the temp of this zone by reaction with NO. An increase of pressure is assumed to displace the free radicals from this zone because of the increase of the collision rate; this leads to a decrease in the local temp, which compensates for the increased thermal conductivity. In a certain range, these two effects cancel, causing the plateau. At even higher pressures the radical mechanism becomes unimportant, so that the combustion rate increases again with pressure. The nonexistence of a plateau in very "hot" proplnts is understood by this mechanism

G.B. Northam, NASA Tech Note **NASA-TN-D-4914** (1968) & CA **70**, 49145 (1969). The combustion of aluminized solid proplnts (polybutadiene-acrylic acid containg 70 wt% AP) was studied in the firing of unidirectional burning slab motors on a ballistics centrifuge. Acceleration levels were varied from 0 to 300g, and the acceleration load was directed normal into and out of the burning surface, as well as at orientations into the burning surface of 0°, 30°, 60° and 75°. The surface condition of each test sample after firing was examined by extinguishing methods. The average proplnt burning rate, the surface pitting and the residues varied directly with the normal acceleration load into the burning surface. At orientations other than normal and into the burning surface, none of these factors showed much change thru the entire spectrum of acceleration levels. At the average chamber pressure of 500psia, the proplnt burning rate increased about 21% over the range of acceleration levels. At the higher pressure levels, the proplnt burning rate was most sensitive to increased acceleration loads. Empirical burning-rate equations are included, and it is concluded that ground-spin-test results should be extrapolated to flight performance with great care, and that changes in proplnt formulations tending to reduce metallic fuel additive agglomeration would be effective in reducing the effects of acceleration level on combustion

R.D. Gould, US Clearinghouse FedSciTech-Inform, **AD-684244** (1968) & CA **71**, 51808 (1969): The effect of variations in the composition of solid proplnts on their tendency to show combustion instability at 1000psi was studied using a T burner. AP particle size can have a large effect on the acoustic response and this is frequency-dependent. TiO_2 is usually added to plastic proplnts to promote stable combustion, and the mechanism of its action was detd. With a view to the potential use of O-balanced proplnts, the effect of varying the oxidizer/fuel

ratio of plastic proplnts was also studied

E.W. Price, 12th IntSympComb (Proc) **14-20 Jul**, 101–13 (1968) & CA **74**, 89283 (1971): A review with discussion and 48 refs, stressing advances since 1964 in the understanding of oscillatory combustion. Price discusses the nature of the combustion zone and warns that generalizations from current knowledge, which pertain mostly to proplnts with AP as oxidizer and rubber as binder, with Al as the metal if any, might not fit other types. The theory of combustion-flow interactions is outlined and the nature of the response function is discussed both in 1-dimensional, homogeneous flame models and in others proposed. Recent combustor stability analyses, esp those modeling low-frequency "nonacoustic" combustor instability, are mentioned. Of the techniques considered for exptl determination of the response function, two that had been used extensively are discussed: the T burner and the nonacoustic burner

M.L. Bernard et al, CRAcadSci, Ser C, **272** (26), 2112–15 (1972) & CA **75**, 101675 (1971): A generalization of the previously described (Bernard et al, 1971) ablation theory (for AP) combustion to include AP-based solid proplnts provides satisfactory fits to the exptl data of M. Summerfield et al (1960), with reproduction of the two distinct pressure regimes observed in the combustion of AP-based powders between 0 and 100 bars. The solid binding agent is assumed to be easily pyrolyzable, with each mol producing several combustible gaseous mols, as in the case of pyrolytically degrading polymers

N.E. Cohen, 13th Symp (Int) Combust (Proc) (1970), 1019–29 & CA **76**, 61471 (1972): To analyze and explain the mechanism of combustion of powdered metals in contact with a solid oxidizer (AP) with the powdered metal dispersed in solid AP (I), the combustion of various compressed I-Al and I-Mg mixts in N_2 under various conditions in a high-pressure window bomb was studied. The regression-rate laws of the mixts at high and low pressures, the pressure limits for deflagration, and the structures of the combustion zone and of the surface were detd. The burning rate of various I-Al mixts, as a function of pressure, I particle size, and mixt ratio was determined by cinematography. The combustion was difficult to achieve under some conditions, and became less and less complete as the mass fraction of Al increased. Addition of 2% powdered Cu_2O as a catalyst markedly improved the ignition and combustion, raised the acceptable metal ratio from 25 to more than 50%, and markedly lowered the limiting combustion pressure. The combustion of I-Mg mixts was smooth below as well as above 1 atm, but with a different mechanism. In subatm combustion the pyrolysis surface melted but did not remain flat, and the Mg particles were harder to ignite. The regression rate of pressed I-Mg-2% Cu_2O samples rose with increase in Mg content, unlike the case with Al. The study of the molten and resolidified pyrolysis surface formed during subatm combustion of I-Mg mixts suggested a possible mechanism for the decompn of I

A.M. Varney & W.C. Strahle, CombustSciTechnol **4** (5), 197–208 (1972) & CA **76**, 61472 (1972): Expts were conducted on quench combustion of 2-dimensional proplnt sandwiches prepared with AP oxidizer and 4 conventional proplnt binders – polysulfide, polyurethane, polybutadiene acrylic acid, and carboxy-terminated polybutadiene. Proplnt sandwiches prepd with both single-crystal sheets and compacted polycryst sheets were burned and quenched at combustion-pressure levels from 300 to 2400psig for binder lamination thicknesses of 25–200μ. The quenched sandwich properties indicate that there is considerable interplay between the binder and oxidizer species on the oxidizer portion of the sandwich surface, primarily because of the ability of the binder to form a flowable melt prior to gasification; sandwiches prepared with all 4 fuels formed a surface melt during combustion at every pressure level. Mass flux data generated indicate that all 4 fuels were effective in increasing the AP deflagration rate in the high-pressure region where AP burning rate vs pressure curve has a negative slope

M.W. Beckstead et al, 13 Symp (Int) Combustion (Proc) 1047–56 (1970) & CA **76**, 61477 (1972): A model developed previously by the authors described the general combustion properties of 3 types of composite proplnts and of 2 oxidizers burning as mono-proplnts. The math limiting conditions of the model correspond to the combustion in various environments of 3 different oxidizers: AP, HMX, and $KClO_4$. The

3 composite proplnts considered contained 78% of one of these oxidizers and 23% polyurethane binder by weight. The first case studied was that of a solid monoproplnt burning with a single premixed flame; apparently AP and HMX burn with a considerable energy release at the burning surface and in the gas phase; both reactions must be considered. The second case was that of composite proplnts containing $KClO_4$. These burn with a primary flame resulting from reaction of the oxidizer and binder decompn products. The third case was that of composite proplnts, such as those containing HMX, which burn with a primary flame and a monoproplnt flame, but no afterburning. Cases 2 and 3 are compared with calcns for a composite proplnt containing AP. The combustion model was compared with exptl data for the burning rates, their dependence on particle size and concn, and on pressure and initial temp, and for the variation of surface temp and of pressure exponent with pressure. In all 3 cases, the model described the general combustion characteristics of the systems

P.G. Willoughby et al, 13th Symp (Int) Combust (Proc), 1033–45 (1970) & CA **76**, 61748 (1972): The photographic study of solid proplnts burning in an acceleration environment supported previous findings that acceleration forces directed onto the burning surface may greatly raise the burning rate of aluminized solid proplnts, probably by heat transfer to the solid below from the burning Al globules held on the surface. The burning of 6 different composite proplnts at 200, 500 and 1000psia, and at accelerations $\leq$100g in a normal direction toward the burning surface, was photographed by high-speed color cinematography. Also, one proplnt was photographed with the acceleration vector oriented at 75° to the surface. Pits were formed in the burning surfaces by the extra heat transferred from the burning globules. All of the aluminized proplnts showed pit formation and growth, but the rate of growth depended on proplnt compn, pressure, and acceleration level. A high-burning-rate proplnt containing a Mg/Al alloy was not acceleration sensitive. The median diams of these agglomerates at 0 acceleration differed widely (130–440μ) for the different proplnts. The diam increased with acceleration and with pressure drop. The proplnts which formed the larger agglomerates were the most sensitive to acceleration. Scanning electron microscopy of residual slag and extinguished proplnt surface showed the slag particles characterized by large numbers of small surface holes and by tubular voids in the interior. Photomicrographs of AP particles in extinguished proplnts suggested subsurface evolution of gas and existence of a liq layer during combustion

Ya.B. Zel'dovich, FizGoreniyaVzryva **7** (4), 463–76 (1971) & CA **77**, 64194 (1972): The influence of turbulence and nonturbulence is examined relative to a proplnt burning in a gas flow. Equations indicate exptl methods for determining the magnitudes of the thermal conductivity and viscosity under turbulent flow, and permit a study of thermal flow distribution and temps in a gas wherein an exothermic chem reaction occurs. Equations for nonturbulent conditions can be used to calculate the distance from the surface of the proplnt to the zone of intense chem reaction and establish the relation of bulk burning rate to the vol reaction rate. A discussion of the theory of erosion burning (wherein the flow of combustion products increases the rate of proplnt burning) confirms the role of the Pobednostev criteria relative to such burnings

V.F. Buldakov et al, FizAerodispersnykh-Sist, No **5**, 77–82 (1971) & CA **77**, 64195 (1972): The results of an exptl study of the burning of 2-component (finely ground oxidizer with a high-polymer compd or a ballistic proplnt) heterogeneous systems under low pressure are presented. At a constant pressure, oscillatory burning was used

Yu.A. Gostintsev et al, FizGoreniyaVzryva **7** (4), 476–82 (1971) & CA **77**, 64917 (1972): Equations are given that indicate the changeover of the temp profile in the condensed phase of transition processes during proplnt burning in a semienclosed vol, and give parameters relative to proplnt and to surface, flame, and gas temps in the chamber. Graphic representations of intraballistic parameters as functions of time are given for four variants relative to such processes

V.A. Strunin et al, FizGoreniyaVzryva **7** (4), 498–501 (1972) & CA **77**, 64201 (1972): Equations relative to stationary burning stability indicate that such stability is greater at

lower activation energy for the chem reaction, and at higher heat of vaporization and initial temp. Instability is characteristic of substances which have a strong relation between rate and pressure. Stability criteria are significantly affected by the temp relation of the heat of vaporization

C.M. Mihlfeith et al, AIAA J **10** (10), 1280–85 (1972) & CA **78**, 6070 (1972): The response function relating mass flux perturbations of a burning solid proplnt to externally imposed periodic thermal radiation was measured over a range of frequencies of 20–80, depending on the fuel binder, oxidizer loading, and proplnt translucence. The compn and oxidizer loading affected the response, which is attributed to changes in the interfacial combustion dynamics. The total character of the response function is affected by changes in the proplnt fuel binder. A lower max response at resonance was noted for polybutadiene-acrylic acid-containing proplnts compared with polyurethane-containing opaque proplnts. Comparison of the measured response functions with predictions of theoretical models, which were modified to consider radiant-heat-flux effects for translucent proplnts rather than pressure perturbations, suggest general agreement between theory and expt. The technique is suggested for study of the effects of proplnt-formulation variations on solid-proplnt combustion dynamics

D.W. Blair, CombustFlame **20** (1), 105–9 (1973) & CA **78**, 113515 (1973): A simple heat-transfer model is coupled with an Arrhenius-type pyrolysis law to study the effect of solid-state heat-transfer losses on burning rates of solid rocket-proplnt strands. Such heat-transfer losses materially affect the burning rates and also cause extinction phenomena similar to some that had been observed exptly. Strand diam and compn, adiabatic burning rate, and the heat-transfer film coeff at the strand surface are important variables. Results of theoretical analysis are applied to AP-based composite solid proplnts

R.A. Battista & L.H. Caveny, USNatlTechInformServ, **AD 753835** (1972) & CA **78**, 161662 (1973): Solid rocket performance during rapid pressure increases differs greatly from predictions based on steady-state burning rate data. Rapid pressurization (150–250kpsi/sec) following a sudden throat-area decrease in a "low L star" combustor produces pressure overshoots of 10% and burning-rate overshoots greater than 50%. A transient internal ballistics model was developed incorporating nonsteady continuity and energy equations for the chamber, nonsteady energy equation for the proplnt condensed phase, and a modified Zel'dovich heat feedback function for the proplnt, which, for the conditions considered, is known to burn in a thin quasi-steady reaction zone

N.N. Bakhman, ArchProcesowSpalania **2** (1-2), 37–43 (1971) & CA **78**, 99930 (1973): Flame propagation along a layer of solid oxidizable polymer or metal powder in contact with a layer of solid oxidizer was investigated. The oxidizer was compression molded into tubes made from the polymer or compressed on the surface of W or Al powder tablets. $KClO_4$, $KClO_3$, BaO_2 and $KMnO_4$ were used as oxidizers. Poly (Me methacrylate) and polystyrene were the principal polymers used. For systems characterized by stable combustion, the flame-propagation rate was determined. The effects of the thicknesses of both layers, the density of the oxidizer layer, and the pressure on the flame-propagation rate were studied. The shape of the recess formed by combustion was compared with that resulting from the theory of diffusion

O.Ya. Romanov & G.G. Shelukhin, Gorenie-Vzryv, MaterVsesSimp, 3rd, 94–9 (1971) & CA **78**, 161665 (1973): A math analysis of the theory is presented on the basis of the combustion rate, the thermal conductivity, the heat capacity, the surface temp of the proplnt grains, and other factors. Expts were made to determine the relation of the combustion rate to acceleration for various proplnts. The rate of combustion at 70 atm was compared with the initial rate. The relation of the critical pressure of transitional laminar combustion to acceleration, and the dependence of the combustion rate of nitroglycol to the pressure at various acceleration rates were determined. Exptl observations were compared with results of theoretical calcns

V.V. Kleimenov et al, GorenieVzryv, MaterVsesSimp, 3rd, 426–28 (1971) & CA **78**, 161666 (1973): Motion-picture and spectral studies of the combustion products from a model rocket engine were conducted to determine the progressive temps, to identify the combustion products, and to establish equilibrium condi-

tions in the system. The emission spectra in the visible and ultra violet regions of the combustion products of gunpowder N without and with addn of 5% Al were determined for incomplete (20–30 atm) and complete combustion (80–90 atm) regimes. Bands and lines of the following radicals and mols were identified in the continuous background of the emission spectrum of the combustion products: N_2, C_2, CO, CN, CH, OH, H_2O, and AlO, AlH, and Al in the case of the combustion of N-Al powder mixts. The electron temps for C_2, N_2, CN and CO were 2200, 2000, 2210, and 1900°K resp. The differences between the measured progressive temps and the calcd electron temps indicate the absence of thermodynamic equilibrium

N. Ryan & A.D. Baer, USNatlTechInformServ, **AD 757234** (1973) & CA **79**, 33259 (1973): Conclusions of previous publications re combustion transients of solid proplnts are restated. The area of studies reported are an evaluation of the hot wire-ignition method for characterizing proplnts; development and study of gas-fueled analog of the solid-proplnt T-burner low-frequency combustion; high-frequency acoustic instability of solid proplnts, the T-burner and the radial-mode, radial-flow burner being used with the same proplnt systems; development and evaluation of a technique for measuring the solid-proplnt response function to external energy perturbations at the burning surfaces; measurement and evaluation of transient temps of proplnt flames during rapid depressurization; and low-pressure combustion of several different solid proplnts, including their low-pressure deflagration limits, the elec conductivity near the surface, the extinction requirements, and spontaneous reignition

R.F. McAlevy, III & R.B. Cole, USNatTechInformServ, **AD 757066** (1973) & CA **79**, 33260 (1973): Investigations over an 11-yr period of the mechanism of composite solid-proplnt deflagration and its component processes are reviewed. Exptl studies and techniques involving diagnostic measurement on analog burners of several types and characterizations of the linear pyrolysis of proplnt ingredients (polymers and AP) are included along with efforts to model the overall mechanism. All publications resulting from the work reported are cited

N.N. Bakhman et al, CombustFlame **22** (1), 77–87 (1974) & CA **80**, 110502 (1974): AP, $KClO_4$, formamidine perchlorate (I) and tetramethylammonium perchlorate (II) were used as oxidizers and poly (Me methacrylate) (III), polystyrene, soot, S and guanidine nitrate were used as fuels. For AP-III mixts, the catalyst effectiveness, $Z = u/u_0$ (where u_0 is the burning rate of an uncatalyzed mixt) increases with pressure. The Z for AP-III and AP-polystyrene mixts decreased with increasing ambient temp. Rapid increases in u and A occurred at small catalyst content but at m_c = 1–5%, Z increased only slightly. The catalyst effectiveness decreased as the u_0 increased; $Z_{max} = A/u_0^{0.65}$, in which A is a constant. AP- and I-based mixts were much more sensitive to catalysis by Fe_2O_3 than $KClO_4$ and II-based mixts, but Fe_2O_3 was an excellent catalyst for II when u_0 was decreased by adding diluents (KCl, NH_4Cl, or Al_2O_3). A diffusion-controlled model is proposed, taking into account the competition of catalytic and homogeneous reactions. The mechanism of catalysis in the burning zone is discussed

H.C. Mongia & L.L. Ambs, CombustFlame **22** (1), 59–69 (1974) & CA **80**, 110503 (1974): Some results are reported of the study of transient burning rate and crit-pressure decay rate required to cause extinction of a steadily burning solid proplnt subject to sudden depressurization. It is possible that the solid decompn products are rich in oxidizer immediately after the beginning of depressurization and rich in fuel afterwards. The calcd transient burning rates agree qualitatively with exptl values reported by Norton and Schulz (1970), Yin & Hermance (1971) and Fletcher & Bunde (1965). A stability analysis using the linear approximation predicts the existence of a min burning-surface temp below which stable combustion of the solid proplnt is not possible. The analysis correctly predicts the crit depressurization rate required to extinguish a burning solid proplnt by sudden venting of the combustion chambers

N.S. Cohen et al, AIAA J **12** (2), 212–18 (1974) & CA **80**, 135471 (1974): The effects of inert polymer binder properties on composite solid proplnt burning rate are described. Surface pyrolysis data for many polymers over a wide range of conditions are used to derive kinetics constants from Arrhenius plots and heat of

decompn from an energy balance. Pyrolysis kinetics varied between the polymers, but were found to be independent of N pressure, the presence of AP or catalysts in the sample, and their combinations. All of the polymers exhibited molten, boiling surfaces mingled with char, to varying degrees; the low activation energies may be associated with the boiling or with a weak-link decompn mechanism. Relevant data were input into the Derr-Beckstead-Price combustion model in order to associate binder properties with known effects on burning rate in simple propellants. Although the effects were predictable, they stemmed from properties other than pyrolysis kinetics. The role of the binder appears to be in controlling the gas phase processes and not the surface pyrolysis properties

J.L. Murphy & D.W. Netzer, AIAA J **12** (1), 13–14 (1974) & CA **80**, 135474 (1974): Color schlieren of AP are photographed in a N-purged combustion bomb at 100–1000psig to study AP deflagration and AP-binder sandwich combustion. The method provides more complete behavioral data during the combustion process

K.K. Kuo & M. Summerfield, AIAA J **12** (1), 49–56 (1974) & CA **80** 135475 (1974): High-speed flame propagation well above the normal deflagration rate is achieved in the combustion of porous proplnts. Gas-penetrative burning of porous proplnts under strong confinement is inherently self-accelerating, but under suitable physical conditions, a constant-speed combustion wave can be produced. The jump conditions and the equiv Rankine-Hugoniot (R-H) relation for porous proplnt burning are derived. Whereas the usual R-H relation forbids the existence of a steady-state combustion wave that has both a pressure rise and a density decrease (called forbidden region on the R-H curve), this restriction can be bypassed here and high-speed compressive-expansive waves are legitimate solutions of the equations. The structure of the wave and its speed of propagation are affected by proplnt porosity, ignition temp, specific burning area, gas permeability and pressure. The flame propagation speed is determined as the eigenvalue of this 2-point boundary value problem

Reactivity

M. Frey, Explosivstoffe **15** (5), 97–105 (1967) & CA **68**, 31678 (1968): The decompn of Ph_2NH in NG and NC was measured at 50–100°. At 90°, samples open to the air decompd more rapidly initially, but more slowly later, and partially closed samples reached an autocatalytic stage in 18 days, whereas closed samples decompd more slowly at first, but continued to decomp and took longer to reach the autocatalytic stage. The disappearance of Ph_2NH was followed by extraction with CH_2Cl_2, drying the extract, dissolving in MeOH, and measuring polarographically. Nitro and nitroso diphenylamine could be measured directly. The 2-nitro and 4-nitro derivatives could be separated by thin-layer chromatography. Residual Ph_2NH could be determined after conversion to the N-nitroso derivative. The Ph_2NH decreased linearly with time at a rate set by the decompn of the NG or NC. The N-nitrosodiphenylamine passed thru a max and the nitrodiphenylamine increased regularly. Based on these data, the energy of activation for the decompn of NC was found to be 29.5kcal/mole with a range of 27.2–34.2 for different samples. Similar calcns from the stability times yielded values of 27.2–27.6kcal/mole. This compares with the literature values for pure NC of 39.2 and 49kcal/mole. Similar expts with NG indicated an energy of activation for decompn of 29kcal/mole. It is suggested that these values can be used to estimate the life of the compns under normal storage temps

G.D. Sammons, Analytic Calorimetry, Proc-AmerChemSymp, 155th, 305–11, Edited by Porter, Plenum Press, NY (1968) & CA **70**, 89323 (1969): The proplnts studied were in the form of disks, 3–5mm in diam and 280–840μ thick. A modification of the Rogers & Morris equation (of CA **64**, 17345) based on the theory of Borchardt & Daniels (of CA **51**, 6296) was used in evaluating the kinetic parameters. The thermogram of the proplnt binder (a linear polybutadiene polymer) shows an exotherm at 570°K (probably due to vinyl polymerization). The average activation energy was 33 ± 3kcal/mole. The thermogram of AP (oxidizer) shows a phase change at 516°K (orthorhombic to cubic), a low temp decompn at about 600°K (30%) and a high temp decompn (100%) at 725°K. The termination at 30% decompn at 516°K is

probably due to a concn of adsorbed ammonia on the surface of the AP. The activation energy for high-temp decompn (127kcal/mole) is in disagreement with that obtained by thermogravimetric analysis (35kcal/mole) and is due to the fact that differential scanning calorimetry is sensitive to many other processes, such as proton transfer, taking place in the sample to which thermogravimetric analysis is not sensitive

H. Selzer, AGARD Conf Proc **52**, 24 (1970) & CA **73**, 100599 (1970): AP-based composite solid proplnts, most commonly used in modern day rocketry, are discussed. Recent work since previous reviews is discussed and areas where additional work is needed are indicated. New facts are given concerning the effects of lattice defects and condensed-phase behavior of the burning process. The findings require revision of the theoretical models to account for lattice defects, for a change from fast to slow decompn, and for spots of high reactivity (size 1–10μ)

J.F. Lieberherr, AGARD Conf Proc **52**, 23 (1970) & CA **73**, 100605 (1970): In hybrid-propint combustion studies, disparities between exptl results and simplified models based on gas-solid heat transfer led to research on other mechanisms. New models, mathematically derived, based on chemical surface reactions are in better agreement with actual results. The surface reactions are less related to simple vaporization than to a melting mechanism, followed by liq flow. The melting rate depends on the gasification rate and has an inverse pressure sensitivity, while the gasification rate has a direct pressure sensitivity. It was concluded that means that will destroy the liq layer and promote combustion efficiency, other than already existing turbulators, are difficult to visualize. One possible way is to make use, as much as possible, of surface reactions and to avoid proplnts that have too low a Prandtl number in the liq phase. Another way would be to take advantage of the particular conditions under which combustion takes place in the injection zone

G.L. Pellett, AIAA J **8** (9), 1560–66 (1970) & CA **73**, 100610 (1970): A pulsed ruby laser-mass spectrometry technique was developed and applied, wherein granular mixts of AP and light-absorbing substrate materials were rapidly flash pyrolyzed (0.8msec) within the low-pressure ion-source chamber of a Bendix TOF mass spectrometer. Gaseous products from AP mixed with carbon black, Cu chromite, Fe_2O_3, and MnO_2 indicated a predominance of high-temp heterogeneous reactions. The first step appeared to be proton transfer dissociation of AP into NH_3 and $HClO_4$. Adsorbed $HClO_4$ underwent rapid heterogeneous decompn on the substrate material; ClO_2 and HCl were evolved as major products, but ClO_3, ClO, and Cl_2 were only minor products. Chemisorbed O and O carriers, such as OH and ClO were likely formed on the substrate simultaneously, however. These could react with adsorbed NH_3 and its dehydrogenated fragments to form H_2O, NO, and HOCl as major gaseous products. N_2, N_2O, and NO_2 were minor products. Low-pressure isothermal decompns of AP and AP/substrate mixts in a glass capillary were utilized to compare product distributions. The site of $HClO_4$ decompn (crystal vs substrate surface) was at least as important as temp and effective residence time in determining the predominant chemistry

K.O. Hartman & R.C. Musso, WestStatesSect-CombustInst (Pap) **WSCI 72-30** (1972) & CA **78**, 113507 (1970): The thermal-decompn kinetics of liq NG dispersed in alkali metal halide disks in the range 90–160° is first order; $k = 2.5 \times 10^{14} \exp(-34{,}400 \pm 1500/RT)\ sec^{-1}$. The rate determining step is probably scission O–N bonds. In the liq phase, the decompn mechanism is more complex with an overall rate of 0.5 order. The thermal decompns of $EtNO_3$ and ethylene dinitrate in halide disks were also studied. The increase in rate from $EtNO_3$ thru ethylene dinitrate to NG is attributed to an increase in th entropy of activation. Thermal decompn of CMDB proplnts containing AP shows autocatalytic behavior; for prolonged storage, a stabilizer is necessary. The rate-controlling process during the induction period is probably decompn of NG. CMDB proplnts containing AP should last 50 years without significant degradation at 40° when stabilized with resorcinol

A.N. Kiselev et al, FizGoreniyaVzryva **8** (4), 595 (1972) & CA **78**, 161672 (1973): The effects of shock waves produced by Ammonite 6Zh expln on powdered AP were examined. The AP, after having been exposed to expln, was studied by DTA (differential thermal analy-

sis) and TGA (thermogravimetric analysis). Although no chemical changes occurred, there was a considerable change in the density of the dislocations, resulting in an increasing number of pores. These changes strongly affect the temp of the beginning of low-temp thermal decompn. The rate of high-temp decompn is not influenced by the shock-wave pretreatment

Detonability & Safety

R. McGill, USDeptCom, Office Tech Serv, **AD 272424** (1961) & CA **60**, 10463 (1964): Expls, proplnts and pyrotechnic safety covering laboratory, pilot plant, and production operation

W.H. Anderson & R.F. Chaiken, ARS (Amer Rocket Soc) J, **31** (10), 1379–87 (1961) & CA **61**, 6849 (1964): A theoretical model of propagation of detonation in proplnts is presented. This model is based on the hypothesis that detonation is propagated by the same rate-controlling chemical reactions that occur during normal burning of the proplnt. In particular, it is assumed that a grain burning of the oxidizer occurs and that the rate of linear-surface decompn (pyrolysis) of the oxidizer can be used to describe the rate of the detonation reaction. Kinetic data on the surface decompn of AP, which were obtained by the hot plate-linear pyrolysis technique, suggest that sublimination of AP (with an apparent activation energy of about 22kcal/mole) is the rate-controlling step in the surface decompn of this oxidizer. A discussion is presented on how these data can be used in conjunction with the detonation model to calculate the min (crit) diam at which detonation can propagate in a cylindrical charge of solid proplnt. The possible effect of various proplnt parameters, ie, oxidizer-binder ratio, oxidizer particle size, and confinement on the detonation process is discussed. The role of ignition, diffusion, and heat conduction processes in the detonation and rapid deflagration of solid composite proplnts is discussed. A preliminary theoretical approach to accelerating burning in porous proplnt is also presented. This approach indicates that porous burning in rocket motors containing solid composite proplnts can lead to very rapid chamber pressure build-up so that an expln could occur within several millisec after porous burning begins

Donna Price et al, IndChimBelge **32** (SpecNo), 506–10 (1967) & CA **70**, 49142 (1969): Solid rocket proplnts were tested for shock sensitivity and detonability by the NOL Standard Card-Gap Test. The proplnts act as high explosives, showing the same trends as conventional explosives of increasing shock sensitivity with increasing porosity or increasing temp. A porosity effect and a temp effect upon detonability were also observed. Some relatively low energy materials are improperly classified as insensitive

H.M. Shuey, AdvanChemSer No **88**, 296–300 (1969) & CA **71**, 51811 (1969): The identification and evaluation of hazards in the manuf of solid proplnts are being brought to a semiquantitative state of the art. Indiscriminate use of routine "approved" tests is being supplanted by analysis of the processes and operations to be used. By identifying the principal stresses involved (as thermal, friction, impact, electrostatic), one can design specific "use" tests resulting in numerical values broad enough to distinguish discrete differences in stimuli necessary to ignite materials tested. Consideration of the consequences of such ignition allows tests to assess the worst catastrophe probable and suggests modifications of process conditions or plant construction to minimize risk to personnel, facilities, and product

N.J. Blay & I. Dunstan, USNatTechInformServ, **AD 744871** (1970) & CA **78**, 6069 (1973): Compatibility and stability problems encountered in the design and development of weapon systems containing expls and solid proplnts are discussed. Safety during storage and reliability in service are emphasized. The effects of materials used near or in contact with the expls and proplnts are considered

Analytical Procedures & Data

M. Roth, USDeptCom, Office TechServ, **AD 296018** (1963) & CA **60**, 10464 (1964): In general, stabilizers function by reaction with proplnt decompn products. A number of methods have been described and a preliminary evaluation of these methods was conducted by several labs under a cooperative program. Based on results from these screening tests, the PicArsn spectrophotometric methods for available stabilizer and primary degradation products were selected for further study. The initial phase of this program was an attempt to standardize the necessary spectrophotometric factors. Significant differences with regard to the factors obtained

existed between labs. It was suggested, however, that these differences would be cancelled if each lab used the factor appropriate to its spectrophotometer

G.N. Kruse et al, USDeptCom, Office Tech-Serv, **AD 297333** (1959) & CA **60**, 10464 (1964): Solid-proplnt combustion products resulting from firing 2.5-inch rockets from F-102 airplanes were found to consist of C, various organic materials, and Mg or MgO. Twenty-nine materials were tested to determine their efficiency in removing heavy combustion-product deposits. Three of these materials, Rocket Cleaners X2-6, X2-9 and X2-11, were suitable for combustion-product removal

W. Stark & B. Hornstein, NASA Doc **N62-12792** (1962) & CA **60**, 10464 (1964): A spectroscopic method for measuring burning rates in an operating solid proplnt motor was investigated. The principle is to detect spectroscopically in the exhaust the appearance of emission from a tracer compd previously embedded in the grain. Li tracer emission was detected against background radiation from Al_2O_3 in the exhaust. The necessary correlation between tracer detection in the exhaust and progress of the burning surface in the motor was partially accomplished; difficulties encountered relate primarily to tracer excitation by the flame front

S.K. Sinha et al, Current Sci (India) **33** (5), 141–2 (1964) & CA **60**, 11835 (1964): The thin-layer technique (CA **60**, 6691) utilizes aliquots of proplnt ether extract (I) and the ether soln (II) of a known mixt. II consists of nitrates of glycerol and glycol, di-Bu or di-Et phthalates, Et or Me centralites, DNT, and diphenylamine. The chromatoplates are made of 85:15 silica gel and plaster of Paris. These plates, containing spots of I and II, are developed with 1:1 C_6H_6-petroleum ether, then sprayed with specific detectors by color. The method is much quicker and easier than chemical analysis and simpler than infrared spectroscopy and column chromatography

J. Tranchant, IndChimBelge **32** (Spec No), 601–5 (1967) & CA **70**, 49146 (1969): A gas-phase method of chromatographic analysis is described for measuring stabilizers and some of their derivatives, as well as a method for the chromatographic sepn in thin layers of nitro and nitroso derivatives, as well as an accurate detn of mixts of Ph_2NH and centralite. With thin-layer chromatography, the gas-phase chromatographic method is a good method for studying the stability of powders during storage

F.I.H. Tunstall, Chromatographia, **11–12**, 477–80 (1968) & CA **70**, 41947 (1969): A knowledge of the nature and amount of gas evolved from stored proplnt compns provides valuable information on the stability, compatibility, handling and storage characteristics of such compns. A gas chromatographic method is described for the sepn and detn of N, O, CO, NO, CO_2 and N_2O employing a single column thermal conductivity detector system. Sepn of N, O, CO and NO is achieved by operation of a 4.5m column packed with Porapak Q at $-70°$ and by rapid heating of the column to $+20°$, CO_2 and N_2O well separated, are eluted. For detection, calibration curves of gas partial pressure against integrated peak area were produced

K. Mehlhose, Explosivstoffe **20** (3-4), 37–70 (1972) & CA **78**, 113513 (1973): Methods developed for detn of H_2O in gun and rocket proplnts are: column distn with n-PrOH and gas-chromatographic analysis of the distillate, corrected for continuous formation of water in decompn reactions; and photometric methods, both based on the reaction of $CoCl_2$ with water. Choice of the methods is based on a critical review (117 refs) of the usual methods of water detn by chemical and physical methods. A theoretical and exptl analysis of the new methods was made and their results compared with those of older methods. Application to mono-, di-, and tribasic and to double-base NC and poly (vinyl nitrate) proplnts is discussed

Miscellaneous

R.L. Bohon, AnalChem **35** (12), 1845–52 (1963) & CA **60**, 1527 (1964): Approx heats of expln, Q_v were detd on mg amounts of proplnts and expls by differential thermal analysis (DTA). Small-screw-cap metal cups sealed with a Cu washer served as constant vol sample containers; the initial cup pressure could be controlled from 0 to approximately 1000psia. The calibration constant was calcd for each run from the total heat capacity of the cup and the relaxation curve, thereby compensating for equipment variations.

Nine runs on JPN proplnt gave an average Q_V of 1110± 140cal/g at 250°. Systems examined included N-5, JPN, ABL-2056, TNT/AN/NaCl, TNT/AN/paraffin, and $C(NO_2)_4$ proplnts; TNT, RDX, PETN, Tetryl, and NG expls. DTA-detd Q_V values can be misleadingly low when evaluating the potential destructive power of a material

R.C. Oliver et al, USDeptCom, Office TechServ, **AD 265822** (1961) & CA **60**, 10466 (1969): Metal additives for solid proplnts: formulas for calculating specific impulse and other proplnt performance parameters are given. A mathematical treatment of the free-energy minimization procedure for equilibrium compn calcns is provided. The treatment is extended to include ionized species and mixing of condensed phases. Sources and techniques for thermodynamic-property calcns are also discussed

E. Kuletz & J.M. Pakulak, Jr, USDeptCom, Office TechServ **AD 291792** (1962) & CA **60**, 10466 (1969): Effects of thermal aging on a cast-composite proplnt: the activation energy, E, frequency factor, A, and specific rate constant, k, were determined for the exposed surface, subsurface, and internal regions of 5 cast-composite proplnt (ANP-2639 AF) motors thermally aged at various temps from 95° to 165°F for different periods. The E values of the exposed surfaces for the 95° and 130°-aged samples were essentially identical (23kcal/mole), while there was a 4kcal/mole increase for the samples aged at 150° and 165°F. For the subsurface regions, 0.005–0.010 inch below the surface, the E values are similar – each is approximately 25kcal/mole. E, as well as A, varies with the aging history of the sample. A comparison of all E values and a study of the relations of temp to a rate factor indicate that, for the thermally aged proplnt grains, the primary component altered at the surface is the binder. In the interior, it is the oxidizer

J.W. Jones, APL Bull Meeting, Interagency Chem Rocket Propulsion Group, Working Group Mech Behavior, 3rd, **1**, 371–94 (1964) & CA **63**, 17781 (1965): Proplnt failure characteristics were measured in uniaxial and biaxial stress states for polybutadiene acrylic acid and Nitroplastisol proplnts, and failure conditions were examined over a wide range of temps. The observed failure conditions were compared for various failure criteria, and it was found that a max tensile stress criterion accurately resolved the data for uniaxial tensile, biaxial tension-tension, simple shear, and biaxial tension-compression stress states. The expts gave indications of the granular reactions of the solids during deformations to failure in tests made in the biaxial tension-compression mode. Examination of the influence of temp on the multiaxial failure characteristics of proplnts gave evidence to support the applicability of the max stress failure criterion over wide ranges of temps. In studies of the effect of binder and oxidizer variations on failure, it was found that reasonable agreement with the max tensile stress criterion was obtained for wide variations in formulations

D.E. Cantey, APL Bull Meeting, Interagency Chem Rocket Propulsion Group, Working Group Mech Behavior, 3rd, **1**, 317–44 (1964) & CA **63**, 17782 (1965): Dielectric spectroscopy was investigated as an analytical tool to assist in the elucidation of chemicophysical effects in solid proplnt systems. Complex dielectric properties were measured over a wide temp range and at frequencies from 50 to 10^5 cycles/sec for polybutadiene-acrylic acid (PBAA), carboxy-terminated polybutadiene (CTPB), and NC-base proplnts and ingredients. The measurement range was extended to low frequencies by measurement of dielectric absorption response to step function dc potentials over time ranges from 10 to 10^6 secs. Spectral response of the complex dielectric constant storage and loss components is interpreted in terms of classical electrical polarization mechanisms

J.N. Lhuillier, IndChimBelge **32** (Spec No Pt 3), 669–75 (1967) & CA **70**, 69708 (1969): A discussion with 10 refs of combustion instability in solid-proplnt rocket engines. Two different types of instability are considered: acoustic and non-acoustic instability

P. Tavernier, IndChimBelge **32** (Spec No Pt 3), 337–46 (1967) & CA **70**, 69709 (1969): A discussion with 14 refs on expls and proplnts considering the thermodynamic characteristics of expl substances, the kinetics of combustion of powders and the effects of catalysts, corrosion, and instability on the kinetics, the occurrence of deflagration on detonation, and forms of solid mixts in view of the augmentation of their performance and the extension of conditions used in their mixts. The importance of modern methods of calcn is stressed

G.A. Fluke, AdvanChemSer No **88**, 165–87 (1969) & CA **71**, 51809 (1969): The processing techniques for manuf of composite solid proplnts are described. The general oeprations of oxidizer prepn, binder and fuel prepn, proplnt mixing, and chamber insulation and lining are illustrated by typical flow sheets and descriptions of the equipment used. Limited data on the performance of this equipment are presented. The importance of characterizing the processability of proplnts is introduced together with an instrumental method for achieving this characterization on a comparative basis. New processing systems, such as pneumatic mixing and inert diluent mixing, are discussed with their apparent advantages and likely limitations

A.E. Oberth & R.S. Brenner, AdvanChemSer, No **88**, 84–121 (1969) & CA **71**, 51810 (1969): Solid proplnt technology as pertaining to polyurethane-based proplnts is presented. Particular emphasis is placed on the newer developments as well as the fundamental knowledge gained in the field. Much of this knowledge is not restricted to solid proplnt technology but is of general nature. This includes contributions to kinetics and mechanism of the urethane reaction, metal catalysis, the effect of fillers on mechanical properties of filled elastomers, tear phenomena in composite materials, the importance of the interface between solid particle and matrix on physical properties, and the mechanism of filler reinforcement. Progress pertaining more directly to proplnt technology includes such topics as catalyst modification to increase the pot life of proplnt batches, calcn of mix viscosities of multinodal dispersions, mechanism and prevention of moisture embrittlement, and others

D.W. Blair & W. Lake, AIAA J **7** (9), 1808–10 (1969) & CA **71**, 126690 (1969): The radiant energy flux emitted thru a small viewing port in the side of an internal burning cylindrical solid proplnt rocket motor is detd, and the data are interpreted in terms of net heat flux to the burning surface, ie, in terms of heat transfer from the gas phase flame zone to the solid surface to provide the enthalpy of heating and vaporization for the solid phase. Data are given for solid fuels comprising AP in a polybutadiene-acrylic acid or polyurethane binder. The radiant energy flux is apparently a significant portion of the total heat flux at the burning surface of the solid proplnt

K. Suzuki et al, KogyoKayaku **30** (3), 126–30 (1969) & CA **71**, 126692 (1969): Composite proplnts composed of AP 65–80, Al 7–8, binder (polybutadiene, polyether, polysulfide) 14–28, and burning catalyst 1–3% by wt were subjected to the following aging test: outdoors, in dry N at ambient temp and 80°; with wetting at 50°, and 30% relative humidity for 12 days, and drying with $CaCl_2$ at 3mm. In summer, the elongation and tensile strength of polysulfide and polybutadiene-based proplnts decrease in outdoor air. In winter, and even in summer, the properties are restored by drying. Proplnts using polyester as binder absorb considerable moisture and depolymerization occurs. No change in mechanical properties is observed in polybutadiene proplnts at ambient temp in dry air, but at 80° a slight change is observed. Polybutadiene proplnts absorb moisture and an increase in elongation and a decrease in tensile strength occur at higher humidity, but these properties are restored by drying

T.L. Boggs et al, AIAA J **8** (2), 370–72 (1970) & CA **72**, 113371 (1970): Scanning electron microscopy is used to study the surface structure of solid proplnts, prepd from AP (I) and polyurethane or carboxylated polybutadiene. Polyurethane proplnts are self-extinguishing at high pressure due to the flow of molten binder over I crystals. I crystals formed a thin surface melt with gas liberation in the molten phase

V.A. Veretennikov et al, FizGoreniyaVzryva **5** (4), 499 (1969) & CA **72**, 123552 (1970): Shock compressibility of compact and porous NB (Ballistite) proplnts: Shock Hugoniots of 60/40 NC/NG were determined at ρ = 1.63 and 1.0g/cc, respectively. Particle velocity, u, was measured:

$U = 1.70 + 1.85u$ for ρ = 1.63g/cc

$U = 0.58 + 1.68u$ for ρ = 1.0g/cc

ΔT at shock front is calcd

V.V. Aleksandrov & S.S. Khlevnoi, FizGoreniyaVzryva **6** (4), 438–43 (1970) & CA **75**, 89714 (1971): Earlier work showed that the surface temp, T_s, of NG powder (a mixt of NC, NG and DNT) in flameless combustion does not depend on the initial temp. On the basis of expts conducted at elevated temps and pressures, the mean heat of vaporization of a volatile com-

ponent was estimated to be about 26kcal/mole, and a formula was derived for the relation between the pressure p and T_S on the assumption that vaporization of these components determines T_S. T_S at p less than 20–30mm calcd from this formula was less than 194–98° vs 300–10° determined exptly. NG proplnt tablets were heated in a vacuum. Surface temps were measured and related to diffusion of the volatile components to the surface followed by their evaporation. They indicated that, upon evaporation of NG and DNT, a surface must form that consists almost entirely of NC and that this surface becomes overheated to a temp above the bp of the volatile components. Calcn showed that if flameless combustion of NG proplnt took place at a T_S equal to the bp of the volatile components (about 200–30°), the combustion rate would be lower by a factor of 18–50 than that observed exptly

A. Sapinski, Arch Procesow Spalania **3** (2), 179–90 (1972) & CA **78**, 99929 (1973): Temp mesurement of a flame containing solid particles by the emission-absorption method: The method was used for investigation of solid proplnts containing Al and Mg powder. The method is described in detail and its errors are analyzed. The effects of solid particles on radiation propagation are discussed

H. Schubert, ChemZtg **97** (9), 486–92 (1973) & CA **80**, 28964 (1974): A brief historical survey of solid rocket proplnts is followed by a description of solid proplnt motors and of the uses of the proplnts. The compn and the process technology of two fundamentally different types of proplnts, ie, homogeneous or double-base solid proplnts and heterogeneous or composite solid proplnts, are described. Their properties are reviewed

Written by **J. ROTH & E. L. CAPENER**

Refs: 1) C.F. Schönbein, SitzungsberNaturforschGesBasel **7**, 27 (1846) 2) J.H. Pelouze, CR **23**, 809, 837, 861, 892 (1846) 3) E. Schultze, DeutscheIndustrie-Ztg **10**, III (1865) 4) F. Volkmann, AustrianP 21/208, 21/257 (1871); also according to O. Guttmann, "Zwanzig Jahre Forschritte in Explosivstoffen", Berlin (1909); & SS **4**, 16 (1909) 5) J. Hartig, "Untersuchungen über den Bestand und die Wirkungen der explosiven Baumwolle", Braunschweig (1874) 6) D. Spill, BritP 1739 (1879) 7) W.F. Reid, BritP 619 (1882) 8) W. Wolf & F. Forster, GerP 23808 (1883) 9) A. Nobel, BritP 1471 (1888) 10) F.A. Abel & J. Dewar, BritP 5614 (1889) 11) P. Vieille, MP **3**, 9, 177 (1890); **4**, 256 (1891); **7**, 19, 30 (1894); **11**, 157 (1901); **15**, 61 (1909–1910); & SS **6**, 181, 303, 327, 441 & 464 (1911) 12) D.I. Mendeleyev, "Sochinenya", Vol **9**, IzdAkadNaukSSSR, Leningrad-Moskva, 1949: Morskoy Sbornik **268**, 38 (1895); **272**, 39 (1896); BullSocd'encourSci (4) **10**, 1100 (1893); & Engineering **63**, 180 (1897) 13) W. VonLenk, according to S.J. Romocki, "Geschichte der Explosivstoffe", Bd **II**, Oppenheim, Berlin (1896) 14) M. vonDuttenhofer, according to H. Brunswig, "Das rauchlose Pulver", deGruyter, Berlin-Leipzig (1926); BritP 6002 (1887) & 8776 (1902) 15) C. Claessen, GerP 256572 (1910–1913) 16) H. Gallwitz, "Die Geschützladung", Heereswaffenamt (1944), according to Technical PB Rept **925** (1945) 17) J. Roth, ProcONRConfOnChem&PhysOfDetonation, 51–61 (1951) 18) B.L. Hicks, JChemPhys **22**, 414 (1954) 19) A. Maček, JChemPhys **31**, 162 (1959) 20) N. Griffiths & J.M. Groocock, JCS **1960**, 4154 21) R. Steinberger, "Preparation and Properties of Double-base Propellants", Chemistry of Propellants, AGARD Panel, Paris (1959) 22) M. Summerfield, Ed, "Solid Propellant Rocket Research", Academic Press, NY (1960), 623 23) Bruce F. Greek, I&EC **52**, 12, 974 (1960) 24) Anon, Propellant Performance Data, Gallery Chemical Co (1961) 25) R.F. McAlevy & M. Summerfield, ARS J **32**, 270 (1962) 25a) V.S. Ilyukhin & P.F. Pokhil, DAN **140**, 179 (1961) & CA **56**, 6229 (1962) 26) H. Allen Jr & M.L. Penns, NASA Lewis Research Center, **TND-1533** (Jan 1963) 27) Anon, "Propulsion and Propellants", **AMCP 706-282** (1963) 28) F.I. Ordway Ed, "Advances in Space Science & Tech", **5**, 60, Academic Press, NY (1963) 29) R. Anderson et al, AIAA Preprint **63-514** (Dec 1963) 29a) S. Wachtell, Preprints, ACS Symp on Explosive Hazards and Testing of Explosives, Vol **7**, No 3, 83 (1963) & CA **63**, 2837 (1965) 30) R. Anderson et al, AIAA Preprint **64-156** (Jan 1964) 31) E. McAbee & M. Chmara, JAppPolymerSci **8**, 3 (1964) 32) L.A. Dickinson & E.L. Capener, "Study of the Origin

and Propagation of Disturbances in Burning Propellant", SRI Project Rept **PRU-2770** (May 1964) 32a) Anon, CPIA/M2 Manual (June 1964) 33) A.M. Ball, "Solid Propellants, Part 1", **AMCP 706-175** (Sept 1964) 34) D.D. Perry, ACS Division of Fuel Chem **9**, 1, 118 (April 1965) 35) M.S. Cohen, ACS Div of Fuel Chem **9**, 1, 100 (April 1965) 36) C.E. Hermance et al, AIAA J **3**, 1584 (1965) 36a) D. Price & J.F. Wehner, CombustFlame **9**, 73 (1965) 36b) Anon, **AFRPL-TR-65-11** (1965) & **AFRPL-TR-67-211** (1967) (Project *SOPHY*), quoted in **AMCP 706-180**, 11-21 & 11-22 (1972) 37) R.N. Chappell, Bulletin 4th MeetingICRPGWorkingGpOnMechBehavior (Oct 1965) 38) G.S. Pearson & D. Sutton, AIAA J **4**, 954 (1966) 39) E.W. Price et al, AIAA J **4**, 1, 1153 (1966) 39a) N.L. Colburn, AIAA J **4**, 521 (1966) 40) E.L. Capener et al, "Propellant Combustion Phenomenon During Rapid Depressurization", **SRI Rept FRU-5577**, July 1 1965–June 30 1966 (Sept 1966) 40a) N.L. Coleburn & T.P. Liddiard, JChemPhys **44**, 1929 (1966) 41) P.E. Gahr & E.W. Madison, "Application of Large Vertical Helical Mixer for Mixing Composite Propellants", Paper AIChE 60th Meeting, Atlantic City, NJ (1966) 42) D.C. McGehee & P.K. Meyers, ChemEngrProgressSympSeries **62**, 6, 19 (1966) 43) S.F. Sarner, "Propellant Chemistry", Reinhold Pub Corp, NY (1966) 44) G.S. Pearson & D. Sutton, AIAA J **5**, 344 (1967) 45) E.L. Capener et al, AIAA J **5**, 5, 938 (1967) 46) N. Fishman, AIAA J **5**, 1500 (1967) 46a) T. Urbański, "Chemistry & Technology of Explosives", Vol **3**, Pergamon Press, NY (1967) 46b) E.N. Aleksandrov et al, FizGoreniyaVzryva **3**, 471 (1967) & CA **69**, 45001 (1968) 47) E.W. Price, 12th IntSympComb, 101 (1968) 47a) A.B. Amster et al, AIAA Paper **68-524**, 3rd Solid Propulsion Conf (1968); not found in CA 48) R.N. Chappell et al, JSpacecraftandRoc **5**, 1, 42 (1968); not found in CA 49) V. Quan, "Analytical Prediction of Delivered Specific Impulse", **NASA CR-1123** (Aug 1968); not found in CA 49a) A.I. Korotkov et al, Combustion, Explosion & Shock Waves **5**, 216 (1969) & CA **72**, 33876 (1970) 49b) A.V. Obmenin et al, Ibid **5**, 317 (1969) & CA **72**, 123574 (1970) 50) E.C. Francis & C.H. Carlton, JSpacecraft&Roc **6**, 1, 65 (1969); not found in CA 51) P.W.M. Jacobs & H.M. Whitehead, ChemRevs **69**, 581 (1969) 52) W.D. Hart et al, JANNAFMechBehaviorWorkingGrp, 8th Meeting (1969); not found in CA 52a) V.A. Veretennikov et al, FizGoreniyaVzryva **5** (4), 499 (1969) & CA **72**, 123552 (1970) 52b) J. Calzia & H. Carabin, 5thONRSympDet, 231 (1970); not found in CA 53) Anon, "Recommended Procedure for the Measurement of Specific Impulse of Solid Propellants", CPIA Publication **174** rev (Aug 1968), **AD 838907** 54) H.M. Fisher, USP 3666575 (1972) & CA **77**, 50942 (1972) 55) M. Fein et al, USP 3698969 (1972) & CA **78**, 32237 (1973) 55a) Yu.V. Frolov, V.F. Dubovitskii et al, CombustExpl&Shock **8**, 296 (1972) & CA **78**, 45823 (1973) 56) N.P. Suh et al, "On the Ignition and Deflagration of Nitrocellulose Based Solid Propellant", PATM **2064** (Dec 1972) 57) T. Merrow et al, USP 3732132 (1973) & CA **79**, 33283 (1973) 58) R.M. Wall, USP 3741830 (1973) & CA **79**, 81028 (1973) 58a) B.J. Alley & H.A. Carter, USP 3745078 (1973) 59) E.W. Vriesen & J.C. Merges Jr, USP 3748199 (1973) & CA **79**, 106554 (1973) 60) Anon, "Computer Programs for Chemical Engineers–1973", Part 1, Chem Eng, 121 (Aug 30, 1973) 61) D.C. Sayles, USP 3764420 (1973) & CA **80**, 61702 (1974) 62) J. Reinhart, USP 3767489 (1973) & CA **79**, 142344 (1973) 63) J.P. Blackwell, USP 3779825 (1973) & CA **80**, 135506 (1974) 64) R.G. Shaver, USP 3779826 (1973) & CA **80**, 122952 (1974) 65) M.G. Baldwin & S.F. Reed, USP 3781178 (1973) & CA **80**, 135502 (1974) 66) R.W. Lawrence, USP 3793097 (1974) & CA **80**, 147448 (1974) 66a) E.J. Mastrolia & H.J. Michigian, USP 3801385 (1974) 67) D.C. Sayles, USP 3811965 (1974) & CA **81**, 108111 (1974) 68) W.E. Hill & L.R. Beason, USP 3811966 (1974) & CA **81**, 65772 (1974) 69) R.W. Lawrence & A.J. Secchi, USP 3822159 (1974); not found in CA 69a) R.R. Bernecker & D. Price, Combust Flame **22**, 119 (1974) 69b) Ibid, 161 (1974) 70) P.G. Butts & W.E. Baumgartner, USP 3861970 (1975); not found in CA 71) T.P. Rudy & H.J. Hayer, USP 3864178 (1975); not found in CA 72) M. Klunsch et al, USP 3862864 (1975); not found in CA 73) J.P. Flynn et al, USP 3865656 (1975); not found in

CA 73a) J.P. Flynn et al, USP 3865659 (1975); not found in CA 74) P.L. Nickols Jr, USP 3870578 (1975); not found in CA 75) J.B. Eldridge et al, USP 3876477 (1975); not found in CA 76) J.W. Lavitt, USP 3890175 (1975); not found in CA 77) D.C. Sayles, USP 3914141 (1975); not found in CA 78) C.W. Huskins, USP 3914140 (1975); not found in CA 79) M.L. Jones & D.W. Booth , USP 3914139 (1975); not found in CA 80) D.C. Sayles, USP 3914142 (1975); not found in CA 81) R. Lantz, USP 3923564 (1975); not found in CA 82) D.C. Sayles, USP 3932241 (1976); not found in CA 83) D.A. Madden, USP 3933543 (1976); not found in CA

Propene and Derivatives

Propene. See under "Polypropylene" in this Vol

Addnl Refs: 1) J.A. Monick, "Alcohols – Their Chemistry, Properties and Manufacture", Reinhold, NY (1968), 492–95 & 500–01 2) E.G. Hancock, Ed, "Propylene and Its Industrial Derivatives", Wiley, NY (1973)

3-Azido-1-Propene. See under "Allylazide" in Vol **1**, A137-L

1,3-Diazidopropene-(1) (Bistriazopropylene or α, γ-Diazidopropylene). $N_3.CH_2.CH{:}CH.N_3$; mw 124.13; N 67.72%; yel liq; bp 78–79° at 26mm; d 1.1572g/cc at 25/4°; RI 1.5202. Volatile in steam. Prepn is by shaking an alc soln of 2-chlor-1,3-diazidopropane with a concd aq soln of K hydroxide for three hrs. The compd is a v sens high expl

Refs: 1) Beil **1**, (84) 2) M.O. Forster et al, JCS **101**, 489 (1912) & CA **6**, 2065 (1913)

Diazopropene (Diazopropylene or Vinyldiazomethane). See under this title in Vol **5**, D1173-L

Aminopropenes and Derivatives. See in Vol **1**, A253-R to A254-L

Nitropropene Polymers. There are two nitropropenes which can be considered energetic materials, 1- and 2-nitropropene polymers

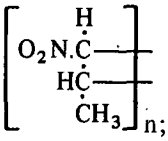
1-Nitropropene-(1) Polymer

Monomer

(Cis- or trans-) 1-Nitropropene-(1) (α-Nitropropylene). $CH_3.CH{:}CH.NO_2$; mw 87.09; N 16.09%; OB to CO_2 −119.42%; the *cis* form is v unstable, hence all measurements are of the *trans* isomer; mobile, pungent colorl liq; bp 37° at 10mm; d 1.0661g/cc at 20/4°; RI 1.4527, 1.4545, 1.4559 (sep measurements). Sol in Na acetate soln, ethanol and hexane. Prepn is by boiling an ethereal soln of β-nitro isopropyl acetate and K bicarbonate and then recovering the prod by shaking with eth. The *trans* monomer is unaffected by ambient storage for one year and will not react with w (Ref 3)

Polymer

1-Nitropropene-(1) Polymer.



n; yel brn, odiferous powd; bp, decompn. Sol in hot glacial acetic acid and NaOH; insol in w and most org solvents. Polymerization occurs *vigorously* on treatment with an alkali such as aq K bicarbonate

Refs: 1) Beil **1**, 203, [173], {715} & ⟨763⟩ 2) M. Levy & C.W. Scaife, JCS **1946**, 1100 to 1104 & CA **41**, 2388 (1947) 3) G.D. Buckley & C.W. Scaife, JCS **1947**, 1471–72 & CA **42**, 4907 (1948) 4) C.E. Redemann et al, JACS **70**, 2582–3 (1948) & CA **42**, 8563 (1948) 5) G.D. Buckley & C.W. Scaife, BritP 595282 (1947) & CA **42**, 3773 (1948) 6) C.W. Scaife, BritP 613853 (1948) & CA **43**, 5411 (1949) 7) Anon, BritP 593109 (1947) & CA **44**, 653 (1950) 8) W.E. Parham & W.R. Hasek, JACS **76**, 799–801 (1954) & CA **49**, 3947 (1955) 9) J. Bryks & J. Ville, MP **41**, 23–6 (1959)

2-Nitropropene-(1) Polymer

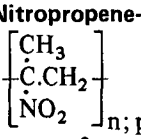
Monomer

2-Nitropropene-(1). $CH_3.C(NO_2){:}CH_2$; mw 87.09; N 16.09%; OB to CO_2 −119.42%; yel liq, strong lachrymatory properties; rapidly turns grn and decomps to a black tar on being

kept in the dark for several days; bp 48–49° at 59.5mm, vigorous decompn at 100° and ambient press; d 1.0492g/cc at 20/20°; RI 1.4292 & 1.4296 (sep values). Sol in eth. Prepn is by pyrolysis of 2-nitropropylbenzoate at 190–95°. The crude nitroolefin is distd off at 110–40° and then extracted from the distillate with absolute eth to give an 83.6% yield

Polymer

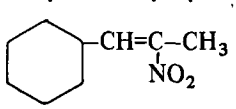
2-Nitropropene-(1) Polymer



n; pale yel crysts; mp, decompn above 200° without melting. Sol in acet, dioxane and acetic anhydride. Prepn of the polymer by vigorous stirring of the monomer with a satd aq soln of K bicarbonate. The crude prod is purified by w washing and air drying. The yield is 93.2%

Refs: 1) Beil **1**, {715} & ⟨764⟩ 2) A.T. Blomquist et al, JACS **67**, 1519–24 (1945) & CA **40**, 58 (1946) 3) A.T. Blomquist & T.H. Shelley, JACS **70**, 149 (1948) & CA **42**, 2228 (1948) 4) H.B. Hass et al, JOC **15**, 8–14 (1950) & CA **44**, 4412 (1950) 5) Anon, BritP 593109 (1947) & CA **44**, 653 (1950) 6) W.D. Emmons et al, JACS **75**, 1993–94 (1953) & CA **49**, 6082 (1955)

1-Phenyl-2-Nitropropene-(1).



mw 163.19, N 8.59%, OB to CO_2 −200.99%; pale yellow cryst, mp 64.5–5.5°; bp 139° at 10mm, d 1.277g/cc. Sol in warm ethanol, warm methanol and w; v sl sol in cold ethanol, diethyl eth, methanol and petr eth. Prepn is by reacting 1.5 moles of benzaldehyde with 1.5 moles of nitroethane plus 13.6g of isopropylamine in a sealed tube heated in a w bath for 2 hrs. Upon cooling and shaking a yellow cryst product is formed. The 57% yield is then w washed and recrystd from warm methanol

The compd decomps at 177°. Its Na or K salts are primary expls

Refs: 1) Beil **5**, 483 2) M.L. Wolfrom, "I. The Preparation and Properties of Some Nitroolefine Derivatives . . .", OSRD **1568**, Ohio State Univ Res Found, NDRC Contract 9-122 (July 1943), 7 & 8

3-Nitropropene-(1) (γ-Nitropropylene or Nitroallyl). $O_2N.CH_2.CH{:}CH_2$; mw 87.09; N 16.09%; OB to CO_2 −119.42%; colorl liq with a sharp bitter odor; bp 125–30°; d 1.051g/cc at 21°; RI 1.4270. Sol in ethanol and eth; insol in w; volatile in hot eth. Prepn is by reacting for three-quarters of an hour at 40°, a mixt of Ag nitrate and sand with 10g of allyliodide dissolved in three times its vol of eth

The sodium salt, $Na.C_3H_4O_2N$, which is v sol in w and sol in ethanol and ether, explds with great brisance at 200°

Ref: Beil **1**, 203 & ⟨764⟩

Propenenitrile. See under "Acrylonitrile" in Vol **1**, A97-R

3-Bromopropene-(1) (γ-Bromopropylene or Allyl bromide). $CH_2Br.CH{:}CH_2$; mw 120.98; liq; mp −119.4°; bp 70° at 753mm; d 1.398 g/cc at 20/4°; RI 1.4697. V sol in ethanol and eth; sol in chlf, carbon disulfide and carbon tetrachloride; insol in w. Prepn is by reacting a 3 molar soln of aq bromic acid (48%) with 1 mole of allylalc at RT; yield is 100%. Expl limits (in air) are 4.4–7.3%; flash pt is −1°.

Refs: 1) Beil **1**, 201, (84), {711} & ⟨753⟩ 2) Bretherick (1975), 355

(*Cis* or *trans*) 1-Chloropropene-(1) (Cis- or trans-Propenyl chloride). $CH_3.CH{:}CHCl$; mw 76.53; see table of properties below

Isomer	Color & State	mp, °	bp,°	d, g/cc	RI	Soluble in
Cis	liq	−134.8	32.8	0.9347 at 20/4°	1.4061	eth, acetone, benz; chlf
trans	liq	−99	37.4	0.9350 at 20/4°	1.4058	eth, acetone, benz; chlf

Prepn of the *cis* isomer is by boiling cis-1,3-dichloropropene-(1) with $LiAlH_4$ in diisopropyl ether. The *trans* isomer is similarly prepd using trans-1,3-dichloropropene-(1). Expl limits in air are 4.5 to 16%, and the flash pt is −6° for both isomers

Refs: 1) Beil **1**, {697} & ⟨737⟩ 2) ChemRub-Hdb (1975), C457 3) Bretherick (1975), 355

2-Chloropropene-(1) (Isopropenyl chloride). $CH_3.CCl{:}CH_2$; mw 76.53; liq; mp −137.4°; bp 22.65°; d 0.9017g/cc at 20/4°; RI 1.3973. Sol in acet, benz, eth and chlf. Prepn is by reacting 1,2-dichloropropane with alc KOH. Expl limits in air are 4.5 to 16%; flash pt is <−20°

Refs: 1) Beil **1**, 198, (82), [169], {698} & ⟨737⟩ 2) Bretherick (1975), 355 3) ChemRubHdb (1975), C457

3-Chloropropene-(1) (Allyl chloride). $ClCH_2.CH{:}CH_2$; mw 76.53; colorl liq; mp −134.5°, −136.4° (sep values); bp 45°, 44.6° (sep values); d 0.9376g/cc at 20/4°; RI 1.4157. Sol in acet, benz, eth and chlf. Prepn is by reacting HCl (d 1.19g/cc) with allylalcohol at RT, or by distg allylalc with HCl (20% concn) in a molar ratio of 1:5. Expl limits in air are 3.3 to 11.2%; flash pt is −32°. Allyl chloride is v toxic. The TLV is 1 ppm or 3mgs/cm of air (Ref 1a)

Refs: 1) Beil **1**, 198, (82), [169], {768} & ⟨738⟩ 1a) Sax (1968), 385 2) Bretherick (1975), 355 3) ChemRubHdb (1975), C-457

1,1,1-Trichloro-3-Nitropropene-(2). $CCl_3.CH{:}CH.NO_2$, mw 190.41; N 7.36%; OB to CO_2 −42.01%; pale yel oil, powerful irritant and lachrymator; mp −4.4°; bp 44–45° at 1mm, 97° or 99.5° (sep values) at 28mm, d 1.5562 g/cc; RI 1.5172. Sol in acet, ethanol, eth and aq soln of NaOH. Prepn is by slowly heating a mixt of 45.0g of P_2O_5 with 150ml of med heavy USP mineral oil plus 36g of 1,1,1-trichloro-2-hydroxy-3-nitropropane to 170°. The mixt is then cooled and the excess P_2O_5 decompd with ice and w. The nitroolefin product separates as a heavy, yel oil on steam distn. After eth extraction of the aq distillate the product is redistd at reduced press giving a 46% yield

The nitroolefin decomps at 150°. The dry (Na or K) salt of this compd is a primary expl

Refs: 1) Beil **1**, {715} 2) M.L. Wolfrom, "I. The Preparation and Properties of Some Nitroolefine Derivatives . . .", OSRD **1568**, Ohio State Univ Res Found, NDRC Contract 9-122 (July 1943), 9 & 10

Propen-2-en-1-ol (Allyl alcohol). $CH_2{:}CH.CH_2.OH$; mw 58.09; OB to CO_2 −220.35%; colorl, mobile liq with a pungent odor; mp −129°; bp 96.9°, d 0.8520g/cc at 20/4°; RI 1.4127, 1.4133, 1.4135 (sep values). V sol in w, ethanol and ether. Prepn is by the high temp chlorination of propene, followed by hydrolysis of allyl chloride. Thus, ". . . Allyl chloride is hydrolyzed at 200psi pressure, 150°C and a pH range of 10–12. Injection of steam forms a water-allyl alcohol azeotrope, which is then treated with diallyl ether to remove water. Final purification by distn leads to a 98% min assay . . ." (Ref 2). Using procedures such as the above, ". . . at least two American companies (Shell Chemical Co and Dow Chemical Co) produce a total of several million lbs per year. . ." (Ref 2)

Allyl alcohol is an expl with expl limits in air of 2.5 and 18%; an open cup flash pt of 32°; a Q_c of 7617cal/g and an autoignition point of 443°

The alcohol has an LD_{50} of 0.064g/kg in rats; an acute toxicity, LD_{50}, of 0.053ml/kg, found by penetration of rabbit skin. The liq is rapidly absorbed by the skin and distributed thru the body. The vap is highly irritating to the respiratory tract and to the eyes (Refs 2 & 3). The TLV is 2ppm or 5mgs/cm of air (Ref 2a)

Refs: 1) Beil **1**, 436, (224), [474], {1873} & ⟨2079⟩ 2) J.A. Monick, "Alcohols – Their Chemistry, Properties and Manufacture", Reinhold, NY (1968), 198–206 2a) Sax (1968), 384 3) Anon, "Fire Protection Guide on Hazardous Materials–6th Edition", NFPA, Boston (1975), 39–40 4) ChemRub-Hdb (1975), C-460

Prop-2-en-1-thiol (Allyl mercaptan). $CH_2{:}CH.CH_2.SH$; mw 74.15; bp 63–6°; d

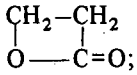
0.9304g/cc at 20/4°; RI 1.4680. Prepn is by reacting allyl bromide with K hydrogen sulfide in aq ethanol. Allyl mercaptan has a flash pt of −10°

Refs: 1) Beil **1**, 440, (226), [478], {1888} & ⟨2095⟩ 2) Bretherick (1975), 367

Propergols and Derivatives. See under "Liquid Propellants" in Vol **7**, L34-R to L44-R

Properties of Detonation Processes. See under "Detonation, Explosion and Related Subjects" in Vol **4**, D137-L to D732-R

β-Propiolactone (Propanoic acid, 3-hydroxy lactone).



O—C=O; mw 72.07; OB to CO_2 −133.20%; liq; mp −33.4°; bp 155°, 162° (rapid decompn) (sep values); d 1.1460g/cc at 20/4°; RI 1.4105. Sol in eth, w and chlf. Prepn is by adding formaldehyde to ketene in the presence of Zn chloride. The lactone has a lower expl level in air of 2.9% and a flash pt of 75°

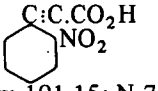
β-propiolactone is the *most* toxic of the lactones. It is a strong irritant and has produced skin cancer in exptl animals. The TLV is *none*

Refs: 1) Beil **17**, 130 2) Sax (1968), 1057 3) N.L. Allinger et al, "Organic Chemistry", 2nd Edn, Worth, NY (1976), 934

Propiolic Acid (2-Propynoic acid, Propinic acid or Acetylenecarbonic acid). $CH{:}C.CO_2H$; mw 70.05; OB to CO_2 −114.20%; liq; mp 9° (cryst from CS_2), 18° (anhyd); bp 144° (decompn); d 1.1380g/cc at 20/4°; RI 1.4302, 1.4306 at 20/4° (sep values). V sol in acet, eth, ethanol, chlf and w. Prepn is by reacting acetylene magnesium bromide with carbon dioxide in ether

Refs: 1) Beil **2**, 477, (208), [449] & {1447} 2) ChemRubHdb (1975), C-461 3) Merck (1976), 1013 (No 7611)

2-Nitro-Phenylpropiolic Acid (2-Nitrophenyl propynoic acid).



mw 191.15; N 7.38%; OB to CO_2 −138.11%; colorl ndles or lfs; mp 157° (decompn); bp, explds. Sol in eth and ethanol; sl sol in chlf. Prepn is by nitration of phenylpropiolic acid or by treating α,β-dibromo-β-[2-nitrophenyl]-propionic acid with an excess of NaOH and then hydrolyzing with HCl to ppt the product

Ref: Beil **9**, 637, (267), [438] & {3067}

Propionaldehyde and Derivatives

Propionaldehyde (Propanal, Propylaldehyde, Propylic aldehyde, Propional or methylacetaldehyde). $CH_3.CH_2.CH{:}O$; mw 58.09; OB to CO_2 −220.35%; colorl liq with suffocating odor; mp −81°; bp 48.8°; d 0.8058g/cc at 20/4°; RI 1.3636. V sol in ethanol and eth; sol in w. Prepn is by treating propyl alc with Na bichromate oxidizing mixt contg sulfuric acid and then distg off the aldehyde. Also, by passing propyl alc vap over Cu at high temp. Propanal has expl limits in air of 2.9 to 17%, a flash pt of −9° to −7°, and an autoign temp of 207°

The aldehyde has a min oral lethal concn in rats of 800mgs/kg and a min inhalation concn for rats of 8000ppm/4 hrs

Refs: 1) Beil **1**, 629, (333), [687] & {2682} 2) Sax (1968), 1058 3) ChemRubHdb (1975), C439 4) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual . . .", The Intnl Tech Info Inst, Tokyo (1975), 442–43 4a) Bretherick (1975), 364 5) Merck (1976), 1013 6) N.L. Allinger et al, "Organic Chemistry", 2nd Edn, Worth, NY (1976), 436

α,β,β-Trinitro-Propionaldehyde, Dipotassium Salt of [Dipotassium-2,3,3-Trinitro propanol-(1)]. $CK(NO_2)_2.CK(NO_2).CHO$; mw 269.25; N 15.61%; OB to CO_2 2.97%; red-yel ndles; mp, v sens, deton violently. V sol in w. Prepn is by reacting 20g of K nitrite with 20g of mucobromic acid in 70cc of ethanol at 30–35°. The salt deflagrates on contact with either concd

sulfuric or hydrochloric acid
Refs: 1) Beil **1**, 634 2) Anon, "Synthesis of New Explosives & Propellants", **Quarterly Progress Rept No 8**, US Rubber Co, Passaic, Contract Nord 10129 (1948), 10 & 11

α,β,β-Trinitro-Propionaldehyde-Anil (Ger). ([β,γ,γ-Trinitro-propylidene]-aniline). $C_9H_8O_6N_4 + C_6H_7N$; mw 361.35; N 19.39%; OB to CO_2 −139.48%; citron-yel crysts; mp, explds at 84–86°. Sol in acet. Prepn is by reacting the dipotassium salt (see above) with aniline acetate in aq soln
Ref: Beil **12**, 189

α,β,β-Trinitro-Propionaldehyde methyl imide ([β,γ,γ-Trinitro-Propyliden]-methyl-amine). $CH_3.N{:}CH.CH(NO_2).CH(NO_2)_2$; mw 206.14; N 27.19%; white crysts. V sol in acet; sl sol in w; insol in eth. Prepn is by reacting α,β,β-trinitro-propionaldehyde suspended in ammonia with an excess of methylammonium chloride. The imide is recovered by acidifying the mixt with HCl

The **mono K-α,β,β-Trinitro-Propionaldehyde-methyl imide** salt; bright yel cryst; explds on heating
Ref: Beil **4**, 56

Propionamide (Propanamide, Propionic acid amide). $CH_3.CH_2.CO.NH_2$; mw 73.11; rh plates; mp 77°, 79° (sep values), bp 213°, d 1.0335g/cc; RI (n_α) 1.42667, (n_β) 1.43574. V sol in w, ethanol, eth & chlf. Prepn is by oxidn of propionitrile with hydrogen peroxide in dil alkaline soln at 32°
Ref: Beil **2**, 243, (108) & [223]

Sodium Propionbromoamide. NaC_3H_5ONBr; mw 173.98; N 8.05%; OB to CO_2 −68.97%; white powd; mp, the salt is unstable and can deton at RT. Prepn is by mixing an ethanol soln of NaOH with propionbromoamide dissolved in chlf, and then pptg the salt with eth
Ref: Beil **2**, 244 & (109)

Propionates and Derivatives

[2-Nitro-Ethyl]-Propionate. $C_2H_5.CO_2.CH_2.CH_2.NO_2$; mw 147.15; N 9.52%; OB to CO_2 −114.15%; colorl mobile liq; mp, when distd above 150° the compd deton; bp 106.0 to 108.2° at 10mm; d 1.1727g/cc; RI 1.4336. Prepn is by reacting at a boil 2-nitro-ethylalcohol with propionic acid in benz solvent, with concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn
Ref: Beil **2**, {524}

[1-Nitromethyl-2-Methyl-Propyl]-Propionate. $C_2H_5.CO_2.CH(CH_2.NO_2).CH(CH_3)_2$; mw 189.24; N 7.40%; OB to CO_2 −164.85%; liq; bp ca 238–45° (decompn); d 1.0655g/cc; RI 1.43563. Prepn is by reacting propionic acid anhydride with 4-nitropentanol at 60° using concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn
Ref: Beil **2**, {529}

[2-Nitro-Propyl]-Propionate. $C_2H_5.CO_2.CH_2.CH(NO_2).CH_3$; mw 161.18; N 8.69%; OB to CO_2 −134.00%; colorl liq; mp, when heated over 150° the compd deton; bp 106.8 to 107.0° at 10mm; d 1.1201g/cc; RI 1.42815. Prepn is by reacting at a boil 2-nitro-propyl alcohol with propionic acid using benz as the solvent, and concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn
Ref: Beil **2**, {525}

Propionic Acid and Derivatives

Propionic Acid (Methylacetic acid, Propanoic acid or Ethyl formic acid). $CH_3.CH_2.C{:}O(OH)$; mw 74.09; colorl oily liq with rancid odor; mp −20.8°, −21.5° (sep values); bp 140.7°, 140.99°, 141.1° (sep values); d 0.9930g/cc; RI 1.3869, 1.3862 (sep values). Sol in ethanol, eth, chlf and w. Obtd from natural gas by the Fischer-Tropsch process; as a by-product in the pyrolysis of wood; by the action of microorganisms on a

variety of materials in small yields. The acid has a flash pt of 54°, an ign temp of 513°, and a Q_c of −367kcal/mole

Propionic acid is an irritant to skin, eyes and mucous membranes. The oral LD_{50} for rats is 4290mgs/kg

Refs: 1) Beil **2**, 234, (102), [212] & {502} 2) Sax (1968), 1057 3) ChemRubHdb (1975), C-445 4) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual . . .", The Intl Tech Info Inst, Tokyo (1975), 443–44 5) Merck (1976), 1014 (No 7615)

α-Azido Propionic Acid Azide. $CH_3.CH(N_3).CO.N_3$; mw 140.13; N 59.99%; OB to CO_2 −79.93%; pungent yel oil. Sol in eth. Prepn is by reacting a soln of acetone-[α-azido-propionyl-hydrazone] in one normal HCl with a concd aq soln of Na nitrite in the presence of some eth. The azide explds on heating

Refs: 1) Beil **2**, (115) 2) T. Curtius & H. Franzen, Ber **45**, 1037–44 (1912) & CA **6**, 2433 (1912)

β-Azido Propionic Acid Azide. $N_3.CH_2.CH_2.CO.N_3$; mw 140.13; N 59.99%; OB to CO_2 −79.93%; pungent yel oil. Sol in eth. Prepn is by reacting a soln of acetone-[α-azido-propionyl-hydrazone] in one normal HCl with a concd aq soln of Na nitrite in the presence of some eth. The azide explds on heating

Ref: Beil **2**, (115)

β-Azido Propionic Acid (L-2-Azido propionic acid or dl-α-Triazo propionic acid). $CH_3.CH(N_3).CO_2H$; mw 115.11; N 36.51%; OB to CO_2 −90.35%; oily liq; mp 0°; bp 97.5° at 3mm; d 1.2502g/cc at 33°. Sol in eth; sl sol in w. Prepn is by shaking an ethanol soln of the ethyl ester with an aq soln of 1 g equiv wt of KOH. The azide explds on heating

The Ag salt, **Silver -β-Azido Propionic Acid**, $AgC_3H_4O_2N_3$; white ndles; sl w sol, also explds on heating

Refs: 1) Beil **2**, 263, (114), [234] & {575} 2) J.H. Boyer, JACS **73**, 5248–52 (1951) & CA **47**, 490 (1953) 3) W.F. Huber, JACS **77**, 112–16 (1955) & CA **50**, 804 (1956)

α-Nitro Propionic Acid. $CH_3.CH(NO_2).CO_2H$; mw 119.09; N 11.76%; OB to CO_2 −60.46%; ndles, mp 61–61.5° (decompn). V sol in w, ethanol, eth, benz, chlf; sl sol in ligroin and carbon disulfide. Prepn is by boiling the ammonium salt of α-nitro ethyl propionate with alc NaOH. The Na salt is then hydrolyzed with HCl

Ref: Beil **2**, (114)

β,β-Dinitro-Propionic Acid [3,3-Dinitro-Propanic acid-(1)]. $(O_2N)_2CH.CH_2.CO_2H$; mw 164.09; N 17.08%; OB to CO_2 −19.50%; viscous grn oil; mp, explds on heating. Prepn is by hydrolysis of β,β-dinitropropionic nitrile with concd HCl

Ref: Beil **2**, 263

3,3,3-Triodopropionic Acid. $CI_3.CH_2.CO_2H$; mw 451.76; OB to CO_2 −19.48%; lt yel prisms; mp 131° (decompn). Sol in eth, ethanol, warm benz (decompn); insol in w. Prepn is by heating iodopropiolic acid with HI (d 1.96g/cc) on a steam bath

Ref: Beil **2**, {575}

Propionic Nitrile. See "Ethyl Cyanide" in Vol **6**, E223-L

Propionyls and Derivatives

3-Pentanone (Propionone, Diethyl ketone or DEK). See under this title in this Vol

Bis-[α(?)-Bromo-Propionyl]-Amine. $(CH_3.CHBr.CO)_2NH$; mw 286.96; N 4.88%; OB to CO_2 −80.84%; ndles (from hot w); mp 148° (decompn occurs at about 152°). V sol in hot w, ethanol and eth. Prepn is by exposure of the α-bromopropionic acid amide bromide to moist air

Ref: Beil **2**, 256

Propionyl nitrite (Nitric acid-propionic acid anhydride). $CH_3.CH_2.CO.O.NO$; mw 103.09; N 13.59%; OB to CO_2 −85.36%; golden-yel liq; bp <60° (decompn). Prepn is by reacting nitrosyl chloride with Ag propionate

The nitrite is a weaker expl than acetyl nitrite. It is quickly decompd by light

Ref: Beil **2**, 243 & (108)

N-Propionyl-Dimethylsulfinimin-Hydrochloride. $C_2H_5.CO.N{:}S(CH_3)_2.HCl$; mw 163.63; N 8.56%; OB to CO_2 −117.34%; crysts; mp 110° (decompn). Sol in w and warm org solvents. Prepn is by reacting N-Chloropropionamide dissolved in eth with dimethyl sulfide dissolved in CCl_4 at below 0°

Ref: Beil **2**, {551}

2-Propyl Acetate, 1,1,1-Trinitro.

$$H_3C.C(O).O.\underset{\displaystyle CH_3}{\underset{|}{C}}H.C(NO_2)_3;$$

mw 237.15; N 17.72%; OB to CO_2 −37.11%; colorl liq; bp 56° at 1 mm; RI 1.4432. Prepn is by reacting nitroform with vinyl acetate. The compd burns quietly with a blue flame and deton weakly from a heavy hammer blow

Ref: 1) Beil, not found 2) Anon, "Synthesis of New Explosives & Propellants", Quarterly Progress Rept No 5, US Rubber Co, Passaic, Contract Nord 10129 (1948), 15–17

Propyl Acrylate (Propylic Acid, Propyl ester). The (theoretical) parent compd for nitroolefin polymers used as proplnts and expls such as "2,2-Dinitropropylacrylate (DNPA)". See under this title in this Vol, N139-R to N140-L. $CH_2{:}CH.C(O_2)C_3H_7$; mw 114.16; colorl liq; bp 122.9°; d 0.91996g/cc at 0°. Prepn is by redn with Zn in sulfuric acid of the propyl ester of α,β-dibromopropionic acid dissolved in n-propanol

Ref: Beil **2**, 400 & {1225}

1,1,1-Trinitro-2-Propyl Acrylate.

$$CH_3.\underset{\displaystyle C(NO_2)_3}{\underset{|}{C}}H.O.C(O).CH{:}CH_2$$

mw 249.16; N 16.87%; OB to CO_2 −48.16%; yel liq; bp 50–60° at 0.4mm; sol in CCl_4. Prepn is by refluxing for one-half hr a mixt of nitroform, paraldehyde and acryl chloride dissolved in 50cc of carbon tetrachloride in the presence of Al chloride. The reacted mixt is then hydrolyzed with w; the CCl_4 layer neutralized with Na bicarbonate soln, dried and vac distd. The yield is 25%. The acrylate will deflagrate on a hot plate and will deton from a blow

Refs: 1) Beil, not found 2) Anon, "Synthesis of New Explosives & Propellants", Quarterly Progress Rept No 18, US Rubber Co, Passaic, Contract Nord 10129 (1952), 4

N- and Iso-Propylamine and Derivatives. See "Aminopropanes and Derivatives" in Vol **1**, A250-L to A251-L

Propyl Aniline and Derivatives

Propyl Aniline (Phenylpropylamine). $C_6H_5.NH.(CH_2)_2.CH_3$; mw 135.21; bp 222°, d 0.9443g/cc at 20/4°; RI 1.5428. Sol in ethanol, eth and ligr. Prepn is by reacting aniline with propyl alcohol over silica gel at 385°

Ref: Beil **12**, 166, (159), [94] & ⟨264⟩

N-Propyl-N,2,4,6-Tetranitro-Aniline (N-Nitro-N-propyl-2,4,6-trinitro-aniline, Propyl Tetryl or Propyl-picryl-nitramine). $(O_2N)_3C_6H_2.N(NO_2).(CH_2)_2.CH_3$; mw 315.23; N 22.22%; OB to CO_2 −73.60; colorl leaflets; mp 98°, 97° (sep values); sol in ethanol. Prepn is by reacting picrylchloride with K propyl-nitramine in warm ethanol. The compd is an expl

Ref: Beil **12**, 771 & (371)

2,4,6-Trinitro-N-(iso-propyl)-Aniline. $(O_2N)_3C_6H_2.NH.CH(CH_3)_2$; mw 270.23; N 20.74%; OB to CO_2 −100.64%; yel ndles; mp 106–7°. Sol in acet and hot ethanol. Prepn is by nitrating 2,4-Dinitro-N(iso-propyl)-aniline with hot anhyd nitric acid. The compd is an expl

Refs: 1) Beil **12**, 764 2) A. Mulder, Rec **25**, 116 (1906) & CA, not found

2,4,6-Trinitro-N-(iso-propyl)-N-Nitraniline (Isopropylpikrylnitramin in Ger).
$(O_2N)_3C_6H_2.N(NO_2)CH(CH_3)_2$; mw 315.23; N 22.22%; OB to CO_2 −73.60%; pale yel crysts; mp 107–8°; d 1.563g/cc at 10°. Sol in ethanol. Prepn is by nitration of 2,4-dinitroisopropylaniline with hot anhyd nitric acid. The compd is an expl
Refs: 1) Beil **12**, 771 2) A. Mulder, Rec **25**, 115 (1906) & CA, not found

Trinitro Propyl Bromide.
$(O_2N)_3C.CH_2.CH_2.Br$; mw 258.0; N 16.29%; OB to CO_2 −12.40%; yel liq. Prepn is by reacting powd Ag γ-trinitrobutyrate and bromine in carbon tetrachloride. The bromide burns rapidly and can be deton with a hammer blow
Refs: 1) Beil, not found 2) Anon, "Synthesis of New Explosives & Propellants", Quarterly Progress Rept No 7, US Rubber Co, Passaic, Contract Nord 10129 (1949), 10 & 11

2,2-Dinitropropyl Trinitrobutyrate (DNPTB).
$(O_2N)_3C.(CH_2)_2.C(O).O.CH_2.C(NO_2)_2.CH_3$; mw 355.21; N 19.72%; OB to CO_2 −29.28%; waxy crysts; mp 93°; d 1.66g/cc. Prepn is by reacting 2,2-dinitropropanol with butyric acid chloride in chlf in the presence of anhyd Al chloride. DNPTB has a hotbar ign temp of 300° and an impact sensy of about that of TNT (151cm for the 50% pt using a 2.5kg wt with No 12 tools in an ERL machine). Vac stab is 0.5ml of gas (100° for 48 hrs)
Refs: 1) Beil, not found 2) W.F. Sager & D.V. Sickman, "Second Report on Research and Development in New Chemical High Explosives", NAVORD **483** (1952), 24 3) D. Jensen, "The Preparation of 2,2,2-Trinitroethyl-4,4-dinitropentanoate", NAVORD **2498** (1952) 4) M. Hill, "Preparation and Properties of 2,2-Dinitropropanol Esters", NAVORD **2497** (1952)

Propyl-[2,4,6-Trinitro-phenyl]-Ether (Picricacid-propyl ether or Propylpicrate).
$(O_2N)_3.C_6H_2.O.CH_2.CH_2.CH_3$; mw 271.21; N 36.87%; OB to CO_2 −91.44%; colorl ndles; mp 43°. V sol in all org solvents. Prepn is by adding a warm soln of picryl chloride dissolved in n-propyl alc to an ice-cold soln of KOH in n-propyl alc. The orange ppt formed is then hydrolyzed with dil aq HCl to form a yel solid. The crude ether is then dissolved in benz and treated with decolorizing carbon. Final pptn is then performed using ligr. The yield is 61%. The lead block test of the ether has shown it to be 68% as powerful as TNT
Refs: 1) Beil **6**, 290 2) H. Blatt & A.W. Bytina, JACS **72**, 3274–75 (1950) & CA **44**, 10673 (1950)

2,2-Dinitropropyl Fumarate (DNPF).
$CH_3.C(NO_2)_2.CH_2.O.CO.CH{:}CH.CO.O.CH_2.C(NO_2)_2.CH_3$; mw 380.24; N 14.74%; OB to CO_2 −58.91%; waxy crysts; mp 84°; d 1.60g/cc. Prepn is by reacting 2,2-dinitropropanol with fumaric acid chloride in chlf soln in the presence of anhyd. Al chloride. DNPF has a hot bar ign temp of 269° and an impact sensy that approaches TNT
Refs: 1) Beil, not found 2) W.F. Sager & D.V. Sickman, "Second Report on Research and Development in New Chemical High Explosives", NAVORD **483** (1952), 27

Propylmalonylazidic Acid.
$CH_3.(CH_2)_2.C(CO_2.C_2H_5)(CO.N_3)$; mw 198.23; N 21.20%; OB to CO_2 −153.36%; yel oil, expl. Sol in eth and CCl_4. Prepn is by reacting the K salt of the half (or mono) ethyl ester of propyl malonic acid with nitrous acid
Refs: 1) Beil, not found 2) T. Curtius & W. Lehmann, "Transformation of alkylated malonic acids into α-amino acids. III. Synthesis of α-aminovaleric acid, propylmalonylazidic acid . . .", JPraktChem **125**, 211–302 (1930) & CA **24**, 3215 (1930)

Propyl Malonic Acid Diazide.
$C_2H_5.CH_2.CH(CO.N_3)_2$; mw 196.20%; N 41.84%; OB to CO_2 −114.17%; yel, v odiferous oil; mp, v unstable. Prepn is by reacting propylmalonic acid-dihydrazide with Na nitrite in cold dil HCl
Ref: Beil **2**, {1730}

Bis(2,2-Dinitropropyl) Nitramine (DNPN). $CH_3.C(NO_2)_2.CH_2N(NO_2).CH_2.C(NO_2)_2.CH_3$; mw 254.21; N 33.07%; OB to CO_2 −44.06%; crysts; mp 187–88° (decompn); d 1.726g/cc. Sol in hot methanol and methyl ethyl ketone. Prepn is by nitration of bis(2,2-dinitropropyl) amine at 30–35° using mixed acid (HNO_3/H_2SO_4/free SO_3 in the following percentages: 35.2/53.4/11.6). The yield is 94%

DNPN has a booster sensy using gaps consisting of Al plates and a LA donor of 0.053″ (Tetryl = 0.0736″); a gap test using Al gaps and Tetryl as the acceptor of 0.177″ (Tetryl = 0.160″); an ignition temp of 236°; an impact sensy of 28.5cm using a 2.5kg wt and a vac stab of:

Temp, °C	cc of gas in 48 hrs
100	0.22
120	0.32 (Tetryl=1.42)
140	6.16 (Tetryl=58.0 in 8 hrs)

Refs: 1) Beil, not found 2) O.H. Johnson, "The Preparation and Properties of Bis(2,2-Dinitropropyl) Nitramine", NAVORD **2448** (1952), 11 & 12 3) W.F. Sager & D.V. Sickman, "Second Report on Research and Development in New Chemical High Explosives", NAVORD **483** (1952), 11

Nitropropylisonitramine, Sodium salt. $C_2H_5.C(NO_2).N.NO_2.\frac{1}{2}H_2O$ $(Na)_2$

mw 202.10; N 20.80%; OB to CO_2 −43.54%; small ndles, deliq; mp, explds with great brisance when heated. V sol in w. Prepn is by reacting nitropropylisonitramine with an alcoholic soln of NaOH

Ref: Beil **1**, 631

n-Propyl Nitrate (NPN). $C_2H_5.CH_2.O.NO_2$; mw 105.125; N 13.33%; OB to CO_2 −98.93%; w white liq; fl p 102°; bp 110.5°; d 1.0538 g/cc at 20/4°; RI 1.3973 (Ref 1), 1.3983 (Ref 4). Sol in ethanol and eth. Gelantinizes NC. Forms azeotropic mixts with butyl alc, acetic acid, heptane, toluene, nitroethane, perchloroethylene, w, etc. Prepn is by reacting propyl alc with concd nitric acid (d 1.41g/cc) dissolved in ethylacetate at 20°, followed by distn of the product. NPN can also be prepd by reacting a continuous stream of propyl alc below the surface of stirred mixed acid (20% nitric acid, 68% sulfuric acid and 12% w by wt) in a cooled (0–5°) open stainless steel vessel. Addnl mixed acid is also simultaneously introduced at about a third of the depth of the liq. An overflow pipe maintains a constant reactant level and the effluent prod is sepd, washed with 10% aq Na carbonate soln and dried by passage thru a Filtrol packed tower. Contact time of reactants can vary from 0.6 to 15 mins using about 50% isopropanol at 0° to yield 66.5% NPN (Ref 3b)

Liq NPN can be detond with difficulty at RT in a Trauzl block using a No 8 blasting cap with w tamping; a mixt with kieselguhr, however, readily detonates with an expansion of 230cc vs 200cc for AN (Refs 1a & 6). By raising the temp of the liq NPN to over 90°, the BuMines was able to propagate deton in a steel pipe of 1-3/8″ ID and 1/8″ wall thickness using a Tetryl charge. The avg deton vel is 5100m/sec (Ref 4)

Much work has been done on the adiabatic compression ignition of NPN vapor mixed with various gases by both NOL (Ref 2) and Brit Imp Chem Inds (Ref 4). A table of compression ratios and resultant temps from the detons of NPN vapor saturated gas mixts is presented below

NPN is completely compatible with the following materials: hard copper, ST aluminum alloy, 2S soft aluminum, K Monel, 303 stainless steel and polyethylene. The compatibility limit for 10-20 cold-rolled steel is one year (Ref 4). However, according to Harvey (Ref 3a), addn of as little as 0.05% of a polyhydric alc such as glycerol to NPN will prevent the corrosion of steel

The work of the BuMines (Ref 5) in measuring the effect of NPN/air compn on deton vel is presented in Table 1

Gas	Air	Nitrogen	Carbon Dioxide
Explosive Ratios	13.5:1 to 21.5:1	33.5:1 to 40:1	No explns at 80:1
Calculated Temps	322° to 695°	890° to 985°	795°

Table 1
NPN Vapors Content vs Detonation Velocity

NPN Vapor, volume percent	Detonation Velocity, m/sec
1.9	no ignition
2.4	no ignition
2.5 (estimated)	215 (deflagration)
2.7	1,455
2.8	1,480
3.5	1,630
4.1	1,520
5.0	1,620
6.7	1,740
21.2	1,900
31.4	1,525

The expln temp under confinement with a heating rate of 5°/min is 190°. The self-ignition temp of a vap/air mixt is 193°. The principle prod of the thermal decompn of NPN is carbon monoxide. The combined molar vol from one mole of NPN of carbon monoxide and carbon dioxide is 1.84 moles (at 305psi and 200°)

NPN has a flash pt (Abel closed cup) of 65°F and (Cleveland open cup) of 78°F

A card gap value of 16 cards has been obtained for NPN using the ERDE procedure (Ref 4) at temps ranging from −14° to +15°. Under the same conditions, a value of 24 cards was found for Nitromethane

The vol of gas evolved from the thermal decompn of 1 kg of NPN is 1000ℓ at 250psi and 1050°

NPN has a Q_c of 4080cal/g (liq H_2O at 25° ref); a Q_d of 400cal/g (liq H_2O at 25° ref); and a Q_f^R of 660cal/g (Ref 4). It has a bond energy level 0 of 37kcal/mole (Ref 8)

NPN is v sl hygroscopic; it is, however, miscible with w in a ratio of 1/3 and 13/7 (w/NPN), forming azeotropes which boil at 84.8° and 107.5°, respectively (Ref 1)

Inpact sensy has been detd for NPN using a modified Imp Chem Ind app (Ref 4) which consists of a sample cylinder 1/2″ in diam and 1″ long, fitted with a piston upon which a wt of 310g is dropped. Results were detd for both air and nitrogen by varying the vol of the gas above the liq NPN. These data are tabulated below

Impact sensy has also been reported on by Médard (Ref 2b). Using a 15mg sample wt, he dropped a 5kg wt a height of 293cm, obtaining a v weak expln in 48 out of 100 drops. The 50% prob pt is 10m, while NG has a 50% prob pt of 0.40m

Again, from the work of Ref 4, power by BalMort is 0.1 (Mk 1 mortar using a No 6 ASA Al CB detonator; PA=100) and 72.9 (Mk IIIC mortar using a No 8 ASA Al CB detonator; PA=100). Power by Trauzl test is 13cc/g (40% of NG)

No explns were obtd in 15 shots each of 0.303 ball or AP ammo against targets consisting of 3 cu inch mild steel boxes with walls of 1/16″, 1/8″ and 3/16″ thickness contg NPN. Ref is 55% explns using eth nitrate as the filler for this rifle bullet impact test

Table 2 correlates data from refs 4 and 5 on the sensy to initiation of NPN

The specific heats of NPN product gases (primarily carbon monoxide and carbon dioxide) arising from combustion are C_p 0.346cal/g/° and C_v 0.252cal/g/° at 300°K. The specific impulse of these gases (calc at 400psi) is 155 lbs/thrust/lb/sec

The result of high temp stability testing shows that at a temp of 150–200° under a press greater than 100psi, NPN will undergo a self-sustained thermal decompn yielding a gaseous mixt comprised primarily of carbon monoxide

A conclusion drawn from the data of both Refs 4 and 5 is that NPN is completely stable at ambient temp and does not deteriorate on prolonged storage. Recommended storage procedures include packaging NPN in polyethylene or lead-lined 55 gal drums constructed of stainless steel, aluminum or aluminum alloys; a temp range that should not exceed 160°F; blanketing under nitrogen; a storage period of no longer than one year; and treatment as a high expl and storage in accordance with the American

Gas in Vapor Space	Air		Nitrogen	
Vol of gas, cc	1.35	0.86	1.35	0.86
Drop height, cm	10 to 15	5 to 10	No expln to 43	No expln to 43
Calcd expln temp, °	<400	<400	–	–

Table 2
Sensitivity to Initiation of NPN

Type of Initiation	Catalytic Cr & Ni Metal Rings	Spark	Hot Wire	Inert Shock
Type of Energy Input	Thermal (elec heaters)	Thermal (ionized gas)	Thermal (elec)	Mech Comprsn
Min Energy Reqd	–	–	∿5Kjoules	755psig/<1 sec
NPN State	Liq spray in air	Vapor	Vapor	Vapor
% NPN in mixt	–	3 in air	3 in air	4.5 in air
Min Temp, °C	200°	34°	34°	30.8°
Min Press, cm Hg	Ambient	120	120	74
Time to initiation, sec	∿1	0.01	> 2	<1 [a]

[a] Ref 8 indicates that a Mach 3 shock initiation of NPN droplets in oxygen can occur in 24.1 microsecs

Table of Distances (Ref 5)

According to Sax (Ref 7) NPN is highly toxic, having a min tolerance level of 25ppm or 110mgs per cubic meter of air

NPN is used as a rocket monoproplnt, a jet motor starting fuel; its hot combustn prod gases are used to drive turbine type motors (Ref 4). It is also used as a degreasing solvent for iron and aluminum (Ref 2a), and as a diesel fuel additive (Ref 3a). Proposed uses for NPN are in expls or ammo monoproplnts (Addnl Refs, limited distribution Nos 1, 2, 4 and 5 to 8)

The viscosity of NPN at 20° is 0.66 centipoise

The vapor press of NPN can be calcd by any one of the three equations shown below. The results of such calcs over a range of temps are given in Table 3 (Ref 4)

(1) $\log_{10}P = 33.42 - 3090/T - 8.7 \log_{10}T$, where P is in mm Hg and T is in °K;

(2) $\log_{10}P = 7.3506 - 1520/(t+230)$, where P is in mm Hg and t is in °C; and

(3) $\log_{10}P = 7.246 - 1444/(t+221)$, where P is in mm Hg and t is in °C

The heat of vapn of NPN is 73.4 to 81.8cal/g (Ref 4)

Table 3
Vapor Pressure of NPN

Temp, °C	Vapor Press (mm Hg) according to Eqn No		
	1	2	3
0	1.2	5.5	5.3
10	15	10.4	10.0
20	26	18.6	17.8
30	43	31.9	30.6
40	69	52.6	50.6
50	106	83.6	81.4
60	157	129	128
70	226	192	189
80	317	280	–

Refs: 1) Beil **1**, 355, [369] & {1419} 1a) Naoúm, NG (1928), 208 2) ADL Pure-ExplCompds I (1947), 31 & 141 2a) W. Klabunde, "Solvent for Degreasing Iron and Aluminum", USP 2435312 (1948) & CA **42**, 2916 (1948) 2b) L. Médard, MP **31**, 131–43 (1949) & CA **46**, 11685 (1952) 2c) B.R. Diplock et al, "Liquid Propellant Rocket Motors", JRoyAeronautSoc **57**, No 505, 19–28 (1953) & CA **47**, 5686 (1953) 3) E. Hogge & J.B. Levy, "Ignition of Normal Propyl Nitrate by Compression of Air-Normal Propyl Nitrate Vapor Mixtures", **NAVORD 4296** (1956) 3a) C. Harvey, USP 2742492 (1956) & CA **50**, 13428 (1956) 3b) J.B. Hinkamp et al, "Propyl Nitrate", USP 2734910 (1956) & CA **50**, 13080 (1956) 4) Anon, "The Properties of Normal Propyl and Isopropyl Nitrates", Imp Chem Inds Ltd, Stevenston (Engl) (1957) 5) M.G. Zabetakis, et al, "Safety Characteristics of Normal Propyl Nitrate", **BuMines RI 6058**

(1962) 6) Urbański **2** (1965), 165 7) Sax (1968), 1063–64 8) P.L. Lu & N. Slagg, "Chemical Aspects of the Shock Initiation of Fuel Droplets", PATR **4153** (1971)

The following *Addnl Refs* are of limited distribution: 1) G.A. Yanyecic, "Decomposition Characteristics of Nitrate Ester Monopropellants", Rept No **TM-705. 9161-03**, Contract NOW-65-0123, Penn State Univ, Univ Park (1968) 2) R.K. Lund, "Encapsulated Liquid Monopropellant Ammunition Feasibility Study", **AFATL TR-69-27**, Contract F08635-68-C-0131, Thiokol Chem Corp, Brigham City (1969) 3) J.A. Letos, "Materials Compatibility with Liquid Rocket Propellants", **Rept No D2-113073-1**, Boeing Co, Seattle (1970) 4) R.F. Bonanno, "Proceedings of the Fuel-Air Explosives Conference (1st), 27 thru 29 October 1971. Volume 1, Book 2", Rept No **AFATL-TR-71-171-Vol 1-Bk-2** (1971) 5) E.B. Vanta et al, "Detonability of Propylene Oxide/Air and N-Propyl Nitrate/Air Mixtures", Rept No **AFATL-TR-73-3** (1973) 6) E.L. Husker, "Tethered Aerosol Detonating Fuze for a Fuel-Air Explosive Munition", **AFATL-TR-73-31**, Contract F08635-72-C-0213, Beech Aircraft Corp, Boulder (1973) 7) H.W. Brown Jr, "Development Tests of a High-Speed Nonretarded Fuel-Air Explosive (FAE)", Rept No **ADTC-TR-73-93**, Elgin AFB (1973) 8) R.C. Weaver et al, "Evaluation of Elliptical Experimental Explosive Charges (Z-Test)", Rept No **USAMERDC-2116** (1974)

2-Nitro Isopropyl Nitrate.

$CH_3.C(NO_2).CH_3$ mw 150.11; N 53.29%; $O.NO_2$ OB to CO_2 −42.64%; colorl oil; bp 71° at 1 mm; d 1.348g/cc at 20/4°; RI 1.447; sol in eth; insol in w. The nitrate is polymerized to the 1-nitropropene polymer (qv) by aq NaOH. Prepn is by reacting propene with N_2O_4 in eth at 0° for 3 hrs. The oily prod is w washed and dried by distn with benz. It is sepd by vac distn from other nitration prods in a 21.4% yield. The nitrate has 75% of the power (lead block) of blasting gelatin and is v insens to friction and impact

Refs: 1) Beil **1**, {1477} & ⟨1497⟩ 2) N. Levy & C.W. Scaife, JCS **1946**, 1093–96 & CA **41**, 2388 (1947)

Isopropyl Nitrate (IPN). $CH_3.(H)C(ONO_2).CH_3$; mw 105.125; N 13.33%; OB to CO_2 −98.93%; w white liq with an ethereal odor; fp −82°; bp 101.5°; d 1.049g/cc at 15.5/15.5°; RI 1.3913. Sol in ethanol and eth. There are four methods of prepn which are used for IPN prodn: a) that of Silva (Ref 2) in which isopropyl iodide and powd Ag nitrate are reacted to give a 69% yield; b) that described by Naoûm in Ref 4 in which acet is catalytically reduced and nitrated; c) also mentioned by Naoûm is a procedure involving useage of the gases from oil cracking stills; and d) a continuous process patented by Allen and Tobin (Ref 4a) and developed almost simultaneously by Desseigne (Ref 5), in which isopropyl alc is nitrated continuously by dropping a mixt of 61% nitric acid with 95% isopropylalc, satd with urea, into a vessel contg boiling 50% nitric acid. The IPN and w formed are continuously distd off at about 98° from the reaction mixt. The vol of the reaction mixt is held constant by drainage of nitric acid and unstable by-products from it as the reactants are added. A curtain of air, nitrogen or carbon dioxide is blown thru the reaction mixt to improve mixing and to facilitate the elimination of the volatile prods. However, a flow of inert gas in excess of 50ℓ/hr decreases the IPN yield. The optimum ratio of nitric acid to isopropyl alc is about 2:1. The IPN yield is 78%

According to Brochet (Ref 8), IPN can be detond in thick-walled tubes of plastic with an ID of 16mm at 20° using a Gevelot P 53A electric igniter coupled to a Briska #8 detonator, used in conjunction with an HE donor (75% PETN). The donor, in turn, is in direct contact with the liq IPN. Under these conditions a deton vel of 5400m/sec is achieved. Ref 6 lists a liq IPN deton vel of 5070m/sec in 1½" mild steel pipes. Also, the conditions under which deton is propagated are stated by Ref 6 to be as follows; viz,

" . . . (a) At 70°C and above when confined in a mild steel pipe 30 inches in length of 1.5 inch ID and 0.2-inch wall thickness and initiated with 3 oz Tetryl

(b) Along the full length of a similar pipe 5 ft in length in which the detonation was initiated in a region at 70°C (top 2 feet) and propagated thru a region at 15°C (bottom 3 ft)

(c) At 35°C when confined in a mild steel

canister 10 inches in diameter and 0.5-inch wall thickness and initiated with 8 oz Tetryl
(d) At 10°C in a container 2 inches in diameter and 1.5-inch wall thickness and initiated with 4 oz Submarine blasting gelatine and 1 oz Tetryl
(e) Between 30° and 45°C and above in stainless steel pipes 30 inches in length and 1.55 inches in diameter and 0.66-inch wall thickness and initiated with 3 oz Tetryl . . ."

Again, according to Ref 6, deton is propagated in a 1½" diam mild steel tube at ambient temp using a No 8 detonator alone when IPN is mixed with kieselguhr or sawdust in the ratio of 1 p solid/2 p IPN by wt. Mixts with sand (4 p/1 p IPN by wt) are detonatable under the same conditions using 1.5 oz PETN

The work of Ref 6 includes parameters affecting the adiabatic compression ignition of NPN vapor mixed with various gases. A table of compression ratios and resultant temps from the detons of the IPN vapor satd gas mixts is presented below

The compatibility of IPN with a great number of matls has also been investigated by the authors of Ref 6. These data are presented in tabular fashion below

I. Metals and Alloys

To serve as a basis for comparison a series of IPN solns were prepd as test matl reactants:
(1) Pure IPN
(2) IPN + oleic acid (0.3%)
(3) IPN + methanol (4%) + oleic acid (0.3%)
(4) IPN + isopropanol (4%) + oleic acid (0.3%)
(5) IPN + Esso Aviation Turbo-Oil 35 (EEL3) (2%)
(6) IPN + methanol (4%)
(7) IPN + isopropanol (4%)
(8) IPN + isopropanol (4%) + EEL3 (2%)
(9) IPN + Shellex 4 (1%)
(10) IPN + isopropanol (4%) + Shellex 4 (1%)
(11) IPN + cyclohexanol (5%)

Table 1 details the effects of exposure of a variety of metals and alloys to the solns enumerated above

	Air	Nitrogen	Carbon Dioxide
Explosive Ratios	13.5:1 to 21.5:1	33.5:1 to 40:1	No explns at 80:1
Calculated Temps	525° to 695°	890° to 985°	795°

Table 1
Compatibility of IPN with Typical Metals and Alloys

Metal	Solution No	Remarks
Stainless Steel 18/8/Ti	1–11	No Corrn
Mild Steel	1, 5	V sl corrn; $2x10^{-3}$mm/yr
	2, 3, 4, 6, 7	Some corrn; pptn of rust
	8, 9, 10	No corrn; a little staining
	11	Corrn; no pptn
Tinplate	1, 2, 3, 4, 8, 9, 10	No corrn; sl staining
	5, 6, 7, 11	Bad staining
"Kynal" P.10 Aluminum	1, 2, 3, 4, 6, 7, 8	No corrn
	9, 10, 11	No corrn
	5	V sl corrn
"Kynal" M35/1 Aluminum Alloy	1, 2, 3, 4, 6, 7, 8	No corrn
	9, 10, 11	No corrn
	5	V sl corrn
"Kynal" M39/2 Aluminum Alloy	1, 2, 3, 4	No corrn
"Kynal" PA.19 Aluminum Alloy	1, 2, 3, 4	No corrn
Electrolytic Zinc	1, 4	No corrn
	2, 3	Hvy white ppt of Zn oleate
Lead	1	No corrn; Pb content of liq <1 ppm
	2, 4	Hvy ppt of Pb oleate
	5	Corrn $5.7x10^{4}$mm/yr; Pb content 7 ppm
	7	Corrn $6.2x10^{4}$mm/yr; Pb content 54 ppm
Cadmium	1	No corrn
	3, 4	Ppt of Cd oleate
Copper	1	No corrn; sl staining
70-30 Brass	1	No corrn; sl staining
Chromium	1	No corrn
Nickel	1	No corrn

II. Rubbers and Synthetic Materials

Table 2
Compatibility of IPN with Rubbers and Synthetic Materials

Material	Results	Recommendation
Silicone rubbers S80, S90, B30	Vol increases (approx 60%) and sample loses elasticity	Unsuitable
Hycar rubber	Vol increases and sample rots	Unsuitable
Chloroprene Acrylonitrile rubber	Vol increases and sample loses elasticity	Unsuitable
Butyl rubber B100	Vol increases and sample softens	Unsuitable
Synthetic rubber JP73	No deterioration	Suitable
Nylon	Sample becomes brittle	Unsuitable
Perspex	Sample dissolves	Unsuitable
Polythene	Sample not attacked	Suitable
Fluon (P.T.F.E.)	Sample not attacked	Suitable
P.V.C.	Sample becomes brittle	Unsuitable

III. Various Common Liquids

Table 3
Compatibility of IPN with Common Liquids

Liquid	Observation
Water	The liqs are only sl miscible
Battery acid (dil sulfuric acid, sp gr 1.3g/cc)	The liqs were heated together for several days. Initially a brn ring formed at the interface, but this disappeared and no further reaction took place
44D Lubricating oil	The liqs are miscible at least up to 15% oil and no interaction occurs. A mixt contg 12% oil could be ignited in a turbo-starter but the reaction was not self-sustaining
RDE/0/463 Lubricating oil	The liqs are miscible at least up to 17% oil and no interaction occurs. A turbo-starter operated on a mixt contg 17% oil
Kerosene	This was mixed with pure IPN and IPN contg the above oils. No reaction occured and a turbo-starter operated satisfactorily
Ethylene glycol	Glycol is only v sl sol in IPN. No interaction occurs

The flash pt for IPN using the Abel closed cup method is 53°F while the Cleveland open cup method gives a value of 72°F. Min spont ign temp range in air on a heated brass, Al, stainless steel or mild steel plate is 245–60°

The following data from Ref 6 present, in tabular form, the limits of flammability of IPN vapor/air mixts over a press and temp range:

Table 4
IPN Vapor-Air Flammability Ranges

Temp, °C	Lower Limit Vol, %	Upper Limit Vol, %	Pressure, psig
18–19	2.4	To Satn Pt 5%	14.7
89	2.2	53	14.7
125	1.8	–	5
125	1.2	–	70
125	1.0	–	250
125	0.95	–	500
125	0.90	–	1000

The ign temps obtd by passing IPN vapor/air mixts thru a heated glass tube are tabulated below (Ref 6):

Table 5
IPN Vapor-Air Ignition Temperatures

Composition (Vol % IPN)	Ignition Temp (°C)
3.2	No ignition up to 500°
3.8	240
4.6	220
12.6	200
28.2	190
46.2	200

IPN gave a ERDE gap test (Scale III) of 16 cards at ambient temp. A value of over 27 cards is indicative of positive sensy to the rifle bullet test. Refs as to gap sensy include ethylene oxide (10 cards), Nitromethane (24 cards) and ethyl nitrate (43 cards)

The vol of gas evolved on the thermal decompn of 1 kg of IPN is 1000ℓ at 250psi and 1050° (Ref 6). The temp obtd by cordite deton ignition of IPN is 1027–1277° (Ref 10)

IPN has a Q_c^v of 4110cal/g (liq H_2O at 25° as ref), a Q_c^p of 4400cal/g (liq H_2O at 25° as ref), a Q_d^p of 630cal/g (w vap as ref at 100°), a Q_f^p of 660cal/g and a Q_{vap} of 70.5 or 79.5cal/g (Ref 6)

Tavernier and Lamouroux (Ref 6a) present a somewhat different set of thermal data; viz, a Q_c^v of 4456.5cal/g or 468.35kcal/mole; a Q_c^p of 4455.1cal/g or 468.206kcal/mole; a F_f^v of 489.3cal/g or 54.429kcal/mole; and a F_f^p of 549.7cal/g or 54.619kcal/mole

IPN has a hygroscopicity at 20° of 0.095% and at –20° of 0.03%

Impact sensy has been found for IPN by a modified Imp Chem Ind app (Ref 6) which consists of a sample cylinder ½ inch in diam and 1 inch long, fitted with a piston upon which a wt of 310g is dropped. Results were found for both air and nitrogen by varying the vol of the gas above the liq IPN. These data are tabulated below:

Gas in Vapor Space	Air		Nitrogen
Vol of gas, cc	1.35	0.86	–
Drop Height, cm	15 to 20	5 to 10	No explns up to 43cm
Calculated expln temp, °C	<400	<400	–

Impact sensy has also been detd by Médard (Ref 4b) using a 17mg sample wt. He dropped a 5kg wt 293cm to obtain v weak explns in 46 out of 100 drops. The 50% prob pt for IPN using this procedure was found to be 10m while NG was found to have a 50% prob pt of 0.4m

Again, from the work of Ref 6, power for IPN by BalMort using a Mk I mortar in conjunction with a No 6 ASA Al CB detonator was found to be 0.4; using a Mk IIIC mortar with a No 8 ASA Al CB detonator the power was found to be 73.9 (Ref of PA=100). Trauzl test values for IPN are tabulated below:

Temp, °C	Vol, cc/g [a]
0	3
10	11
20	16.5
30	19

[a] ethyl nitrate values over this temp are 41–42cc/g

Table 6 presents the data from Ref 6 on the initiation sensy of IPN

Table 6
Sensitivity to Initiation of IPN

Type of Initiation	Catalytic (Ni & Cr oxides in coke granules)	Spark	Hot Wire	Expl Shock
Type of Energy Input	Thermal (burning of air-fuel mixt)	Thermal (ionized gas)	Thermal (electrical)	Thermal (comprsn)
Min Energy Required	–	4.0millijoules	5.34Kjoules	∿10Kjoules
IPN State	liq spray in air	vapor/air mixt	liq	liq
% IPN in Mixt by Vol	100	5	100	100
Min Temp, °C	200	ambient	926	> 250
Min Press, cm Hg	ambient	ambient	ambient	> 1250psig
Time to Initiation, sec	∿1	0.5	2.170	<0.001

The specific heats of IPN product gas (primarily carbon monoxide and methane) arising from combustion are C_p 0.333cal/g/° and C_v 0.246cal/g/° (both calcd at 250psi and 300°K). The specific impulse of these gases (calcd at 400psi) is 155 lbs/thrust/lb/sec

The following data is the result of a series of high temp storage (stability) expts conducted by (Brit) Imp Chem Inds Ltd (Ref 6) on IPN:

a) A summary for a series of pressure development tests involving a steel vessel of 100cc capacity, half filled with IPN, and maintained at a given temp for four hours is presented below:

Temp, °C	Heating Period, Hrs	Pressure Developed, psi
100	4	12
120	4	15
135	4	23
142	4	80
150	4	100
160	2	Explds

b) In another series of tests on IPN involving a 500cc steel vessel, the rate of temp rise was recorded at the temps shown. The elapsed time required before decompn occurred at each temp is also shown. The conclusion reached in Ref 6 is that IPN is stable for prolonged periods at storage temps below 100°; at 120° IPN is reasonably stable for periods up to 3 hrs; above that temp, however, decompn occurs

Temp, °C	Time, Hours	Reaction After "Time"
120	3	Decompn
130	2	Decompn
150	< 0.5	Decompn

c) In an attempt to stabilize IPN at 140°, a series of additives were evaluated, unsuccessfully, using a 500cc steel vessel. From the data presented in Table 7 it was concluded that no additive would stabilize IPN since decompn occurred in the vap phase rather than the liq phase

Table 7
Evaluation of Additives for IPN Stabilization

Additive (%)	Mean Rate of Pressure Increase, (psi/min)
Ethyl iodide (2%)	0.6
Lead tetraethyl (0.1%)	0.7
Oxamide (satd)	1.0
Urea (satd)	1.0
Methyl centralite (1%)	1.1
2-Nitrodiphenylamine (1%)	1.1
None	1.2
Acetone (2%)	1.7
Carbon tetrachloride (2%)	1.8
Acetamide (satd)	2.4
Trichloroethylene (2%)	6.1

Table 8
IPN Storage Stability Tests

Test No	Relief Valve Setting, psig	Heating Time Reqd for Valve Operation, min	Temp Increase Range Of IPN, °C	Volume IPN Lost, %
1	15	60	130–143	55.05
2	40–45	28	145–150	26.77
3	No Relief Valve – Disc Burst at 110psig	33½	145	100
4	No Relief Valve – Disc Burst at 200psig	52	> 159	100

d) In a final series of tests on IPN high temp storage conditioning, a 2-gal aluminum container filled with IPN and filled with a bursting disc relief valve, thermocouples and a press gauge, was heated by total immersion in an oil bath maintained at 150°. The results of these tests are shown in Table 8

IPN storage recommendations are the same as for NPN (see the previous entry)

The toxicity of IPN is evaluated by Ref 6 as follows: (a) When inhaled as a vapor or adsorbed thru the skin, IPN acts as a vasodilator and produces a headache in the same manner as other organic nitrates; (b) When injected subcutaneously into rats at the rate of 4cc/kg body wt, it was concluded that the max allowable concn is 100ppm; and (c) When rats were exposed to different concn levels of IPN in air the following resulted:

(1) At 4% by vol deep anesthesia occurred in 30 mins and death in 2 hrs (3 rats); (2) At 2% by vol deep anesthesia was reached in 4 hrs, but the rats recovered within 24 hrs, after a total exposure of 6 hrs; and (3) At 0.2% by vol no ill effects were observed from 10 exposures of 6 hrs each

IPN is used as a rocket monoproplnt, a jet motor starting fuel, and its hot combstn prod gases are used to drive turbine type motors (Refs 6, 8 and 9). Other uses are in expls and proplnts (Addnl limited distribution Refs 1 to 4)

The viscosity of IPN at 20° is 0.66 centipoise

The vap press of IPN can be calcd by either one of two equations shown below. The results of such calcns over a temp range are given in Table 9

(1) $\log_{10}P = 29.08 - 2780/T - 7.3 \log_{10}T$, where P is in mm Hg and T is in °K; and

(2) $\log_{10}P = 7.303 - 1457/(t+227.5)$, where P is in mm Hg and t is in °C

Table 9
Vapor Pressure of IPN

Temp, °C	Vapor Pressure (mm Hg) according to Eqn No		Vapor Pressure Measured, mm Hg (Ref 4c)
	1	2	
–10	–	–	5.2
0	13	7.3	9.9
10	23	14.6	17.4
20	40	26.5	–
30	62	44.5	–
40	96	72.1	–
50	143	113	–
60	208	172	–
70	293	256	–
80	404	–	–

Refs: 1) Beil **1**, 363, [382] & {1465} 2) R.D. Silva, Ann **154**, 254 (1870) 3) A. Egerton & S.F. Gates, JInstPetrTechn **13**, 280 (1927) & CA **21**, 2555 (1927) 4) Naoûm, NG (1928), 209 4a) W.G. Allan & T.J. Tobin, "Isopropyl Nitrate", USP 2647914 (1953) & CA **48**, 7623 (1954) 4b) L. Médard, "Shock Sensitivity of Liquid Nitrate Esters", MP **31**, 131–43 (1949) & CA **46**, 11685 (1952) 4c) R. Vandon & M. Laudy, "Measurements of Vapour Pressure", MSCE **40**, 187 (1955) & CA **51**, 16027 (1957) 5) G. Desseigne, "A Procedure for the Continuous Fabrication of Isopropyl Nitrate", MP **37**, 97–110 (1955) & CA **50**, 17453 (1956) 6) Anon, "The Properties of Normal Propyl and Isopropyl Nitrates", Imp Chem Ind Ltd, Stevenston (Engl) (1957) 6a) P. Tavernier & M. Lamouroux, MP **39**, 344, 345 & 254 (1957) & CA **54**, 21974 (1957) 7) Urbański **2**, 165 (1965) 8) C. Brochet, "Monopropellant Detonation: Isopropyl Nitrate", Astronautica-Acta **15** (5–6), 419–25 (Eng), Pergamon Press, London (1970) & CA **74**, 89303 (1970) 9) L. Bretherick, "Handbook of Reactive Chemical Hazards", CRC Press, Cleveland (1975), 370 10) J.F. Griffiths et al, "Pyrolysis of Isopropyl Nitrate-II. Decomposition at High Temperatures and Pressures", Combustn & Flame **26**, 385–93 (1976) & CA **85**, 145393 (1976)

The following *Addnl Refs* on IPN are of limited distribution: 1) Anon, "General Synthesis. The Ludion Question. The Ludion Sustentator", Rept No **FSTC-HT-23-573-69** (1969) 2) B.H. Bonner, "Ullage Requirements for Packageable Propellants", Rept No **RPE-TM-533**, Rocket Proplsn Est, Westcott (Engl) (1970) 3) M.G. Farey, "The Gas Chromatographic Determination of Isopropyl Nitrate in Slurry Explosives", Rept No **ERDE-TN-41**, Waltham Abbey (Engl) (1971) 4) J. Diederichsen & B.H. Bonner, "Continuous Detection of Propellant Vapours", Rept No **RPE-TM-603**, Rocket Proplsn Est, Westcott (Engl) (1972) 5) R.E. Hull, "Ignition Limits of IPN Vapour/Air Bubbles in Tubes of 25.5mm Diameter", **DRIC BR-41608**, Rocket Proplsn Est, Westcott (Engl) (1973) 6) A. Clarkson & D. Wilson, "The Examination of Combustion Residues of Isopropyl Nitrate. Part I", **DRIC BR-52659**, Ministry of Defence, London (1975) 7) R.E. Hull, "The Adiabatic Compression of Isopropyl Nitrate Vapour/Nitrogen Bubbles in a U-Tube at Temperatures Between Ambient and 60°C", **DRIC BR-53761**, Rocket Proplsn Est, Westcott (Engl) (1976)

n-Propyl Nitrite (Nitrous acid n-propyl ester). $CH_3.CH_2.CH_2.O.NO$; mw 89.09; N 15.72%; OB to CO_2 −134.70%; liq; bp 47.75°; d 0.8864 g/cc at 20/4°, 0.935g/cc at 21°; RI 1.3592, 1.3613 (separate values). Sol in ethanol and eth. It forms azeotropic mixts with acet, carbon disulfide, pentane, propyl chloride, etc. Prepn is by reacting a mixt of n-propanol and Na nitrite with dil sulfuric acid. Coml prepn (Ref 2) consists of spraying an excess of nitric acid on vaporized propane at 400 to 1300°F and from 115 to 175psi in an adiabatic reactor

Vap inhalation causes vasodilation, smooth muscle relaxation and hypotension

N-propyl nitrate is used as a jet proplnt

Refs: 1) Beil **1**, 355, (178), [369] & {1419} 2) J.C. Reidel, OilGasJ **54** (No 36), 110–14 (1956) & CA **50**, 9003 (1956) 3) Merck (1976), 1018 (No 7654)

Iso-Propyl Nitrite (2-Propanol nitrite or Nitrous acid isopropyl ester). $(CH_3)_2CH.O.NO$; mw 89.09; N 15.72%; OB to CO_2 −13.470%; pale yel oil; bp 40.0°; d 0.844 at 25/4°; RI 1.3520. It forms azeotropic mixts with methylol, carbon disulfide, isopentane, isopropyl halides, isoprene, etc. Prepn is by treating isopropyl alc with nitrosyl chloride. Also, by passing NO_2 into isopropyl alc at 25–30°. Coml prepn is similar to that of n-propyl nitrite (above). The nitrite has a flash p of < 10°

According to Merck (Ref 5), ". . . isopropyl nitrite can cause vasodilation with fall in blood pressure, tachycardia, headache. Large doses can cause methemoglobinuria with cyanosis. Severe poisoning results in shock which can end fatally . . ."

Iso-Propyl nitrite is used as a jet proplnt, a jet proplnt additive and as an additive to diesel fuels

Refs: 1) Beil **1**, 362, (184), [382] & {1464} 2) T.F. Doumani & C.S. Coe, USP 2645079 (1953) & CA **47**, 9598 (1953) 3) J.C. Treacy, USP 2739166 & CA **50**, 15575 (1956) 4) Bretherick (1975), 369 5) Merck (1976), 684 (No 5077)

Propyl Nitrolic Acid. See in this Vol, N135-R

N,N′-Bis(Trinitropropyl) Oxamide. $(O_2N)_3.C.CH_2.CH_2.NHCO.CONH.(CH_2)_2.C(NO_2)_3$; mw 442.26; N 25.34%; OB to CO_2 −25.32%; crysts; mp 195–97° (decompn); d 1.692g/cc. Prepn is by reacting 3,3-trinitropropylamine with oxalyl chloride. The oxamide has a hot bar ign temp of 215° and an impact sensy about that of Tetryl
Refs: 1) Beil, not found 2) L.T. Carleton & M.B. Frankel, "Explosives Research", **Rept No 711**, Aerojet-Genl Corp, Azusa, ONR contract N7onr-462 (1953) 3) W.F. Sager & D.V Sickman, ". . . Research and Development in New Chemical High Explosives", **NAVORD 486** (1954)

N,N′-Dinitro-N,N′-Bis(Trinitropropyl) Oxamide. $(O_2N)_3.C(CH_2)_2.N(NO_2).CO.CO.N(NO_2).(CH_2)_2.C(NO_2)_3$; mw 532.26; N 26.32%; OB to CO_2 −6.01%; crysts; mp, exists in two isomers with different mp's, 125–26° and 128–29°. Prepn is by nitration of N,N′-bis(trinitropropyl) oxamide. The oxamide has a hot bar ign temp of 202° and an impact sensy approaching that of PETN
Refs: 1) Beil, not found 2) L.T. Carleton & M.B. Frankel, "Explosives Research", **Rept No 711**, Aerojet-Genl Corp, Azusa, ONR contract N7onr-462 (1953) 3) W.F. Sager & D.V. Sickman, " . . . Research and Development in New Chemical High Explosives", **NAVORD 486** (1954)

Propylpentaerythritol Trinitrate Ether. See in this Vol under "Pentaerythritol Propyl Ether Trinitrate"

Iso-Propyl Peroxides. See under "Peroxides" in this Vol

2,2-Dinitropropyl Phosphate. $CH_3.C(NO_2)_2.CH_2O_3.PO$; mw 463.30; N 18.14%; OB to CO_2 −56.98%; crysts; mp 155°. Prepn is by reacting 2,2-dinitropropanol with P pentachloride. The phosphate has an impact sensy about that of Comp A
Refs: 1) Beil, not found 2) W.F. Sager & D.V. Sickman, "Second Report on Research and Development in New Chemical High Explosives", **NAVORD 483** (1952)

Propyl isopropylether, 3,3,3-Trinitro. $(O_2N)_3C.CH_2.CH_2.O.CH(CH_3)_2$; mw 237.19; N 17.72%; OB to CO_2 −70.83%; liq; bp 53–56° at 1 mm; RI 1.4380. Prepn is by reacting nitroform with vinyl isopropylether. The ether burns readily and deton with a heavy blow
Refs: 1) Beil, not found 2) Anon, "Synthesis of New Explosives & Propellants", Quarterly Progress Rept No 4, US Rubber Co, Passaic, Contract Nord 10129 (1948)

Bis (2,2-Dinitropropyl) Succinate. See Vol **5**, D1500-L (information incomplete). $CH_3.C(NO_2)_2.CH_2O_2.C.(CH_2)_2.CO_2.CH_2.C(NO_2)_2.CH_3$; mw 382.28; N 14.66%; OB to CO_2 −62.78%; crysts; mp 84–85°; d 1.51g/cc. Prepn is by reacting dinitropropanol with succinyl chloride. The ester has a hot bar ign temp of > 400°
Refs: 1) Beil, not found 2) W.F. Sager & D.V. Sickman, ". . . Research and Development in New Chemical High Explosives", **NAVORD 486** (1954)

Bis(Trinitropropyl) Sulfone. See under "3,3,3,3′,3′,3′-Hexanitropropyl-sulfone. . ." in Vol **5**, D1501-L

Bis(Trinitropropyl) Urea. See under "Dipropylureas and Derivatives" in Vol **5**, D1501-L & R

[N′-Isopropyl-Ureido] -Acetic Acid Azide (5-Isopropyl-hydantoin acid azide). $(CH_3)_2CH.NH.CO.NH.CH_2.CO.N_3$; mw 185.22; N 37.82%; OB to CO_2 −133.89%; mp ca 100° (deflagrates quickly when heated). Prepn is by reacting [N-isopropyl-ureido] -acetic acid-hydrazide with Na nitrite dissolved in aq HCl
Ref: Beil **4**, {1169}

Propylene and Derivatives. See Propylene under "Polypropylene" in this Vol. The Derivatives are listed under "Propene and Derivatives", also in this Vol

Propylene Dinitramine (PDNA). See under "Diaminopropane and Derivatives" in Vol **5**, D1143-R

Propyleneglycols and Derivatives. See under "1,2- and 1,3-Propane Diol and Derivatives" in this Vol. For "Propyleneglycol", see under "Glycols and Derivatives" in Vol **6**, G112-L to G114-R. Addnl propyleneglycol compds of interest are presented next

3-Azido-1,2-Propyleneglycol Dinitrate (3-Azido-1,2-propanediol dinitrate or Dinitroazidohydrine). $(O_2NO).CH_2.CH(ONO_2).CH_2.N_3$; mw 207.13; N 33.82%; OB to CO_2 −19.3%; liq; mp, explds on heating. Prepn is by reacting glycerin monochlorohydrin with Na azide, and then nitrating the resulting prod. The azide has a calcd power of 162% PA and is extremely sensitive

Refs: 1) Beil, not found 2) Blatt, OSRD **1085** (1942), 3 3) ADL Punch Cards **I** (1947), 48 4) Ibid **II** (1954) (Conf)

Di[2,2-Dinitro-1,3-Propyleneglycol]-Trinitro Butyrate. $(O_2N)_3.C.(CH_2)_2.C(O).O.CH_2.C(NO_2)_2.CH_2.O.(O)C.(CH_2)_2.C(NO_2)_3$; mw 576.31; crysts; mp 144°; d 1.68g/cc. Prepn is by the addn of nitroform to the acrylate ester of 2,2-dinitro-1,3-propylene glycol or by the addn of acrylyl chloride to the glycol. The compd has an ign temp of 235° and an impact sensy about that of Comp A. It was hoped that the ester could be used as a casting medium, but its high mp and low d were unsatisfactory for mil purposes

Refs: 1) Beil, not found 2) W.F. Sager & D.V. Sickman, "Second Report on Research and Development in New Chemical High Explosives", **NAVORD 483** (1952), 15

Nitropropylenes. See under "Propene and Derivatives" as 1-, 2-Nitro and Di-Nitro Propenes in this Vol

Propylene Oxide (1,2-Epoxypropane, Methyloxirane or Prepene Oxide).



$CH_2CH.CH_3$; mw 58.08; OB to CO_2 −220.39%; colorl liq, ether-like odor; mp −104.4°; bp 35°; d 0.859g/cc at 0/4°; RI 1.3670. V sol in ethanol, eth and w. Prepn is by treating propylene chlorohydrin with an aq soln of KOH. The oxide has expl limits in air of 3.1 to 27.5%, 2 to 22% (separate values); an autoign temp of 465°; a flash pt (open cup) of −37°; a Q_c^v of 7771.3cal/g. The compd deton weakly and burns with a clear blue flame. It may flash-back a great distance from an ign source. It also polymerizes in contact with highly active catalysts such as bases, releasing v large amts of heat resulting in an expln when confined

Propylene oxide has an LD_{50} (oral-rat) of 1140mgs/kg and a respiration lower tolerance level vol of 100ppm (Refs 7, 8 & 9)

It is used as an intermediate in the synthesis of various chemicals; as a low-boiling solvent for gums, resins, NC, etc; it is also considered a candidate for use in fuel-air munitions

Refs: 1) Beil **17**, 6, (4) & [12] 2) H. Moureu & M. Dode, BullFr **4** (5), 637 (1937) & CA **31**, 4884 (1937) 3) D. Porret, Helv **30**, 701–06 (1947) & CA **41**, 5779 (1947) 4) Anon, "Synthesis of New Propellants & Explosives", Quarterly Progress Rept No 5, US Rubber Co, Passaic, Contract Nord 10129 (1948), 36–37 4a) G.O. Curme, Jr & F. Johnston, "Glycols", ACS Monograph No 114, Reinhold, NY (1952) 4b) A.F. Gait, "Propylene Oxide" in E.G. Hancock, Ed, "Propylene and Its Industrial Derivatives", Wiley & Sons, NY (1973), 273–97 5) R.C. Crews, "Effects of Propylene Oxide on Selected Species of Fishes", **AFATL TR-74-183** (1974) 6) Bretherick (1975), 364 7) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The Intl Tech Info Institute, Tokyo (1975), 449–50 8) Merck (1976), 1017 (No 7645) 9) CondChemDict (1977), 727–28

Propyleneoxozonide. $C_3H_6O_4$(structure ?); mw 106.11; OB to CO_2 −75.39%; a sticky oil of unknown odor; bp 28–34°, d 1.0672g/cc at 22°; RI 1.37978 at 22°. Prepn is by reaction of propene and ozone dissolved in ethyl chloride and cooled using a mixt of carbon dioxide and ether. The ozonide is a strong expl
Ref: Beil **1**, (82)

Bis-Propylene Pseudonitrosite.
$CH_3.CH.CH_2.NO_2$
N.O.O.N
$CH_3.CH.CH_2.NO_2$ (Ref 2); mw 236.22; N 23.72% (calc), 26–26.9% (found); OB to CO_2 −81.28%. Prepn is by reacting N_2O_3 with propylene in eth at a temp of 5 to 20°. Marshall (Ref 2) proposed the compd for use as a base charge
Refs: 1) Beil **1**, 198 & {260, 695}, listed as the propylene pseudo nitrosite ($C_3H_6N_2O_3$)
2) J. Marshall, USP 1473825 (1923) & CA **18**, 588 (1924)

Iso-Propylidene-Dicyclohexylidene-Triperoxide. See in Vol **2**, B144-R

Iso-Propylidene-2,4,6-Trinitro-Phenylhydrazine (Acetone-[2,4,6-trinitro-phenyl hydrazone] or Acetone-picrylhydrazone).
$(O_2N)_3.C_6H_2.NH.N:C(CH_3)_2$; mw 283.23; N 24.73%; OB to CO_2 −93.21%; yel ndles; mp 125°, decomps at 130°. V sol in benz, chlf, acetic acid and eth acetate; sol in ethanol and eth. Prepn is by boiling a mixt of picrylhydrazine and acet in ethanol
Ref: Beil **15**, 495

Propyne. See under "Methyl Acetylene" in this Vol, M94-R
Addnl Ref: A.R. Hall & R.A.M. Straker, "The Methyl Acetylene (Propyne) Decomposition Flame at Pressures of 10, 20 and 40 Atmospheres", **RPE Tech Note 192**, RPE, Westcott (Engl) (1960)

Prosperit V. An older Brit permitted expl contg AN 60, Na nitrate 5, meal 4, nitrotoluenes 6, alkali chloride 21, and NG 4%. OB to CO_2 +2.7%; Pb block expansion 235cc
Ref: Naoûm, NG (1928), 434

Proteins, Nitrated. Proteinaceous or albuminoid materials (glue, bones, hides, leather, hair, feathers, etc) can be nitrated in a two-stage process to yield expl yel oils. Thus, glue is treated first with 3.6 pts by wt of 66°Bé sulfuric acid and 2.7 pts of 36°Bé nitric acid. The resultant oil is sepd from the heavier spent acid and nitrated further with 3 pts of oleum and 2.6 pts of 36°Bé nitric acid. Both nitrations are conducted at 15–20°, and never above 40°. The resulting oily expl can be used alone or mixed with other materials

To prepare a gelatinous expl, mix with stirring 4 pts of collodion cotton dissolved in 10 pts of acet, 6 pts of "nitrated glue", and 1 pt of castor oil (to increase the flexibility of the product). After evapg the acet, the mass can be cartridged

To prepare a granular expl, the above procedure is used, except that the castor oil is replaced by an equal wt of mononitronaphthalene. About 80% of the acet is evapd, and the mass extruded in any desired shape. Or, the acet can be almost completely removed, and the mass rolled into sheets which can be cut to any desired size
Refs: 1) V. Gallarati, BritP 358116 (1930) & CA **26**, 6141 (1932) 2) M. Bonotto, USP 2411145 (1946) & CA **41**, 865 (1947)

Protol or Protoglycerin. See Fermentol in Vol **6**, F14-R

Proving Ground (PG). An area or location where equipment, ammo, or weapons are tested or proved
Ref: Anon, OrdTechTerm (1962), 239-L

Proximity Fuze. See Vol **4**, D918-R to D921-R

"PRP" Wax. A waxy substance composed of a mixt of petroleum, rosin and paraffin. It was used in Dynamite manuf for coating grains of AN to render them non-hygroscopic

Sorenson patented an expl suitable for blasting operations which contained AN 100, Mn dioxide 15, petroleum naphtha 6, rosin 15, paraffin 6, potato flour 8, Al 30, and NG 100 pts
Ref: E. Sorenson, USP 1709498 (1929)

Prussian Fire (Feu Prussian in Fr). See under Wigfall Powder

P.S.G. and P.I.G. See under P.I.G. and P.S.G. in this Vol

PTX-1. An expl developed at PicArsn during WWII for use in land mines and demolition charges. It contained Tetryl 50, RDX 30 and TNT 20%; mw 252; OB to CO –9%, to CO_2 –45%; mp, eutectic 67°, pouring temp 90–95°; d (cast) 1.68g/cc; exudes at 65° and above; sol in acet. Prepd by adding the appropriate wt of w-wet RDX to 40/60 Tetrytol previously melted in a steam-jacketed melt kettle. Heating and stirring are continued until all the w is evapd and the mixt is uniform in compn. It can also be prepd by adding Tetryl to Composition B
Blast. Relative to TNT in air; impulse 109%, peak press 111%
Brisance. Sand test, 54.8g vs 43.0g for TNT; plate dent test, method B, 127% TNT
Compatibility with metals. Does not affect Al or mild steel, wet or dry
Detonation velocity. 7400–7655m/sec for an unconfined cast charge 1 inch in diam, d 1.68 g/cc; vs 6900m/sec for TNT
Fragmentation test. In 3-inch HE shell, wt of charge 0.864 lbs, d 1.63g/cc: total number of fragments 685 vs 514 for TNT
Fragment velocity. At 9 ft, 2690ft/sec; at 25.5 ft, 2460ft/sec
Hygroscopicity. Wt gain after 15 days at 30°, 95% RH: nil
Impact sensitivity. BuMines app, 2kg wt, 44cm vs 100+cm for TNT; PicArsn app, comparable to Tetrytol
Initiation sensitivity. Can be detonated by 0.23g of MF or 0.22g of LA; does not require a booster
Rifle bullet sensitivity. About 40% of trials affected by 0.30 cal bullet fired at 90 ft
Stability. 100° Vać Stab test: 3cc/5g/40 hrs
Note: A **PTX-3** compn, prepd by the addn of Haleite to 40/60 Tetrytol, also offered promise in applications where the charge would not be required to withstand 65° storage without exudation
Refs: 1) W.R. Tomlinson, Jr, PATR **1402** (1944) (PTX-1 loading study) 2) L.H. Eriksen, PATR **1506** (1945) (Exudation study of PTX-1) 3) Anon, "Allied and Enemy Explosives", Aberdeen Proving Ground (1946), 131–32 4) Anon, EngrgDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971)

PTX-2. An expl developed at PicArsn during WWII intended to replace the more sensitive Pentolite. There were two types, with almost identical properties:

	% by Wt	
RDX	44	41
PETN	28	26
TNT	28	33
mw	244	243
OB to CO	–3%	–4%
OB to CO_2	–33%	–36%

mp, eutectic 75°, pouring temp about 95°; d (cast) 1.71g/cc; does not exude at 65°

Its properties, as examined at PicArsn, were as follows:
Blast. Relative to TNT in air; impulse 113%, peak press 113%
Brisance. Sand test, 56.9g vs 53.0 for Pentolite and 43.0 for TNT; plate dent test, method B, 141% TNT for cast unconfined PTX-2, d 1.71g/cc
Compatibility with metals. Does not affect Al, dry or wet; does not affect mild steel, dry
Detonation velocity. 8000–8065m/sec for an unconfined cast charge 1 inch in diam, d 1.70 g/cc; vs 7500m/sec for Pentolite and 6900m/sec for TNT
Fragmentation test. In 3-inch HE shell, wt of charge 0.897 lbs, d 1.70g/cc: total number of fragments 750 vs 514 for TNT
Fragment velocity. At 9 ft, 3020ft/sec; at 25.5 ft, 2850ft/sec

Friction sensitivity. Crackles with steel shoes
Hygroscopicity. Wt gain after 15 days at 90% RH: nil
Impact sensitivity. BuMines app, 2kg wt, 35cm vs 100+cm for TNT; PicArsn app, 10 inches vs 9 inches for Pentolite and 14 inches for TNT
Initiation sensitivity. Can be detonated by 0.21g of MF, and does not require a booster
Power. BalMort test, 138–45% of TNT, 130% Pentolite
Rifle bullet sensitivity. About 60% of trials affected by 0.30 cal bullet fired at 90 ft, vs 92% affected for Pentolite
Shaped charge effectiveness. Steel cone, hole volume 130% TNT
Stability. 100° Vac Stab test: 2.6cc/5g/40 hrs; 120° Vac Stab test: 11+cc/5g/40 hrs
Uses. Shaped charges and fragmentation weapons. Field tests showed that PTX-2 is superior to Pentolite

PTX-2 can be prepd by adding the appropriate wt of w-wet RDX to 30/70 Pentolite previously melted in a steam-jacketed melt kettle. Heating and stirring are continued until all the w is evapd and the mixt is uniform in compn. It can also be prepd by adding w-wet PETN to Composition B
Note: A **PTX-4** compn, prepd by the addition of Haleite to 30/70 Pentolite, also offered promise, but because of borderline stability in accelerated stability tests, it was decided that PTX-4 must be proven by long term storage to be acceptable for use in standard ammo
Refs: 1) W.R. Tomlinson, "Properties of Ternary Mixtures of High Explosives," PATR **1414** (1944) 2) A.J. Phillips, "The Manufacture of PTX-2 by the Slurry Precipitation Process", PATR **1445** (1944) 3) Anon, "Allied and Enemy Explosives", Aberdeen Proving Ground (1946), 131–32 4) Anon, EngrgDesHndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971)

Pudrolithe (Rockpowder). Blasting expl patented in 1872 and manufd in Engl and Belg. A typical formulation contained K nitrate 68, S 12, charcoal 6, sawdust 5, Ba nitrate 3, Na nitrate 3, and spent tan bark 3%
Ref: Daniel (1902), 653

Pullivitz Explosive. A Ger permissible expl patented in 1896 contg AN 92.0, phenanthrene 5.5, and K dichromate 2.5%
Refs: 1) Daniel (1902), 659 2) PATR **2510** (1958), Ger 152-L 3) Guia, Dizionario **6** (1959), 375

Pulvarent Ammonium Dynamite. NG 20, AN 25, Na nitrate 36, and dry rye flour 19%
Ref: Daniel (1902), 659

Pulverin. French for meal powder. A special, finely pulverized BlkPdr consisting of K nitrate 75, S 12.5 and charcoal 12.5%, prepd by rolling the ingredients with Pb or lignum vitae balls in a hardwood barrel. It has been used in pyrotechnic applications
Refs: 1) G. Cavaignac, "Livraison de Pulverin aux Artificiers", MP **3**, 29 (1890) 2) Daniel (1902), 659 3) Davis (1943), 45

Pulvis Fulminans. An older expl, differing in compn from BlkPdr, contg K nitrate 50.0, S 16.7 and K carbonate 33.3%
Ref: Daniel (1902), 659

Punch Test for Explosives (Stanzprobe in Ger). See under Brisance Test Methods in Vol **2**, B299-R

Punshon Explosive. Patented in 1870; consisted of NC soaked for 12 hrs in a sugar soln, and an oxidizer, such as a nitrate. Another expl, patented by the same inventor in 1875, was a 70% Dynamite contg either peat or toasted peas as absorbants, to which pulverized NC could be added. The third expl patented by Punshon (1880) consisted of nitric and picric acids absorbed on a porous material such as asbestos, and loaded into cartridges which were painted with a mixt of Na silicate and powdered glass

Punshon was also the inventor of *Oxonite* and *Victorite* (qv)
Ref: Daniel (1902), 659–60

PVA-4. A semi-plastic expl of Canadian origin, developed during WWII by Dr. Sutherland of Shawinigan Chemicals, Ltd. It contained RDX 90, PVA (polyvinylacetate) 8, and dibutylphthalate 2%. Mw 217; white solid; OB to CO_2 −37%, to CO −10%; softening pt 92°; d (pressed) 1.60g/cc

A practical method of prepg this compn was by the addition of a soln of the coating agent to an aq RDX slurry. Based on the quality of the product and the pellet densities obtained, a procedure of adding an acet soln of PVA + DBP to a hot w slurry of RDX, under agitation, was adopted as standard

In evaluating various types of PVA commercially available in the US, a type obtained from Union Carbide and Carbon, under the trade name "AYAT" was the most promising coating for RDX in the above proportions

Its properties; as detd at PicArsn, were as follows:

Brisance. Sand test, 58.5g vs 43.0 for TNT

Detonation velocity. 7910m/sec for a cast, unconfined sample 1.0″ diam at d 1.60g/cc

Explosion temperature. No cap used; 375° (decomps) after 5 secs; 330° after 1 sec

Friction pendulum test. Unaffected by fiber shoe, crackles on steel shoe

Hygroscopicity. Wt gain at 30° and 90% RH, 0.20%

Impact sensitivity. BuMines app, 2kg wt, 39cm vs 100+cm for TNT; PicArsn app, 9″ vs 14″ for TNT

Initiation sensitivity. Can be detonated by 0.22g of Pb Azide, and does not require a booster

Loading. Cast or extruded; plasticity 0.3 at 25°, cracked at −40°

Rifle bullet sensitivity. In 5 trials with 0.30 cal bullets fired at 90 ft, 20% explns, 60% burned, 20% unaffected. In 100 trials at −46°, all unaffected

Stability. 100° Heat test: Wt loss 0.10% during first 48 hrs, 0.06% in second 48 hrs; no expln after 100 hrs

Volatility. 0.03% wt loss after 6 hrs at 55° under vacuum

Uses. Demolition charges

Ref 1 states that PVA-4 has sensitivity and stability characteristics considered satisfactory for a demolition expl, and has greater brisance than Composition A or Tetrytol. It undergoes embrittlement when cooled to −40°, but is nonvolatile, non-hygroscopic, insol in w, and has such a high softening pt that exudation in storage is extremely unlikely

Refs: 1) S. Livingston, "Characteristics of Explosive PVA-4", PATR **1532** (1945) 2) H. Aaronson, "Semi-Plastic RDX Compositions", PATR **1634** (1946) 3) Anon, EngrgDes-Hndbk, "Explosives Series, Properties of Explosives of Military Interest", **AMCP 706-177** (1971), 312–14

PVN. Acronym for Polyvinylnitrate (see in this Vol)

PW (Poudres de Wetteren). BlkPdrs used by the Fr Navy in larger cal guns. Prior to this, the so-called "Poudres A" were employed

Ref: Daniel (1902), 660

PW. Acronym for White Phosphorus (see in this Vol under Phosphorus, White)

Pyridine and Pyridinium Compounds

Pyridine. C_5H_5N; mw 79.10; flammable, colorl liq, characteristic disagreeable odor, sharp taste; mp −42°; bp 115–16°; d 0.9780 at 25/4°; RI 1.50920 at 20°. Flash pt 20° (closed cup); ignition temp 482°; flammable limits 1.8–12.4%. Vapor may travel considerable distance to a source of ignition and flash back. Vapor forms expl mixts with air (Refs 4 & 5)

There are many methods of prepn of pyridine (Ref 2). It is misc with w, alc, eth, petr eth, oils and many other organic liqs

Pyridine may cause central nervous system depression, irritation of skin and respiratory tract. Large doses may produce gastro-intestinal disturbances, kidney and liver damage (Refs 3 & 4)

Refs: 1) Beil **20**, 181, (54) & [96] 2) E. Klingsberg, Ed, "Pyridine and Its Derivatives", Interscience, NY (1960) 3) E. Browning, "Toxicity and Metabolism of Industrial Solvents", Elsevier, NY (1965), 304–09

4) Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical Information Institute, Tokyo (1975), 452–53 5) Merck (1976), No 7752

Pyridine Chlorate. $C_5H_5N.HClO_3$, mw 163.57, N 8.56%, mp 142° (with decompn). Was prepd by Datta & Choudhury (Ref 3) by evapg on a w bath a mixt of a slight excess of pyridine and concd perchloric acid. The resulting crystals of the salt were washed with a small amt of cold w and recrystd from alc. It is sol in w and alc, and insol in non-dissociating organic solvents. When heated, it burns with a sudden flash; it flames when brought into contact with concd sulfuric acid

Pyridine Perchlorate. $C_5H_5N.HClO_4$; mw 179.5; N 7.8%; OB to CO_2, Cl_2 and H_2O –80.2%; mp about 288° (without decompn). Can be prepd by treating pyridine with 20% perchloric acid, and then adding alc to ppt the perchlorate

Sl sol in w (9.49g in 100ml of soln at 19°); v sl sol in alc (100ml of satd soln in abs alc contains, at 19°, 0.454g; in 95% alc, 1.20g)

Pyridine Perchlorate is almost as powerful as TNT (Pb block expansion 95% TNT, 87% PA), but is much more sensitive to impact (FI 40% PA), being comparable to PETN in this respect (Refs 4 & 5). Kuhn (Ref 7) states that it can be detonated on impact, but is normally considered a stable intermediate, suitable for purification of pyridine. Occasionally explns have occurred when the salt was disturbed (Ref 11), which have been variously attributed to the presence of ethyl perchlorate, AP or chlorates. A safer preparative modification is described (Ref 8). It explds on heating to above 335°, or at a lower temp if AP is present (Ref 10). According to Mellor (Ref 9), the salt can expld violently in contact with metals, while Zacherl (Ref 6) describes a lab expln which occurred during the distn of pyridine liberated from its perchlorate

Pyridine Picrate. $C_5H_5N.C_6H_3O_7N_3$, mw 308.22, N 18.2%, gold-yel needles from alc, mp 167–68°. It was prepd by Ladenburg (Ref 2) by mixing concd solns of pyridine and PA. The salt is difficultly sol in w. It explds when heated rapidly above its mp

Refs: 1) Beil **20**, 200 & 208, (58 & 81), [104, 122 & 154] 2) A. Ladenburg, Ann **247**, 5 (1888) 3) R.L. Datta & J.K. Choudhury, JACS **38**, 1083 (1916) 4) Blatt & Whitmore, OSRD **1085** (1942), 78 5) Blatt, OSRD **2014** (1944) 6) M.K. Zacherl, MikrChem **33**, 387–88 (1948) & CA **42**, 6537 (1948) 7) R. Kuhn et al, ChemZtg **74** (1950), 139 & CA **44**, 6129 (1950) 8) F. Arndt et al, ChemZtg **74** (1950), 140 9) Mellor **2**, Suppl 1 (1956), 603 10) J.C. Schumacher, "Perchlorates, Their Properties, Manufacture and Uses", ACS Monograph **146**, Reinhold, NY (1960) 11) Anon, Chemiearbeit **15** (3) (1963), 19

Pyridine Compounds with Metallic Salts.

Pyridine combines with many inorganic salts to form additive compds. Some of these are expl, eg:

1) $2C_5H_5N.Cu(N_3)_2$; green crysts changing to brown; explds violently ca 202–03° [Beil **20**, 191; A. Cirulis & M. Straumanis, ZAnorgChem **251**, 350 (1943)]

2) $2C_5H_5N.HgCr_2O_7$; orange crysts; expld on heating above 300° (Beil **20**, 199)

3) $3C_5H_5N.Cr(N_3)_2$; green crysts; expld violently when heated [Beil **20**, (62)]

4) $6C_5H_5N.Cu(ClO_4)_2$; bluish-violet crysts; expld violently when heated (Beil **20**, [104–05])

5) $2C_5H_5N.Cd(CON)_2$; yellowish crysts; expld weakly when heated (Beil **20**, [109])

6) $C_5H_5N.CrO_3.HF$; orange-yel crysts; expld when heated (Beil **20**, [113])

7) $C_5H_5N.MnClO_4.3H_2O$; nearly colorl crysts; expld when heated (Beil **20**, [115])

8) $4C_5H_5N.Zn(ClO_4)_2$; prisms; expld weakly when heated (Beil **20**, [108])

Pyridine Complexes of Metallic Permanganates.

Pyridine, C_5H_5N, like ammonia, forms complexes with various metallic permanganates. In general, they are more or less sol in w and very sol in pyridine. When heated rapidly they expld, but decompose when heated slowly. They burn vigorously when moistened with sulfuric acid or when suddenly compressed. They are unstable and lose pyridine even at RT, and for this reason should be prepd and dried at 0°

Cadmium complex. $4C_5H_5N.Cd(MnO_4)_2$; violet tubular crysts, apparently rhombic. It was prepd by mixing concd solns of pyridine (4 moles) and $Cd(MnO_4)_2$ (1mole) at 0°. V sol in w; explds at about 65°
Cobalt. Could not be prepd
Copper. $4C_5H_5N.Cu(MnO_4)_2$; violet crysts; expld at about 65°. Was prepd by adding a small quantity of pyridine to an aq soln of $AgNO_3$ and $KMnO_4$, mixed in equivalent proportions
Nickel. $4C_5H_5N.Ni(MnO_4)_2$; blk pdr; very unstable; decomps at about 65°. Was prepd in the same manner as the cadmium salt
Silver. $5C_5H_5N.2AgMnO_4$; violet needles; explds at about 100°. Was obtained by pouring a mixed soln of $AgNO_3$ + $KMnO_4$ into an excess of pyridine, or by gradually adding w to a 50% soln of $AgMnO_4$ in pyridine
Silver. $2C_5H_5N.AgMnO_4$; violet microscopic crysts. Was prepd by adding a small quantity of pyridine to an aq soln of $AgNO_3$ and $KMnO_4$, mixed in equal proportions. V sl sol in w; decomps or explds at about 65°
Zinc. $4C_5H_5N.Zn(MnO_4)_2$; violet crysts; v sol in w; explds at about 65°. Was prepd in the same manner as the cadmium salt
Refs: 1) Beil **20**, 200 & 203 2) T. Klobb, CR **118**, 1271–73 (1894) & JCS **66** (I), 548 (1894)

"Pyro". Abbreviation for Pyrocellulose

Pyrocatechol. See under Dihydroxybenzene and Derivatives in Vol **5**, D1270-R ff

Pyrocellulose. See under "Pyrocellulose, Pyro or Pyrocotton" in Vol **2**, C105-L ff

Pyroclok. Trademark for a slow-burning delay train which furnishes a 5-minute delay time in about 10 inches of column length
Refs: 1) H. Ellern & D.E. Olander, USP 2954735 (1960) 2) Ellern (1968), 199

"Pyrocollodion" Powder. A smokeless powder developed in Russia about 1891 by Prof. D.I. Mendele'eff, based on NC contg 12.44% N (Pyrocellulose). Its degree of nitration was slightly lower than that of decanitrocellulose, $C_{24}H_{30}O_{10}(ONO_2)_{10}$, which has N=12.75%. The reason for using "Pyrocollodion" was that it contained just enough oxygen for combustion to CO and H_2O. In actual tests, however, some CH_4 and CO_2 were also present in the combustion gases

Trials conducted at Okhta (near St Petersburg) showed that Pyrocollodion powder was fairly stable, and burned slowly and uniformly. When a 40kg projectile was fired from a 150mm cannon, a muzzle velocity of about 785m/sec was obtained. A Krupp armor plate 36.8cm thick was pierced by a shell weighing 225kg when projected by "Pyrocollodion" from a 250cm cannon

This powder was so successful that it was adopted not only in Russia (in preference to Vieilles' "Poudre B", developed in Fr), but also by the US Navy. Its introduction in this country was due to Lt. Bernadou, US Naval Attaché in St. Petersburg at that time. Soon after its introduction in the USA (1895–96), the powder was manufd at the Naval Powder Factory, Indian Head, Md. It should be noted that Bernadou improved the powder by using NC with a slightly higher N content (12.6–12.7%), and this became known as "Pyrocellulose Powder". Its use by the US Army began about 1899

Pyrocollodion and Pyrocellulose powders belong to the single-base type because they contain only NC and about 1% of a stabilizer, diphenylamine. Both are nearly completely sol in eth-alc mixts. According to microscopic observations conducted by Sapojnikoff (Ref 5), Pyrocollodion powder is much more uniform than the Fr "Poudre B", both CP_1 and CP_2 types

Both Pyrocollodion and Pyrocellulose powders were much "cooler" than powders contg NG (such as Ballistite and Cordite) and caused much less erosion

According to Pérez Ara (Ref 5), the following countries used single-base proplnts until about the beginning of WWII: France, Russia, USA, Argentina, Mexico, Spain, Cuba, Belgium, Switzerland and Rumania, while other countries used either double-base powders exclusively (such as England and Italy), or both single and

double-base powders (Germany and Japan)
Note: Prior to and during WWII, the Germans developed several "cool" proplnts in which NG was replaced by Ethyleneglycoldinitrate (EGDN) or Nitroguanidine. They also developed proplnts which contained neither NC or NG, such as "Tetrasalz" proplnts, which contained Tetramethylammonium nitrate
Refs: 1) Daniel (1902), 660–61 2) C.G. Storm, ArmyOrdn **2**, 217 (1922) 3) Van-Gelder & Schlatter (1927), 780 & 835–36 4) Davis (1943), 259 5) A. Pérez Ara (1945), 448–51 6) Urbański **2** (1965), 215

Pyrocore. See Vol **4**, D763-L
Addnl Refs: 1) Ellern (1968), 191–92 2) K.O. Brauer, "Handbook of Pyrotechnics", Chem Publishing Co, NY (1974), 58–59

Pyrocoton or Coton Pyrique. An expl mixt consisting of NC and picrates, proposed in 1883 by Parozzani as a bursting charge for projectiles
Ref: Daniel (1902), 661

Pyrocotton. Same as Pyrocellulose

Pyrodex. Tradename of a close substitute for BlkPdr, invented by D. Pawlak and distributed by the Hodgdon Powder Co, Shawnee Mission, Kansas intended primarily for use with replica sporting firearms. It can be loaded volume-for-volume with BlkPdr, producing similar pressures and velocities. It smokes, smells and fouls somewhat like BlkPdr, and it is claimed that Pyrodex is actually safer to handle and store than modern smokeless powder (Refs 1 & 3)

Pyrodex comes in several types: RS for rifles and shotguns, P for handguns, C for BlkPdr cannon, and CR for BlkPdr centerfire cartridges. It requires very firm bullet-seating, hot percussion caps, and a strong hammer-spring for good ignition – it is not recommended for flintlocks (Ref 3)

Pyrodex is classified as a Class B explosive by the Bureau of Explosives of the Association of American Railroads (Ref 5)

Four persons, including inventor D. Pawlak, were killed in a fire that swept the Pyrodex Corp plant in Issaquah, Washington, on 27 Jan 1977. The plant had been in operation for 13 months. The cause of the fire was not known, and no decision had been made on whether or not to resume operations (Ref 4)
Refs: 1) C. Askins, Guns & Ammunition (July 1976), 74 & 84–85 2) Anon, American Pyrotechnist Fireworks News **9**, No 5 (Sept 1976), 758 3) J. Wootters, Field & Stream (Jan 1977), 59 4) Anon, Gun Week (Feb 7, 1977) 5) G. Cohn Ed, Expls & Pyrots **10**, No 1 (Jan 1977) & 10, No 3 (March 1977)

Pyrodialites or Pyrodialytes. A series of expl mixts, patented in Fr by Turpin, beginning in 1881, and contg as principal combustible ingredients, tar (goudron), rosin, etc; and as oxidizers, K chlorate alone or in mixt with K or Na nitrates. The following examples are taken from Daniel (Ref 2): *Extraforte No 0:* K chlorate 88, tar 10, charcoal 5, Na or Amm bicarbonate 2–3ps; *Lente No 2:* K chlorate 40, Na nitrate 48, tar 20, charcoal 5, Na or Amm bicarbonate 4–5ps. These expls were too "hot", and were not approved for use in gaseous coal mines

In 1888, Turpin prepd a series of "cool" expls which were permissable, by incorporating materials such as alkali chlorides, Na or K bicarbonate (up to 50% content), fluorides, acetates, oxalates, Ba carbonate.$10H_2O$, chromates, hyposulfites, stannic acid, boric acid, borates, etc, in the expls listed above; eg, a) K chlorate 45, double salt of Ca and K acetochlorate 35, tar 18, charcoal 5, and alkali bicarbonate or oxalate 15ps; b) K chlorate 15, double salt of K and Amm chlorobichromate 35, K or Na nitrate 10, tar 18, charcoal 5, and K or Na bicarbonate 15ps

Due to the fact that chlorates are very sensitive to mechanical action, Turpin replaced them with perchlorates, eg, a) K perchlorate 80, tar 10, and Amm trinitrocresylate 10%; b) K perchlorate 60, tar 10, & Amm Picrate 30%; c) Amm Perchlorate 85 & tar 15%; d) Amm Perchlorate 75, tar 10, & Amm trinitrobenzoate 15%; and e) Amm Perchlorate 50, tar 10, & Guanidine Nitrate 40%

As an antiacid, 2.5 to 5% Na or Amm bi-

carbonate was added to these compns. By incorporating a cooling agent, such as an oxalate or bicarbonate, permissible expls could be obtained

Turpin's expls were soon superseded by Cheddites (see Vol **2**, C155-L to C164-R), introduced by Street in 1897

Refs: 1) Commission des Substances Explosives, MP **11**, 53–56 (1901) 2) Daniel (1902), 661 3) Pepin Lehalleur (1935), 345 4) Davis (1943), 360

Pyrofulmin or Mercuric Pyrofulminate. See in Vol **6**, F223-L

Pyrofuze. See in Vol **4**, D762-R to D763-L

Addnl Refs: 1) Ellern (1968), 207 & 279 2) K.O. Brauer, "Handbook of Pyrotechnics", Chemical Publ Co, NY (1974), 17–18, 23–26, 77, 110, 137–39, 143, 291–92, 304–05

Pyrogels. A class of US oil-and-metal incendiary agents. Like napalm (qv), the pyrogels consist essentially of thickened gasoline. The thickener is usually isobutyl methacrylate, and may include natural rubber. Powdered Mg is added to increase the temp of combustion which can reach as high as 1600°, though the pyrogels tend to burn more quickly than napalm. The same type of disseminated incendiary effect is obtained as with napalm-type oil incendiary bombs, but asphalt is added as a binder to overcome the shearing strains resulting from high altitude bombings (Ref 4)

Pyrogels used by the US armed forces include: (1) **PT1**, which is a complex mixt based on a paste of Mg and an oxidizer, bound with petroleum distillate and asphalt. Isobutyl methacrylate is used as a thickener. (2) **PT2**, which contains 5% isobutyl methacrylate as a thickener, together with Ba nitrate and a small quantity of asphalt. (3) **PTV**, which is described as an improved oil and metal incendiary mixt composed of 5% polybutadiene, 6% Na nitrate, 28% Mg, and a trace of p-aminophenol in 60% gasoline (Ref 5)

Refs: 1) V. Torrey, Popular Science (May 1945), 103 2) Anon, ChemIndustries (July 1945), 79 3) R.W. Hufferd, ChemEngrg **53** (10), 112 (1946) 4) E.W. Hollingsworth, Armed-ForcesChemJournal **4** (3), 26–32 (1951) 5) Anon, "Incendiary Weapons", MIT Press, Cambridge (Mass), 98 (1975)

Pyrogen Igniter. Pyrotechnic igniters contg conventional solid proplnt grain rather than pyrotechnic pellets, used mainly in ignition systems for large solid-proplnt rocket motors. For solid-proplnt rocket motor applications that require spreading the flames from the whole surface of the main charge container of the igniter, a pyrogen igniter with a perforated tube can be used

Refs: 1) Ellern (1968), 189 2) K.O. Brauer, "Handbook of Pyrotechnics", Chemical Publ Co, NY (1974), 289

Pyroglycerina (It). The name given to Nitroglycerin by its discoverer, Ascanio Sobrero, in 1847 (see in Vol **6**, G99-R)

Pyrolithe. A type of inexpensive "black" powder patented in the 19th century by Matteen. Daniel (Ref 1) states that it contained K or Na nitrate and sawdust, to which could be added Na carbonate or sulfate to the extent of 6%. Pepin Lehalleur (Ref 2) gives the compn as K nitrate 60, Na nitrate 16, sulfur 25 and charcoal 9%

Refs: 1) Daniel (1902), 664 2) Pepin Lehalleur (1935), 287

Pyronite. One of the names for Tetryl (qv)

Pyronitrines. Expls patented in 1880–81 by Prodhomme and examined in 1884 by the Commission Française des Substances Explosives. They contained Na nitrate 35–18, K nitrate 35–45, spent tanbark 15, Na sulfate 2–3, sulfur 6–9, charcoal 3, rosin 4–3, and tar 7%

Refs: 1) Anon, MP **6**, 74 (1893) 2) Daniel (1902), 664

Pyronome of DeTret. An inexpensive mining expl patented in Engl in 1859 contg Na nitrate 71.5, sulfur 13.5, and charcoal 15% (Refs 1 & 2). A subsequent Pyronome of Salle & Sandoy was patented in Fr in 1881 and contd K nitrate 69; sulfur, charcoal, metallic Sb & K chlorate 15%; the balance being rye flour contg a small quantity of K dichromate (Ref 1)
Refs: 1) Daniel (1902), 664 2) Pepin Lehalleur (1935), 287

Pyropaper (Pyropapier or Papier Fulminant in Fr). An expl prepd by plunging unglazed paper into a mixt of nitric and sulfuric acids for 2 minutes. After submitting the paper to the usual process of stabilization and drying, it was cut into small pieces and used in primers for needle rifles (fusil à aiguille in Fr) (see in this Vol, N22-R)
Ref: Daniel (1902), 665

Pyrophoric Incendiary Agents. Pyrophoric agents are as a class capable of igniting spontaneously in air. They are often used as igniters of other incendiary agents and to some extent as antipersonnel weapons or as weapons for use against targets contg highly inflammable substances

There are three main types of pyrophoric agents: white phosphorus and other inorganic non metals, finely divided metals, and certain organometallic compds

White Phosphorus (WP). See under Phosphorus (White or Yellow) in this Vol. The most important pyrophoric incendiary agent is WP (Ref 7, p 98). Chevalier in Fr noted the incendiary possibilities of WP in 1789, but it was only used sporadically in warfare until WWI. The first air attacks in WWI by hydrogen-filled dirigibles (Zeppelins) were soon abandoned because P-filled bullets spelled death to lighter-than-air aircraft (Ref 4, p 218). It was used extensively in small arms incendiary bullets and in hand and rifle grenades by all the principle belligerents; the Fr and the Ger used larger cal P shells and the Brit and Americans, trench-mortar bombs

Prentiss (Ref 1) comments on the effects of WP as an antipersonnel agent during WWI: "When scattered from overhead bursts of grenades and trench-mortar bombs, the phosphorus rained down in flaming particles, which stuck to clothing and could not be brushed off or quenched. The larger particles quickly burned thru clothing and produced painful burns that were slow and difficult to heal. These properties soon became known to troops, and phosphorus was justly dreaded and always caused a demoralizing effect beyond the actual casualties produced"

In the late summer of 1940, Brit airplanes carried NC sheets, 2-inches square and covered with yel P (kept in w prior to release), and dropped them in the region of the Black Forest in Ger. The fire leaves or "visiting cards" did little damage because of cold weather, which often led to slow oxidation rather than to ignition. Similarly, Jap efforts in WWII to do damage by means of small balloons carrying P, which drifted toward the northwestern US. coastal region, were ineffectual (Ref 4, p 219)

For many military purposes so-called "plastic white phosphorus" (PWP) is used. The properties are essentially the same as WP. Granules of WP are bound together in a rubbery soln which prevents their breaking up to the same extent when dispersed by an exploding munition. PWP is prepd from a slurry of WP granules in cold w with a viscous soln of synthetic rubber (Ref 7, p 100)

Zirconium. While almost any metal in the finely divided state exhibits pyrophoric properties, a few metals when abraded emit a shower of sparks of sufficient temp to ignite hydrocarbon vapors. Cerium is the best known metal of this kind for commercial purposes, such as gas lighter flints. For military purposes Zr is the most used. It has found applications in HE and armor-piercing incendiary ammo, the lining of shaped-charge rounds, and in incendiary cluster bombs (Ref 7, pp 100–01)

Though the element was discovered in 1789 it was not prepd in the pure state until 1914. It may be prepd commercially by the reaction of zirconium chloride with magnesium (the Kroll process) and other methods. The principle ore is zircon, deposits of which are found in the USA, Australia and Brazil. A number of special properties, such as exceptional resistance to corrosion and a low absorption cross section, have led to the use of Zr or alloys contg Zr, in many

specialized applications in the chemical, nuclear and manufg industries

For use in munitions Zr may be alloyed with other metals such as Ti and Pb in approx equal proportions. Fine particles of the metals may be mixed and bound in a synthetic rubber compn. To give added durability to this incendiary core it may be surrounded by a similarly bound compn of Fe and Ni carbonate powder (Refs 2 & 4, p 32)

Depleted Uranium. In the natural state U is a mixt of isotopes from which two, U_{235} and U_{238}, are extracted for use in nuclear reactors and weapons. What remains after the extraction is known as *depleted uranium* which now exists in large quantities and for which few uses have so far been found. One property of U is its high d – it is heavier than Pb – and this has led to the investigation of its military applications

Pellets, slugs or flechettes made of U have very good powers of penetration. However, U is softer than steel so that in the process of penetrating an armored steel plate it is partially pulverized. Since in this form U is pyrophoric (self-igniting), such projectiles have an incendiary as well as a penetrating effect. According to one account of flechettes made of depleted U: "... darts penetrate conventional steel plate better than tungsten tipped weapons. The darts also burn as they go through steel plate and spew flames inside the tank" (Ref 8)

In the process of burning, toxic compds are formed, which may produce delayed effects on personnel exposed to the smoke (Ref 7, p 101)

Triethylaluminum (TEA). A number of organometallic compds are spontaneously inflammable in air. Others, like organosodium and organopotassium compds, are not only spontaneously inflammable in air but react violently with w and carbon dioxide (Ref 4, p 24)

One member of this class of compds, known to be used as an incendiary agent, is *triethylaluminum* [$Al(C_2H_5)_3$]. Similar agents, such as trimethylaluminum or trimethylmagnesium, might also have possible military applications as incendiaries. Diethyl zinc has been employed as an igniter (Ref 3)

Triethylaluminum is a colorl liq which burns with a bright flame reaching temps of up to 2300°, which are comparable to those attained by the metal incendiaries. However, it burns very rapidly and the effects on material are limited. For weapons use it is thickened with polyisobutylene, a very long chain polymer, certain fractions of which are very tacky and are used as adhesives for pressure-sealing tapes. Polyisobutylene-thickened TEA is comparable to napalm in that it has two components: a thickener and an inflammable agent. The term "thickened pyrophoric agent" (TPA) is sometimes used for agents of this kind (Ref 7, p 102)

Production of TPA is much more complex than that of napalm, limiting it to those nations with an advanced petrochemical industry. Because of the reactivity with air, production is usually carried out in an inert atm of nitrogen or helium. Polymerization of isobutylene is also a complex process, requiring catalysts such as Al, Ti or Mo

TEA is currently being used in small incendiary rockets which can be fired from the shoulder by a lightweight launcher, designed to replace conventional flamethrowers. It is the incendiary agent in several prototype large cal incendiary projectiles for use by armored vehicles (Ref 7, p 102)

Expts have shown that if TEA is thickened with only 1% polyisobutylene (instead of the usual 6%) it is possible to produce a chemical fireball which radiates sufficient thermal energy to destroy or damage military targets. It is reported that such a weapon could cause third degree burns on occupants of bunkers within a few seconds, whether or not the agent hit individuals. Previously only nuclear weapons were able to produce damaging levels of thermal radiation (Ref 5)

The concept of the "controlled chemical fireball" is said to have significantly advanced the potential effectiveness of incendiary weapons. Theoretical studies have indicated that a great many applications may be possible, since, by changing the blend of the chemical constituents so as to achieve predetermined rates of combustion, the incendiary agent may be adapted to various operational requirements

In order to permit safe handling and storage, TEA may be made non-pyrophoric by the addition of soluble siluents (for example, n-hexane). "The diluent is expected to flash off when the flame weapon is employed rendering the basic TEA payload pyrophoric again. An effective

delayed, combined flameblast effect should result from the flaming TEA and the deflagrating n-hexane vapor cloud" (Ref 6)

Inorganic Substances Which Ignite in Water. Na is a very reactive substance which is never found free in nature. It is not generally used as an incendiary agent as such but, because of its tendency not only to float on w, but also to ignite spontaneously in contact with it, it may be added to napalm for use against river targets or enemy positions in rice paddy fields or in snow (Ref 7, p 103 & Ref 4, pp 28–29)

K also has the property of igniting spontaneously in w. The pure metal is more difficult to ignite than is Na. Ba, Ca and Li also ignite in the presence of w, though not as vigorously as Na. Li is the lightest of all metals and has the highest specific heat of any solid. It can burn with a temp of up to 1350°. Li was used for the case of a WWII Jap 70kg P incendiary bomb (Ref 7, p 103)

New Incendiary Agents. A great many other substances have been investigated in a search for new incendiary agents. Most interest at the present time seems to be focused on agents which ignite spontaneously, thereby avoiding the need for a fuse. Agents of this kind are particularly suitable for use in small rockets, artillery projectiles and aircraft bomblets which can be distributed over a large area

In addition to pyrophoric organometallic compds of the TEA type, a number of B compds are pyrophoric, including aluminum borohydride, pentaborane and the B alkyls, such as triethylboron. An alternative means of ensuring spontaneous ignition is to utilize a hypergolic oxidizing agent, that is, an agent which generates so much heat while oxidizing a fuel that the fuel ignites. Agents which are hypergolic with petrol are the interhalogens, chlorine trifluoride, bromine trifluoride, and bromine pentafluoride (Ref 7, p 103)

Many of these substances have been investigated in the context of rocket propulsion technology, since, chemically, the combustion of rocket fuels is related to the combustion of incendiary agents. Though by-products of rocket research may be theoretically of interest as potential incendiary agents, it remains to be seen whether they are feasible economically (Ref 7, p 103)

Refs: 1) A.M. Prentiss, "Chemicals in War", McGraw-Hill, NY (1937) 2) C.C. Balke & W.S. Graff, USP 2801590 (1957) 3) L.F. Fieser, "The Scientific Method: A Personal Account of Unusual Projects in War and Peace", Reinhold, NY (1964) 4) Ellern (1968) 5) Anon, "Laboratory Posture Report", US Army Munitions Command, RD&E Directorate, Dover, NJ (1972) 6) Ibid (1973), I-D-23 7) Anon, "Incendiary Weapons", MIT Press, Cambridge, Mass (1975) 8) Anon, "Armament Data Sheets", Aviation Studies Atlantic, London (no date)

"Pyro" Powder. A term used for smokeless powder prepd from Pyrocellulose

PYROTECHNICS

Introduction

Pyrotechnics is the technology of utilizing exothermic chem reactions when these are, generally speaking, non-expl, relatively slow, self-sustaining and self-contained

Pyrotechnics is usually distinguished from its sister technologies, expls and proplnts, even though their functions frequently overlap. There has grown up around the sciences of expls and of propulsion such a large body of specific knowledge that the scientific contributions of pyrotechnics are frequently obscured

Pyrotechnic reactions are employed for the sake of the evolved heat, sound, or smoke; for the generation of high temp, flames, colored light, a working gas or a propagating reaction front. Pyrotechnic devices tend to be storable, compact, and capable of being triggered by a small external force while being in complete isolation from external influences for prolonged periods

Historically, military pyrotechnics had their origin as incendiaries. The Bible refers to the use of firebrands (Judges 15; 4, 5) and to the action of water on naphtha and burnt lime (II Maccabees; 20–36) (I Kings 18; 31–38). Such self-igniting systems were known as "automatic fire" (Ref 130, p 5) and culminated in Greek Fire (Vol **7**, H117). Crucial to the further develop-

ment of pyrotechnics is the discovery of K nitrate and its synthesis from animal products (this Vol, N34-R), followed by the making of BlkPdr (Vol **2**, B165-R), first as an incendiary and then as a proplnt and as an expl. The invention of the cannon placed the combatants beyond the reach of effective incendiary agents which were not again to play a significant role in warfare until the present era. Meanwhile, pyrotechnics continued to be developed as a source of amusement in fireworks, and as a weapon in the form of rockets as used by the Moguls (Vol **7**, I67 & Ref 130, p 220) and by Great Britain (Vol **3**, C498-R). These rockets utilized BlkPdr as proplnt, fuse (Ref 122) and as an expl. Up to the middle of the last century the history of pyrotechnics is the history of BlkPdr. Even now, as will be discussed in Section 7, large quantities of BlkPdr are used as an igniter. By the late 18th century a new age in pyrotechnics commenced thru the synthesis of K chlorate (Vol **2**, C190-R), the discovery of Fulminates (Vol **6**, F216-R) and the identification of the minerals which would impart color to a flame. The discovery of electricity brought about pure chemicals and hence, better flame colors, new oxidizers such as perchlorates (qv in this Vol), the availability of cheap and plentiful Mg, Al and P, and in our own time, Zr and Ti

We observe that the development of general technology is accompanied by a corresponding development in pyrotechnics, and we have reason to believe that this process will continue

The military employment of pyrotechnics on a large scale other than by the use of BlkPdr is a fairly recent development, dating back to WWI, because pyrotechnic warfare is, as we shall see, mainly a product of high technology. Recognizing the interdependence of pyrotechnics and related disciplines, pertinent prior citations in the Encyclopedia as well as recent developments thru 1976 in the field have been collected and grouped into the following sections:

1) Flares and Signals
2) Colored and White Smokes
3) Tracers and Fumers
4) Incendiaries
5) Delays and Fuses
6) Photoflash Compositions
7) Igniters and Initiators
8) Advances in Pyrotechnics
9) The Literature of Pyrotechnics

1) Flares and Signals

Photometry

The inherent complexity of photometry is made greater by the confusion in use and in the naming of the earlier units (Ref 134, p 6-17)

Quantities of interest in describing the performance of light are the intensity, I, (candela, cd), the illuminance, E, (lumen/square meter, lm/m^2), the light output, C, (lumen/watt, lm/W) and the light efficiency. Intensities of flare compns are detd exptly (MIL-C-18762), and facilities for these measurements are found at all major military arsenals. The illuminance is defined in terms of the height of the burning flare, h, (or the distance from the surface to be illuminated) and the radius of illumination, r, such that (Ref 134, Fig 6-12)

$$E \approx I\,h\,(r^2 + h^2)^{3/2}$$

The light output per unit energy in terms of the heat of reaction of the flare mix burning in air, Q, having a mass, m in time, t, is (Ref 149, p 232)

$$C \approx 4\pi It / Qm$$

A means for describing the volumetric efficiency of a flare is the radiant energy per steradian per unit flare volume (W–sec/ster cm^3), the *RED* (Ref 133, p 227), such that the RED, the burn time of the flare and the curve of the spectral distribution constitute, for most purposes, a full description of a flare

Flares have modified grey body spectral distributions, although in some current applications the chief interest is in the long wave length components. One method for discarding the visible spectral component (as one would in a decoy) is to burn the flare within a long cylindrical transparent tube in which the inner walls are protected by an air stream. The transparency of the tube is regulated by infrared windows. The second approach requires that a quasi-gasless reaction take place in an enclosed chamber which is coated with a refractory possessing desirable optical properties (Ref 133, pp 223–47)

Present developments in electro-optical devices has increased the understanding of the spectral characteristics of flare light. Image intensifiers and low level light television employ photo emitter surfaces which have enhanced performance in the red or near infrared spectral region. The admixt of alkali nitrates other than Na results in light in the near infrared, see Table 1. The ground cover is more reflective in the

infrared than in the visible part of the spectrum so that the apparent lower brightness of the Na-free flares is effectively compensated (Ref 134, Table 4-2)

Table 1
Infrared Flare Formulas (from Ref 121)

	Wavelength Emitted		
Component	0.76μm	0.79μm	0.8-0.9μm
Silicon	10	10	16.3
KNO_3	70	–	–
$CsNO_3$	–	–	78.7
$RbNO_3$	–	60.8	–
Hexamethylene Tetramine	16	23.2	–
Epoxy Resin	4	6	5

The spectral component of a Mg/alkali nitrate flare is a continuum with a broad max about 0.01 μm on either side of the resonance line (Ref 35)

The mechanism of radiative transfer in flares was found to depend on compn, flare diameter and pressure (Ref 69). The flare efficiency calcn is complicated by the drop-off in intensity at increasing altitudes and at very large diameters owing to the lower reaction temps (Ref 11, p 13) and the narrowing of the spectral emittance band (Ref 35). The prediction of the light output in terms of compn and pressure (ie, altitude) is now possible using a computer program which computes the equilibrium thermodynamic properties and the luminance (Ref 104)

Flare Formulations

The intensity of a flare is largely determined by its temp, which in turn depends on the stability of the reaction products. In order to generate grey body radiation which encompasses the spectral sensitivity of the human eye (0.4–0.74μm), 3000°K should be exceeded. Whereas this is possible using nitrates and perchlorates with alkaline earth metals as well as Zr, Ti and Hf (Ref 34) (H, C, B, Si and P form oxides which dissociate at high temps), in practice Mg and Al are found to be best in terms of heat output, cost, and transparency to visible radiation

The illuminating characteristic of the flare is only partly determined by the thermal radiation from the oxide particles, a second factor being the spectral emission from excited metals. Metal oxidizers contribute their energy in the form of spectral emission at characteristic frequencies. The human eye has the greatest sensitivity to the Na emission. For this reason, Mg-Na nitrate flares are selected as the best intensity light source

Compns for illuminating shells and flares contain 53–58% Mg (MIL-P-14067A), 36–40% Na nitrate (MIL-STD-1233) and 4–8% Laminac binder (alkyd-styrene resin MIL-R-7575A) (Ref 138, pp 357–62). The thermodynamic data for flare compns is given in Ref 134, p 6-38. Further data on illuminating devices and compns is found in Vol **7**, I31. The work on providing safer flare formulations is continuing and it was described in Ref 85. A major theoretical analysis of the physical principles of flare performance coupled with an exptl verification program was published by the Aerospace Research Corp (Ref 27)

Signal Formulations

Typical formulations and designs of signal flares are described in Vol **6**, F63, and for Star Shells in Vol **7**, I32 and Vol **4**, D959. The purpose of signals differs from that of flares (illuminants) in that the signal light source must be discriminated from the background illumination. As such signals are generally colored, the problem is enhanced by fog, snow, and rain. The subject of visibility is discussed in Ref 134, p 4-1

Because signals are generally fired in a prearranged sequence, their deployment is open to imitation by the enemy. By using a combination of spectral components, the color of the flame is different when viewed thru a filter than the color of the unfiltered signal. Such a signal compn is given in Table 2 of Ref 105

Table 2
Red-Green Flare System, Parts by Weight

Barium Nitrate	30
Strontium Nitrate	13
Potassium Perchlorate	9
Magnesium	30
Dechlorane	12
Polyvinyl Acetate Resin	4

Unfiltered, the green and red region combine to produce a yellow color which resembles the color of a pure yellow flare

A special type of a flare is a thermal decoy which has a strong emission in the infrared. *Decoys* may utilize the Mg-fluorocarbon reaction which form hot carbon particles as the source of radiant energy (see sample equil calcn, Section 4 of the article) (Ref 59)

Ellern (Ref 138, p 181) also describes pyrotechnic means of producing explosive and whistling sound. Recent advances in the art of generating oscillating light signals are described in Section 8 of this article

2) Colored and White Smoke

Screening Smoke

The pyrotechnic generation of smoke is almost exclusively a military device for screening and signaling. While first encountered on a significant scale in WWI, its importance was not realized until early in WWII when the bulk of the presently known data were collected. In the last 30 years studies of smoke have continued at a reduced rate

Screening smokes are generally white because black smokes are rarely sufficiently dense. Signal smokes, on the other hand, are colored so as to assure contrast and be distinct in the presence of clouds and ordinary smoke

Smoke has been found to aid the daytime observance of tracer projectiles and also for tracking space vehicles during launch. Specific smoke tracers for training pilots have been produced (See Section 3 of this article). The 0.50 caliber M48 spotter-tracer was developed specifically to take advantage of the appearance of a smoke puff at the point of impact which persists for a longer time than does the flash

Whereas smokes are often characterized by the mode of their formation, any concd suspension of particles ranging from 0.01 to about 5.0 μm can be considered a smoke. These particles, when suspended in air, reflect, scatter and absorb radiation in a complex manner. A comprehensive model of these interactions in terms of visibility under various conditions was described recently (Ref 62)

The following are pyrotechnic methods for smoke generation as opposed to mechanical methods such as atomization of fog oil, of Ti tetrachloride (FM smoke) or of S trioxide. This discussion is drawn from Ref 134, which should also be consulted for earlier references:

"a. Venturi Thermal Generator Type

The smoke producing material and the pyrotechnic fuel block required to volatilize the smoke material are in separate compartments. The smoke-producing material is atomized and vaporized in the venturi nozzle by the hot gases formed by the burning of the fuel block

b. Burning Type

Burning-type smoke compositions are intimate mixtures of chemicals. Smoke is produced from these mixtures by either of two methods. In the first method, a product of combustion forms the smoke or the product reacts with constituents of the atmosphere to form a smoke. In the second method, the heat of combustion of the pyrotechnic serves to volatilize a component of the mixture which then condenses to form the smoke

c. Explosive Dissemination Type

The smoke producing material is pulverized or atomized and then vaporized, or a preground solid is dispersed by the explosion of a bursting charge"

An important example of the first type is the oil smoke pot which is powered by a slow burning, gassy pyrotechnic mixt such as amm nitrate and amm chloride with a small amount of carbonaceous fuel. The resulting gas jet pulls a stream of oil from a reservoir and injects it into a venturi where the formation of the aerosol takes place

White P, either in bulk or in soln, is a good example of the burning type of smoke generator. The resulting colloidal suspension of P pentoxide is quickly hydrolyzed by moisture to become phosphoric acid droplets which are the actual visible constituent of the smoke. Various other burning type smoke generators exist such as those used for signaling purposes and which use red P, metallic phosphides, or P trichloride as the source of the particulate cloud

Another important burning type of smoke generator is the HC smoke mixt which has been prepd with a number of combinations of Zn with a chlorine carrier to form, on combustion, Zn chloride. For example,

$$2Al+C_2Cl_6+3ZnO \rightarrow Al_2O_3+2C+3ZnCl_2$$

HC mixts are used in the AM-M8 Smoke Hand Grenades, in the HC floating smoke pot (M4A2) and in the M1 Smoke Canister

The expl dissemination type of smoke gene-

rator may contain metallic chlorides which upon dispersal hydrolyze in air. Examples are Ti, Si, and stannic tetrachloride. An effective smoke agent, whether it be mechanically dispersed from an aircraft spray tank or vaporized thermally, is a mixt of S trioxide and chlorosulfonic acid (FS smoke agent) which upon hydrolysis forms sulfuric and hydrochloric acid dispersions. Of course, all such formulations are highly corrosive, and, if not outright toxic, then conducive to pulmonary edema

The so-called "standard smoke" is a smoke of such a density that a light of 25 cd intensity is just invisible when observed thru a layer of approx 30 meters. The amount of smoke agents required to produce one cubic meter of standard smoke is given in Table 3

Signal Smokes

The preferred method of dispersing colored smokes involves the vaporization and condensation of a colored organic volatile dye. The problem has always been one of selecting dyes which are thermally stable and which vaporize without decompn at temps below 400°. There are a very large number of dyes which have been studied and some of these have been collected in Ref 134, p 7-34. The following are representative of dyes selected by the US as satisfactory agents for producing burning type colored smokes.

Yellow: Auramine Hydrochloride
Green: 1,4-di-p-toluidinoanthraquinone with auramine hydrochloride
Red: 1-Methylanthraquinone
Blue: Not suitable for signaling because of excessive light scatter

These dyes are mixed to the extent of about 50% with a fuel such as lactose (20%) and an oxidizer (30%) for which K chlorate is preferred. If the mixts should still burn too hot (and thereby destroy the dye), Na or K bicarbonate are added as cooling agents. Colored smoke compns are usually used in a compressed state without a binder

A major concern at present is the reported carcinogenic nature of organic dyes (Ref 91) and elaborate programs have been initiated for their destruction (Ref 119)

In addition to the smoke grenades which function by burning, others produce smoke by volatization of the dye from a separate dye compartment. These dyes should have preferably melting points below 150° and be stable in the vapor phase. The following are currently used dyes:

Orange: 1-(4-Phenylazo)-2-naphthol
Yellow: N,N-Dimethyl-p-phenylazoaniline
Blue: 1,4-Diamylaminoanthraquinone
Mixts of these dyes produce muddy colors of various hues

Lastly, dyes can be dispersed by expl charges. These generate colored clouds (about 10x20m) which are formed instantaneously and which have a life expectancy, depending on environmental conditions, from 65–85 seconds, whereas aerial burning of the aforementioned burning type produces streamers about one meter across and which last for about 57–120 seconds

Table 3
Amount of Smoke Agent per Cubic Meter of Standard Smoke

Material	g/m^3
White Phosphorus	0.064
Sulfur Trioxide	0.099
FS agent	0.116
HC Mixture	0.127
FM agent	0.159
Crude Oil	2.11

3) Tracers and Fumers

The principle small arms application of military pyrotechnics is in tracer munitions, where they serve as incendiaries, spotters and as fire control. A thorough review of tracer munition design was prepared by Frankford Arsenal (Ref 33)

Tracer munitions are the most effective means of fire control for rapid firing small arms. When used in machine guns, they are belted in a predetermined sequence, depending on the mission, with ball rounds, incendiary rounds or armor-piercing rounds. More recently, the trend in 20–30mm rounds has been to accommodate combined armor-piercing–incendiary–tracer functions which has resulted in every round being a tracer

Historically, storability, ignitibility and burn time have been recurring problems in tracer munition fabrication. The endothermic decompn of metal salt oxidizers and the brief exposure to the propInt flame (0.5–2msec) brought about the need for special igniters and

subigniters. Furthermore, the desire to hide the position of the gun at night by delaying the ignition for a short distance from the muzzle, caused the development of dim igniters. The mechanism of tracer reactions is a complex one as the burning rate and the brightness of the trace increases with spin rate of the bullet, but decreases with altitude. The reaction equilibria were examined (Ref 90) and it was found that the solid phase is principally Mg oxide, the Sr oxide being converted to the volatile chloride by the action of PVC. Hence, the color strengthening chlorinated additives function by volatilizing the spectrally active compd. The reaction products are mainly gaseous, being rich in Mg vapor and CO. The trace brightness originates therefore in the plume reaction. Attempts at minimizing the side visibility of the plume by using gasless reactions have also reduced the trace visibility (Ref 82). Compns for use with electro-optical devices have also been developed (Ref 40). These compns consist of Ca resinate, Ba and Sr peroxides and Mg carbonate

The color of tracers is not judged by a numerical color value but on the basis of visual observation in daylight and at night. Acceptance is based on visibility over a range of 1000m for 5.56 and 7.62mm and up to 2500m for 20mm rounds. Red tracers are more visible to the human eye as longer light waves penetrate haze, dust and fog better, and hence these are most commonly used. The Vietnamese are said to have used green tracers so that, in addition to providing fire control, the tracers helped identify the combatants in night-time encounters

The compn of tracer mixts used in the United Kingdom, as well as a discussion of their burning characteristics in spinning projectiles, is given in Ref 81. A good review of the USSR developments in tracer technology is given by Shidlovski (Ref 149, p 303). Ellern (Ref 138, p 362) lists the compn of artillery tracers. With the trend toward smaller caliber ammo for hand held weapons, the loading of miniature tracer cavities became difficult. For instance, the XM216 is a dart-like finned projectile (flechette) with a 1.52mm diameter opening and 15.9mm cavity depth. The charging problem was overcome with *Visacore* (Refs 20 & 52), a mixt of 65% 23 μm Zr, 30% K perchlorate and 2–5% vinyl alcohol acetate resin (VAAR), blended in ethyl acetate solvent. This mixt is swaged in a Pb tube to the desired diameter, and inserted into the tracer cavity, trimmed and consolidated. A tracer formulation for external application to sabot type projectiles was recently patented (Ref 114). These rely on sintered depleted U and Ni powder and provide a trace of 2000m visibility

Hypergolic reaction systems have been proposed (Refs 46 & 73) for 5.56mm ammo, specifically triethylaluminum (TEA) together with inorganic oxidizers. This system is self-igniting in air, but is compatible with some nitrates, chlorates and perchlorates

A recent development is the use of gas generating tracers ("fumers") for base drag reduction (Refs 74, 75 & 84). The base drag develops because a partial vacuum is created behind a moving projectile, causing a ballistic mismatch between tracer and ball rounds. Fumers utilize the gaseous products of a burning tracer, resulting in increased range and decreased time of flight. A logical extension of the fumer concept is a rocket assisted bullet which would have the advantage of a flat trajectory, min recoil and max velocity at impact. Such small arms rockets with as little as 3mm diameters and 35mm lengths, having foil wrapped casings, perforated double-base proplnt grains and a thermite igniter, have been developed as an anti personnel weapon (Ref 39)

Extension of the visible range for 20mm rounds to ranges beyond 2500m has been made possible by the folded cavity tracer capsule (Ref 102) which is illustrated in Fig 1. The folded cavity is designed to function as follows: the proplnt gases ignite the igniter charge as in all tracer ammo; then, the igniter material ignites the initial tracer charge in the central cavity. As the flame front reaches the bottom of the central cavity, it transfers to the annular cavity containing the downrange tracer charge. As this charge burns, the central (Al) column melts partially or totally, contributing increased fuel to the process. The concept is said to work with any tracer compn, although those which are rich in PVC are favored (see Table 5)

Other uses of tracer rounds have been to initiate a self-destruct charge (Vol **7**, I10) which prevents unexploded antiaircraft shells from falling to the ground. A recent development introduced the inclusion of oxamide to slow the

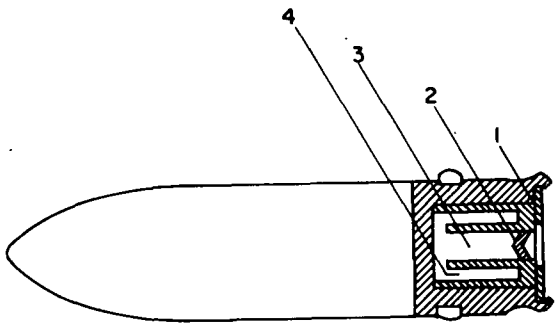


Fig 1 20mm Extended Range Tracer with Folded Cavity Concept (from Ref 102)
1 Metering Disk
2 Igniter
3 Initial Tracer Composition
4 Down Range Tracer Composition

rate of the tracer burn (which in this case operates as a delay column) (Ref 38)

Smoke tracers which leave a colored smoke trail are used by aircraft gunners as practice rounds, the typical trace length being about 600m. The compns contain about 70% Sr peroxide, 10% each of Ca resinate and catechol, the remainder being methylaminoanthraquinone in red smoke trails, and auramine for greenish-yellow smoke trails. In recent years the carcinogenic nature of the dyes has prompted extensive work in the recovery and disposal of pyrotechnic smokes and tracers (Refs 119 & 125). A dye-free blue tracer and smoke generator was recently described (Ref 101)

Whereas generally U is considered to be an incendiary fragment generator, one patent was issued for the inclusion of about 50% depleted U with such oxidizers as $KClO_4$, $Ba(NO_3)_2$ or NH_4NO_3 (Ref 17) for use in spotting rifle projectiles

4) Incendiaries

The history of incendiaries and incendiary projectiles thru WWII was reviewed earlier (Vol 7, I65). The principal advances in the intervening years have been in the wider use of metals which are known to yield pyrophoric fragments, in the fabrication of incendiary bombs, and in the use of Zr, Ti and mischmetal. Early small arms incendiary mixts are reviewed in Ref 134, Table 5-7. As a pyrotechnic metal, Zr has become available only in the last two decades as an intermediate component of nuclear reactor development. The metallic form of interest to pyrotechnics is the sponge which is easily pulverized and which is possessed of a high surface area. Compacted sponge is preferable to wrought metal as it forms incendiary fragments more easily (Ref 128)

The characteristics of a metal which contribute to a good incendiary capability are not yet fully understood nor have they been completely defined. Hillstrom (Ref 64) found that pyrophoricity is related to the ratio of the oxide volume to the metal volume, a ratio above one giving rise to the "popcorning" effect which is

Table 5
Typical Formulas for Igniter and Tracer Compositions (from Ref 33)

Ingredient	Delay Action Igniter, I-136	Dim Igniter, I-194	Daylight (Bright) Igniter, I-276	Red Tracer R-257	Fumer (Ref 75) R-284
Strontium Peroxide	90	–	–	–	–
Magnesium	–	6	15	28	28
I-136 Igniter	–	94	–	–	–
Calcium Resinate	10	–	–	4	–
Barium Peroxide	–	–	83	–	–
Zinc Stearate	–	–	1	–	–
Toluidine Red (Identifier)	–	–	1	–	–
Strontium Nitrate	–	–	–	40	55
Strontium Oxalate	–	–	–	8	–
Potassium Perchlorate	–	–	–	20	–
Polyvinyl Chloride	–	–	–	–	17

Table 6
Properties of Pyrophoric Metals

Metal	ΔF, $\frac{kJ}{mol\ O}$	$\frac{Oxide\ Vol}{Metal\ Vol}$	Electronic Structure
U	– 536	3.10	$6d^1\ 7s^1$
Th	– 587	1.36	$6d^2\ 7s^2$
Zr	– 512	1.55	$4d^2\ 5s^2$
Hf	– 577	1.62	$5d^2\ 6s^2$
Ce	– 486	1.23	$5d^0\ 6s^2$
La	– 641	1.11	$5d^1\ 6s^2$
Pr	– 621	1.12	$5d^0\ 6s^2$
Nd	– 617	1.12	$5d^0\ 6s^2$
Sm	– 431	1.06	$5d^0\ 6s^2$
Y	– 427	1.44	$4d^1\ 5s^2$
Ti	– 426	1.78	$3d^2\ 4s^2$
Be	– 582	2.77	– $2s^2$
Al	– 526	1.28	– $3p^1$

thought to aid in the self-propagation of oxidation. Furthermore, the free energy of the oxide formation (per unit oxygen atom) should exceed 400kJ/mole O. Some elements, such as Al and Be, possess these desired properties but in fact fail to burn spontaneously except as fine powders. For such boundary line cases the electronic structure (see below) may play a deciding role. Table 6 lists these properties of the best candidates

The design characteristics, reaction modeling, target simulation and thermodynamic parameters are exhaustively reviewed in a four volume study by the Denver Research Institute (Ref 129). A variant ignition mechanism, based on shock compression along a Hugoniot curve, was proposed as a source of the ignition energy (Ref 76). Distended metals in the form of powders and sponge are seen to be of particular pyrophoric value, not only because of their high degree of dispersion, but because relief of pressure behind a shockwave passing thru compressed powder creates a persistent hot zone, so as to promote their ignition

Pyrophoric elements are characterized additionally by largely unfilled d shells. Certain alloys spark particularly well when alloyed, as for example, ZrSn and FeCe. It appears that those alloys spark best which are eutectics, and in which the compn is rich in the pyrophoric element, but that such pyrophoricity is lost when the alloying agent forms an intermetallic compd, even though compd formation is accompanied by increased frangibility. Compds do not have electrons in the conduction band, and the change in pyrophoricity may be connected therewith

Pyrophoric penetrators equal in effectiveness to those containing U are reportedly provided by those containing spark sintered bodies of 49–95% W, 4–50% Zr and a binder of ductile metal such as Ni, Fe, Co or Cu (Ref 115). Even though U is the most pyrophoric of all elements, it is not expected to see use as an incendiary because of its toxicity and its great value as a nuclear fuel

Incendiary munitions for use against supersonic aircraft require rapid initiation of long burning incendiary fragments. Whereas this problem has never been solved in a satisfactory manner, coarse particles (20–60 mesh) of Zr sponge are known to ignite on impact and to burn about 300msec. Less dense and more inexpensive Ti will only initiate when the fragments are substantially smaller than 60 mesh, only to burn too quickly (Ref 129, p 317). The data comparing the performance of Ti and Zr tend to be contradictory because the degree of purity of the metals is rarely specified. Several methods are known for initiating coarse (20–60 mesh) Ti sponge which then will burn for up to

300msec. One method consists of admixing 25% K perchlorate, 25% Al–Mg alloy and 50% coarse Ti sponge (Ref 19), resulting in a burst duration of 275msec. Alternately, one may compound the coarse Ti sponge with Teflon or a similar fluorocarbon, which ignite when subjected to shock (Ref 76). The development of fluorocarbons as oxidizers has been one of the principle new developments since WWII, prompting extensive theoretical and exptl work. The volumetric heats of reaction of pyrophoric elements with fluorocarbons are listed in Table 7

Table 7
Maximum Volumetric Heats of Reaction for Metals Reacting with Fluorocarbons (from Ref 8)

Metal	Product	kJ/cm^3 (*)
Be	BeF_2	– 24.0
La	LaF_3	– 21.0
U	UF_3	– 19.8
Mg	MgF_2	– 19.8
Hf	HfF_3	– 19.0
U	UF_4	– 18.9
Zr	ZrF_3	– 18.6
Zr	ZrF_4	– 18.6
Hf	HfF_4	– 18.2
Ti	TiF_3	– 17.0
Ti	TiF_4	– 14.6

(*) The numerical values are strongly affected by the stoichiometry and by the effective densities of the reactants

Enhancement of reactivity of incendiary components has been claimed by the introduction of impurity states, particularly into metallic oxides (Refs 56 & 86). Impurity states have a twofold effect: they disturb the lattice structure of the oxide (and so increase the diffusivity of the reactants), and they disturb the electronic distribution on the surface as well as in the bulk. The argument is made that by "doping" the oxide, or by controlling the formation temp, one may change an oxide from an n-type to a p-type semiconductor and hence cause it to become a better electron acceptor, and vice versa

A promising discovery for increasing the ignitability of Thermite (Vol **7**, I73-R & Ref 134, pp 3–5) mixts has been the admixture of Ni powder (Ref 29). The basis for this finding is the highly exothermic formation of the intermetallic compd NiAl, which proceeds progressively after ignition at 650° (Refs 45 & 68)

The theoretical study of incendiary reactions has been aided by the use of computer programs for the study of the equil products (Refs 15 & 41), as well as for the prediction of the adiabatic reaction temps. An example of the complexity of the reaction products of a fluorocarbon, compounded with 5% epoxy binder, is given by Tanner (Ref 80). It will be observed, that only the carbon remains as solid product, and that the effect of the fluorine is one of increasing the fraction of gaseous products, as well as to provide the thermal energy (see Table 8)

Table 8
Equilibrium Composition of the Product of the Reaction of Magnesium with a Fluorocarbon at 1200°K

C(s)	0.45316	C_2N	0.00118
C	0.00078	MgF	0.03023
CF	0.00755	C_3	0.00485
CF_2	0.00206	F	0.03197
CN	0.00224	MgF_2	0.44743
C_2N	0.00118	N_2	0.01115

Adiabatic Reaction Temperature: 3400°K

5) Delays and Fuses

A delay element is a self-contained pyrotechnic device consisting of an initiator, delay column and an output charge or relay, all assembled into a specially designed inert housing. It provides a predetermined interval between initiation and functioning of a device

Delay elements have been described earlier (Vol **3**, D50 & Vol **4**, D863 & D872). Work on delay systems continues because the existing delay mixtures do not store well, and scale-up is not as flexible and as precise as is desired. A basic reason is that gasless delay mixts are not truly gasless in that gaseous reagents are present in the flame front or in the ignition mix which contribute to the pressure in the column (Ref 32), so that the burn time is not strictly a linear function of the column length. Some workers have called this phenomenon the "anticipatory effect" (Ref 10 & Ref 134, Table 5-17, 18)

The almost universal chromate oxidizers are claimed to be carcinogenic (Ref 67) for which

the manufacturers desire substitutes. The aging problem is known to reside with the metallic fuel (Refs 21 & 60) which tends to corrode in the presence of moisture. The evidence is conflicting whether protective coating or selection of dry components affords the best solution (Ref 51). It appears that the corrosive effect of moisture is in part compensated by the inhibiting effect of the chromate such that in the case of Mn mixts, the burn time stabilizes after an initial increase. Gorbunov (Ref 116) studied many non-toxic, non-corrosive systems over pressure ranges of 1–100 atm, and finds that the burning rates of Na nitrate and carbonate, and K carbonate and sulfate are independent of pressure when reacting with Mg. Intermetallic reaction systems, chiefly Ti–B and Ni–Al, have been studied in recent years (Refs 68 & 106). Reasons for the instability of gasless reactions have been ascribed to "oscillatory burning" (Refs 1, 44 & 107)

A significant discovery was a new commercial product, Pyrofuze (Ref 5 & this Vol) which consists of very thin clad sheets of Pd (or Pt).on Al, or very finely swaged Pd wires which have an Al core. Attempts to incorporate Pyrofuze in delays have met with limited success (Ref 30). Reasons for this have been analyzed (Ref 120) and are ascribed to adverse heat transfer phenomena

The historical developments in delay formulations have been traced by G. Weingarten (Ref 133, p 254), who also tabulated a wealth of performance data

The interest continues in accurate delay compns for use at high altitudes and at extreme temps. Ternary compn diagrams of Ba and Pb chromates with B, Mg, Ti, Ta and Nb, all as function of burn time, have been published (Ref 36) as have burn times with Zr–Ni alloys (Ref 49). Over large ranges of proportions these systems are excessively gassy. An important system is one employing W, Mo or Cr together with perchlorates (Ref 7). These mixts have a wide range of burn times, depending on the compn, but tend to be gassy. Problems related to the variability in delay train performance have been addressed by Valenta (Ref 58)

As propagation rates of gassy reactions are pressure dependent, so are gasless reactions temp dependent. This temp dependence has been ascribed to the effect of temp on the diffusion rate in the solid phase (Ref 66) or to classic kinetic parameters (Ref 47), but no satisfactory method for compensating for the temp effect has been found. The usual approach is one of raising the temp of the reaction (Refs 5 & 89) so as to reduce the percentage change of the exponential term in the Arrhenius expression

An interesting finding was that diatomaceous earth (SiO_2) has a stabilizing effect on the aging characteristics (Ref 60) and an accelerating effect on Ba chromate containing mixts which may be due to the lowering of the decompn temp of Ba compds by $Si\,O_2$ (Ref 26)

Improvement in the precision of delay trains is claimed by the use of swaged cords as opposed to pressed columns (Refs 18 & 55), provided that such cords are reasonably long. Another approach consisted of placing a number of delay columns in parallel so as to decrease the spread of the burn times (Ref 22)

Ellern (Ref 138, p 197) has reviewed the theory and technology of pyrotechnic and non-pyrotechnic delay trains, and he stresses problems in obtaining precise long delays in obturated systems and pressure sensitive (vented) systems, while listing the advantages of pyrotechnic delays in terms of reliability and cost. Non-pyrotechnic systems rely on the corrosion or dissolution of a restraint by acid or by a solvent, causing a spring loaded pin to strike a primer or an electric switch to be functioned (Ref 138, p 210)

A recent review relating the pyrotechnic reaction mechanism, particle size, stoichiometry, temp and compaction density to burning rate is Ref 66, and a study of the effect of multi-dimensional heat transfer on the rate of flame propagation is Ref 120, which showed that the material of the delay body has no effect on the performance of most delay compns, a finding which agrees with test data

Statistical controls in testing delay components are described in Refs 2 & 152

Table 9 lists the chief performance characteristics of the most important delay compns. In general, the burn time is controlled within the stated limits by adjustment of the fuel fraction. Other variables are the particle size of the fuel and the presence of additives such as Pb chromate, silica and Viton. Many perchlorate containing mixts are friction and spark sensitive,

Table 9
Survey of Delay Mixtures

Mixture	Application	Mil Spec	Illustrative Composition	Burn Time Range, sec/cm	Temperature Coeff, %/°K	Delay Time Change on Storage, sec/year-cm
D–16	Navy Mk4Mod0 Delay Cartridge	MIL-M-21383	Mn 29 $PbCrO_4$ 26 $BaCrO_4$ 45	0.8–5.4 (obturated)	0.17	0.02
T–10	Army M112 Photo Flash Cartridge Fuze		B 3–15 $BaCrO_4$ 97–85	0.23–0.32 (obturated)	0.23–0.32	0.15–0.38
Zr–Ni Delays	Grenade Fuze, Navy Mk18 Cable Cutter Cartridge, Army 20-sec Cargo Release Cartridge	MIL-C-13739	Ni–Zr 26 $BaCrO_4$ 60 $KClO_4$ 14 Up to 10% CeO_2	0.8 for 70/30 Zr–Ni, 4.6 for 30/70 Zr–Ni, 7.8 with CeO_2 (vented)	0.16	0.06
Tungsten-Viton	Mk279Mod2 Igniter	WS 12607	W 30 $BaCrO_4$ 55 $KClO_4$ 10 Diat Earth 4 Viton 1	Approx 0.8–6.2 (vented)	0.1	Not known, not suitable for storage in high humidity
UMNOL Tungsten Delay		MIL-T-23132A	W 30 $BaCrO_4$ 55 $KClO_4$ 10 Diat Earth 5	0.04–16 Up to 24 with CaF_2 (vented)	0.1	sensitive to moisture

explaining the intended role of Viton and similar additives in reducing sensitivity

6) Photoflash Compositions

Photoflash powders are loose mixts of powdered oxidizers such as Ba nitrate and K perchlorates with metallic fuels, principally Mg, Al and Zr. These ingredients have such small particle sizes that they burn with expl violence for durations of less than 0.1 sec. At present photoflash powders are used exclusively in military aerial photography, whereas civilian applications are served by electrically ignited Zr or Hf wire containing flashbulbs. Since 1970, non-electric, pyrotechnically functioned, flash cubes have appeared on the market (USPs 3535063, 3540813 & 3674411)

Photoflash bombs and cartridges are pyrotechnic items which are classified with bombs (Vol **2**, B229) because of their explosive effect. The various devices are similar, differing principally in size and the amount of delay. When fired, each photoflash cartridge, after 1, 2, or 4 seconds, produces a flash having a peak intensity of approx 50 million cd with a total output of 5 million cd-sec, whereas photoflash bombs generate above 5×10^9 cd

The literature on flash compns is particularly voluminous, giving rise to the need of correlating or predicting their performance. Comprehensive studies since WWII have shown that Al and Mg are the best fuels at sea level (Ref 134, p 6.62). While atomized Mg gives higher intensities in consolidated compns, atomized Al performs better in loose compns than do other fuels. K perchlorate produces the highest heat of reaction with atomized Al. The output is highest for fuel rich compns and alkaline earth nitrates which are far superior to alkali metal nitrates. Constant Al particle sizes of $22 \pm 8 \mu m$ resulted in optimum efficiency (cd sec/g) at all altitudes. At high altitudes, Zr performs better

Photoflash compns containing Hf and K perchlorate possess greater luminous efficiency on a volume basis than do other formulations (Ref 128). Zr, for example, when burned in oxygen has an average color temp of 4883°K compared with 5235°K for Hf when measured at peak intensity (Ref 65). In pyrotechnic flash units, substitution of Al with Hf and Ti produced comparable peak output, but inferior output when Zr and Ce were substituted (Ref 37). Little work is known to have been done otherwise in the last decade on photoflash compns, which continue to be the single most hazardous class of pyrotechnic mixt, both because of the expl character of its combustion and because of the large quantity deployed in any one device. Current emphasis at PicArsn is on improving the handling safety of the powder. A significant engineering advance consisted in the elimination of the preblending step thru layering the separate components within the bomb, followed by vibrating and tumbling as the means of blending (Ref 12)

Typical photoflash compns as well as some of their performance data and device specifications are given in Ref 134, Tables 6-16 to 6-25

7) Igniters and Initiators

The many aspects of ignition and igniters have been widely covered in this Encyclopedia (Vol **7**, I5-R to I9-R). The igniters given in Vol **4**, D774-L for tracer munitions are no longer correct (the current compns are given in Section 3 of this article); moreover, the wording "barium oxide" should read "barium peroxide". Igniters for incendiary bombs are reported in Vol **4**, D1016-R and for rim fire ignition on page D1053-R. The description for dim igniters on page D774-L is likewise no longer valid, having been superseded by the mixt described in Table 5 of this article. Typical initiation mixts for expls are listed by their Chemical Abstract ref number in Vol **7**, I17. The problem of prime ignition was reviewed in Vol **4**, D758 with listings of match compns on pp D760–D761, of BlkPdrs on D763, of starting mixts on D764, of ignition mixts on D766, and first fires on D767. Additional systems are described by Ellern (Ref 138, pp 189–96), Shidlovsky (Ref 149, pp 463–73), and Robertson (Ref 139). A major review of air and water actuated (ie, self-igniting) systems was also published (Ref 24)

A special category of ignition system is the cartridge actuated device (CAD) also known as the Propellant Actuated Device (PAD) which serves to generate the mechanical force to close switches (in the manner of a squib) or to perform otherwise mechanical work (Vol **2**, C70-R & Ref 138, p 167)

The development of ignition systems is one

of tailoring static, shock, and temp sensitivity to the allowable ignition delay, high altitude ignitability and compatibility. As with other pyrotechnic devices, new ignition systems are constantly being developed to meet specific tasks. Examples of such developments are fluidic expl initiators (Vol **6**, F111-R & Refs 57, 103 & 111), exploding bridgewires (Vol **6**, E353-R), laser energized expl devices (Vol **7**, L5), ignition of intermetallic and gasless reaction mixts (Refs 48 & 78), spontaneous ignition kits (Ref 25), as well as the synthesis of coordination compds to take the place of temp sensitive primary expls (Ref 77)

Ignition mixts of lower static sensitivity have been prepd from Ti hydride and K perchlorate (Refs 117 & 123). It was found that the hydride tends to react with the perchlorate at elevated temps and that such a reaction is progressive, particularly with high hydride concns. No data have been found on Zr hydride mixes, but it is expected that the behavior will be similar. It seems, however, that performance variations are common in Zr mixts, but that these can usually be traced to hydride contamination in the Zr, and that such problems can be solved by heating the Zr in vacuum at about 200° (Ref 128)

The pyrotechnic literature does not contain a critical evaluation of the ignition response time of primary initiators in terms of their compn, temp tolerance and shock sensitivity. In general, primary expls such as Pb Azide or styphnate are selected whenever a brief (microsecond) response is desired, while, for instance, Pb thiocyanate-chlorate mixts are selected when high temps and high radiation environments are encountered, and presumably a longer ignition delay is the price which is paid for the extra margin of safety

The military practice is one of preference for the styphnate-based types, even though for pyrotechnic applications they tend to be brisant. When in about 1960 the requirement for high temp resistant primary compns (1000 hrs at 37°) was established, the G 11 type mixts were developed. These mixts are desensitized by a humid environment and are much less sensitive than the styphnate compns so as to require increased firing energy. The brisance is comparable with Pb styphnate mixts. Table 10 lists the composition of the most important percussion primers, while Table 11 compares the characteristics of the formulations based on a report by Lake (Ref 31)

Table 10
Composition of Typical Percussion Primer Compositions

Component	FA-70	PA-101	G-11
Lead Styphnate	–	53	–
Barium Nitrate	–	22	–
Potassium Chlorate	53	–	53
Antimony Sulfide	17	10	25
Calcium Silicide	–	–	12
TACOT (*)	–	–	10
Lead Thiocyanate	25	–	–
TNT	5	–	–
Aluminum	–	10	–
Tetracene	–	5	–

(*) A proprietary secondary expl by DuPont de Nemours & Co

Whereas once BlkPdr was the universal proplnt and expl, today it finds application chiefly as an igniter. The annual military procurement in the US in 1968 was about 3000 tons, reflecting the requirements of the Vietnamese war, whereas in 1976 consumption dropped to less than 500 tons (Ref 42). Civilian applications

Table 11
Percussion Primer Property Chart after Lake (Ref 31)

Primer Mix	Max Continuous Temperature	Rel Primer Violence	Firing Sensitivity (Drop Height ± 5σ) x Wt
Thiocyanate/Chlorate	70°C	soft	1.53 kg-cm
Styphnate/Chlorate	95°C	brisant	1.98 kg-cm
G-11	200°C	brisant	6.86 kg-cm

in fireworks, muzzleloading weapons and as a proplnt in model rocketry consume another 500 tons of domestic production, although the amount derived from imports is many times this figure. Recently the allowable quantities of BlkPdr which may be stored in a home without a permit has been increased to 50 lbs (22.7 kg) (Title XI, Public Law 91-452)

The US Army is the primary consumer of BlkPdr in the US where it is used as an igniter in flash tubes for artillery shells (Vol **4**, D775-R) above 40mm, where besides being effective as a flash reducer it is known to be a better igniter for smokeless powder than the smokeless powder itself (Ref 110). Minor uses of BlkPdr are as a proplnt/igniter in flare and smoke cartridge ejection systems (Vol **4**, D959), as a delay element (D857) and as an incendiary igniter (D942)

Numerous accidents, coupled with decreased consumption of BlkPdr reduced the domestic US sources to one. Consequently, the US Army has contracted to build a fully automated plant which employs the novel Loevold process (see below), which uses high velocity air to break up and blend the ingredients (Refs 53 & 63). This remotely controlled process is claimed to be safe (Ref 95). The product is to meet US military specifications (Ref 79), although this remains to be demonstrated

The traditional (batch) milling process, essentially unchanged in centuries, grinds the raw material in a wheel mill for many hours, causing pulverization and intimate contact of one component with the other. The resulting mixt is pressed, granulated ("corned"), dried, polished and glazed. In the new Loevold process the raw mixt is injected as a continuous stream into a jet mill, shown schematically in Fig 2, where collision of particles causes pulverization to < 15 μm, as according to Loevold (Ref 95) the fine particle size provides assurance of close particle contact and equivalence in performance with the mill process powder. The resulting raw powder is then pressed, granulated, glazed and screened as before. Another jet mill process for the fabrication of BlkPdr was patented recently (Ref 108)

From the dimmest past to the present, BlkPdr (Vol **2**, B165-R) has been the subject of prolific scientific work, the earlier part of which was reviewed by Urbański (Ref 14). Recent studies

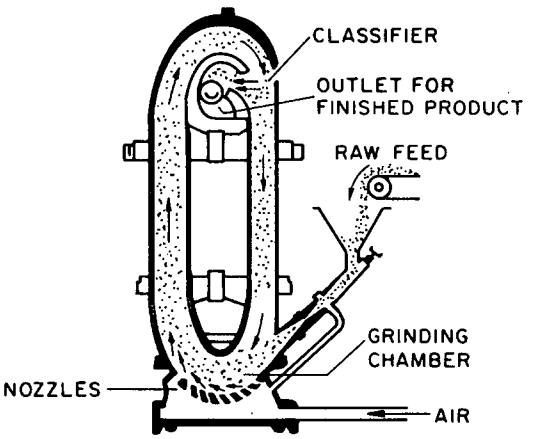


Fig 2 Jet Mill for the Compounding of Black Powder

dealt with the role of S in lowering the pressure limit of BlkPdr ignition, as well as the profound effect of charcoal volatiles content on the performance (Refs 3 & 109). Description of BlkPdr is frequently in terms of the burning rate, which depends on whether it was measured on loose powder or on compressed, single grains. Confined loose powders burn in a manner which can be described as a low order detonation, velocities of 170m/sec for coarse powders (Ref 70) to 950m/sec for fine powder (Ref 9), and 1500m/sec for sulfurless powder having been reported (Ref 9). A more meaningful criterion is the relative quickness, or the rate of pressure rise as determined in a constant volume bomb (Ref 109)

When BlkPdr is used as a pressed grain, surface normal burning rates can be defined. These studies continue as an important tool in examining the complexities of the burning mechanism. These and other properties of various BlkPdrs have been compared (Ref 72), as has the temp dependence of the burning rates. The enormous volume of published data deals, however, only with conventional, mill process, powder, while the corresponding data on the jet mill powder await the completion of ongoing studies

A new replica BlkPdr is Pyrodex (Ref 110) which, containing 6% sulfur, 10% charcoal, 83% K nitrate and 1% Ca carbonate, has an ignition temp above 260° compared with an ignition temp of 125° for BlkPdr and 135° for smokeless powder

8) Advances in Pyrotechnics

Computer Applications in Pyrotechnics

Since 1968 the availability of theoretical calcns from optical spectra, the results of mass spectrometer studies of volatile species and computer programs for the study of high temp equilibria (Refs 15 & 41) has made possible the analysis of complex pyrotechnic reactions. Such techniques will see expanded use in the examination of the spectral characteristics of signals and flares (Ref 80), although prediction of kinetically controlled reaction rates and ignition energies await further mechanistic studies

For much of the last two decades the science of shock physics was applied to thermomechanical effects in expls (Refs 118 & 147) and proplnts. The further extension of such studies to pyrotechnics (Ref 76) may provide further insights into the functioning of improved incendiary munitions by multidimensional analysis of wave propagation into distended matter (Refs 135 & 151). Similarly, propagation rates and ignition energies in condensed phase reactions have also been modeled (Refs 66, 78 & 120)

Application of Solid State Physics to Pyrotechnics

Modification of the reactivity of metallic oxides by doping (Refs 56, 86 & 96) may result in safer igniters, initiators and reaction mixts. In devices which can tolerate moderate ignition delay, further development of non-primary initiators (Refs 31, 77, 97 & 112) will extend the storability, the manufacturing safety, the electromagnetic field and spark sensitivity and the high temp compatibility of pyrotechnic devices

Pyrotechnic Laser Technology

It is not surprising that the reliability, portability and rapid energy release of pyrotechnic systems should have suggested their use in laser technology, both as light source for pumping and as the source for the inversion population. It was realized that pyrotechnic laser devices might be inexpensive single shot laser weapons. Stokes and Steng (Ref 16) suggested the burning of cyanogen as the light source for pumping Nd and ruby lasers, whereas Kaminskii and Bodretsova (Ref 23) studied $KClO_4$ and Zr flash compns. A recent review discusses the feasibility of using the shock driven $CS_2 + O_2$ reaction for use in a gas dynamic laser (Ref 162)

Although no operating data were found on pyrotechnic gas dynamic lasers, Douda (Ref 43) explored some of the theoretical requirements. Of the systems which he considered (principally flare compns), the alkaline earth lasers are the most interesting in that the MOH and MCl radicals are removed from their ground state by further chemical reaction to the bivalent molecule. The concn of the transient species is, as reported (Ref 90), a strong function of temp, suggesting that a possible lasing action could be achieved by "freezing" of radicals thru adiabatic expansion. If a direct inversion does not occur, the species may have to be pumped using possibly nitrogen and nitric oxide. Both molecules are capable of being excited vibrationally to an energy level which is nearly resonant with the excited levels of MOH or MCl where M is either Ba or Sr. The above schemes await exptl verification

Electromagnetic Field Effects

The initiation characteristics of primary expls have profound implications for the storage and functioning of pyrotechnic devices. Specifically, the sensitivity to static electrical discharges and to the presence of RF electrical fields is many orders of magnitude greater in terms of energy required to initiate (Vol **5**, E43) than if the same initiation were to take place thermally or by shock initiation of thin wafers (Ref 118). Significant advances have taken place in the study of this phenomenon. H.D. Fair and D.S. Downs at PicArsn have shown that electronic processes can be used to achieve direct non-thermal initiation of both primary and secondary expls (Ref 87). The electronic energy levels in expls were determined by low temp optical absorption techniques and the electronic transport properties were obtained by photoconduction and related solid state measurements (Ref 71). The description of an expl as a semiconductor suggests a new mechanism for initiation of primary and secondary expls, proplnts and pyrotechnics, because a combination of a low-intensity static electric field coupled with radiation from ultraviolet light (Ref 13), from gamma and X-rays (Ref 127, p 2) or from electron beams (Ref 100) was found to result in initiation

Incident radiation produces linear changes in electrical conductivity with dose (Ref 113) by the production of photocarriers. Initiation then

Table 12
Compositions of Pulsating Pyrotechnic Systems (from Ref 124)

White Composition		Red Composition		Green Composition	
Barium Nitrate	65%	Strontium Nitrate	65%	Barium Nitrate	60%
Al/Mg Alloy	20%	Al/Mg Alloy	18%	Al/Mg Alloy	20%
Nitrocellulose	7%	Dicyandiamide	8%	Amm Perchlorate	7%
Amm Perchlorate	5%	Amm Perchlorate	6%	Potassium Perchlorate	5%
Sodium Oxalate	3%	Potassium Perchlorate	3%	Nitrocellulose	5%
				Barium Perchlorate	3%

Table 13
Pulsating Reactions (from Ref 98)

Dependence of the Pulse Frequency on the Fuel Composition

30% Pentaerithritoldinitrodiacrylate
50% Strontium Perchlorate-tetrahydrate
20% Fuel

Fuel	Pulse Frequency, cps
Methacrylate-methyl ester	1
Methacrylate-ethyl ester	300
Acrylic acid-methyl ester	700
Acrylic acid-ethyl ester	500
Methacrylic acid-isobutyl ester	0.5
Methacrylic acid-n-butyl ester	10

Dependence of the Pulse Frequency on the Perchlorate Concentration

A { Methacrylate-methyl ester 60%
Pentaerithritoldinitrate-diacrylate 40%

B Strontium Perchlorate-tetrahydrate

Ratio of A to B		Pulse Frequency, cps
70	30	0.1
60	40	0.2
50	50	1
40	60	10
30	70	400

occurs in response to an applied field. In the Russian literature this photoelectronic initiation is referred to as the "chemical avalanche effect" because of the dependence of the field intensity at initiation on the specimen thickness (Refs 50 & 61). Charge injection is known to cause a memory effect in Pb Azide (Ref 88)

Whereas currently most studies deal with azides, a similar effort devoted to other metal salts such as nitrates and chlorates would be an important step toward understanding electrical initiation of pyrotechnics, and conversely to making possible safe, non-expl igniters. For instance, a study by Maycock (Ref 4) shows that those azides, perchlorates, and nitrates in which the solid state shows absorption on the long wavelength side of the anionic excitation band in soln, are the most unstable members of the respective series. Consequently, there is a direct relationship between the absorption spectra of pyrotechnic oxidizers and their respective sensitivities

A promising approach toward controlling the static and impact sensitivity of initiators has consisted of co-precipitating the primary expl on a carrier or doping it in a manner which affects its solid state characteristics (Ref 97)

Oscillatory Reactions

Occasionally new pyrotechnic phenomena are discovered (Refs 98, 99 & 124) which may see application in special situations. An example is the devlopment of pulsating burning pyrotechnics which constitute the optical analogue to the familiar whistling compds (Ref 138, Formulas 156–60). Whereas pyrotechnic whistles have a frequency of 2000 to 5000 cps, the new compns burn in the range of 0.1 to 700 cps and are therefore well suited for acquisition by electro-optical devices

Pulsating burning systems were described by Gol'binder in 1961 (Ref 6) but which proved to be unsatisfactory. Siderov and Kravcenko published descriptions of their green and red flash compns (Ref 28) which are said (Ref 99) to be bright. New pulsating burning compns are reported by Wasmann (Ref 124) for white, red and green compns (Table 12). Copper chromite catalysts were used to adjust the pulse frequencies. The trick in making these reactions oscillate is said to be the selection of the correct Al/Mg alloy particle size distribution. Variation of signal frequency is reported by the use of the esters of acrylic acid and methacrylic acids and nitrate alcohols, as shown in Table 13. The explanation of the pulsating phenomenon remains unsatisfactory, and further study should be rewarding

A composition for producing flickering signals was recently patented (Ref 126) which employs ingredients similar to those listed in Table 13

New Technology

New process technologies (Ref 53) such as jet mills (Fig 2) and co-precipitation (Ref 97) may allow safe compounding of sensitive or toxic formulations. New analytical tools such as neutron radiography (Ref 92) afford improved non-destructive testing of devices. X-ray fluorescence (Ref 93) and neutron activation (Ref 94) provide quantitative analysis of pyrotechnic compns and their trace contaminants

9) The Literature of Pyrotechnics

Military pyrotechnics, in contrast to civilian pyrotechnics, is well documented, although much of the useful device-oriented literature is either outdated or classified. Pyrotechnics as a science sees only limited attention and much current work is reported only in proceedings of meetings because, with some exceptions, there are few recognized journals which are suited to the subject

Periodically, useful generalized reviews and explanatory expositions are published such as the series of books by A.A. Shidlovsky (Ref 149), by H. Ellern (Ref 138) and by G.W. Weingart (Ref 140); of these, Ellern's book is the most current and filled with a wealth of background information

Among the more specialized books is the recent "Handbook of Pyrotechnics" by K.O. Brauer (Ref 152) which covers, its title notwithstanding, chiefly aspects of ordnance engineering as it applies to space technology, unlike the "Aerospace Ordnance Handbook" (Ref 133) which contains useful information on pyrotechnics which is not restricted to space applications. For civilian pyrotechnics, the Rev. R. Lancaster's book (Ref 145) is current, while the history of pyrotechnics in antiquity was scholarly presented by J. Partington (Ref 130)

General encyclopedias are usually poor sources of information except for Ullmann's

(Ref 136) discussion of civilian pyrotechnics, of matches, and of explosives. Twenty years ago the Denver Research Institute prepared an exhaustive review of small arms incendiary munitions (Ref 129). In order to fill the gap in the missing basic data on specialized applications, the US Army has published an "Engineering Design Handbook Series" (Refs 131, 132, 134, 143, 146, 147, 150 & 158). Of a long list of Government issued manuals, one on "Small Arms Pyrotechnics" (Ref 33) and one entitled "Joint Munitions Effectiveness Manual, Weapons Characteristics" (Ref 159) are recommended for complete description of the design and performance of US Military pyrotechnic devices. Corresponding data on space shuttle hardware is available from NASA (Ref 157). The Bermite Corporation published a collection of igniter compns (Ref 139)

Fundamental research in pyrotechnics is published in the US in "Combustion and Flame" by the Combustion Institute, and in the UK in "Combustion Science and Technology" and in "Fuel". Germany has the new journal, "Propellants and Explosives" (German Chemical Society), which is the successor to the discontinued "Explosivstoffe". A necessary caveat is that these journals are strongly oriented toward combustion or propulsion so that only rarely do they yield pyrotechnic information. Likewise, the various publications of the learned societies contain much data on thermodynamics, spectroscopy, and instrumental analysis which are useful in the study of pyrotechnics. In the USSR the situation is somewhat better as "Physics of Combustion and Explosion" (Fizika Gorenia i Vzryva) of the Siberian Branch Academy of Sciences USSR is exclusively oriented toward subjects of interest, as several scientific institutes are primarily devoted to research in pyrotechnics. The same authors do publish also, however, in the journals of the Academy of Science USSR (of which there are several) as well as in the corresponding journals of the academies of the various republics, so that the impression is created of a high level of activity

The principal means of information exchange in the US has been at meetings which have been sponsored biannually by the Franklin Research Institute (Refs 142, 154 & 161), and by the Denver Research Institute (Refs 137, 141, 144, 153 & 160). Patent literature is often a convenient reference source. Itemized references and general references follow. The appended numbers with the prefix AD signify that the document is available from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314

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Pyrotolites. Cast or pressed mixts of Tetryl and TNT, first studied and proposed in Fr in 1907 by Koehler and Marqueyrol, but not used at that time. Following is a list of the mixts proposed by them:

Tetryl	TNT	Fusion Point, °C
0	100	80.7
10	90	68.0
20	80	59.5
30	70	65.5
40	60	67.5
50	50	68.0
60	40	67.0
70	30	73.5
80	20	72.5
90	10	106.0
100	0	128.5

These mixts were later used in the USA and other countries (See under Tetrytol)
Ref: L. Desvergnes, MP **19**, 265–66 (1922)

Pyroxalam. The name given by Uchatius in the 1830's to a white powder obtained by nitrating starch with a mixt of nitric and sulfuric acids, and which contained about 11.1% N. It was Nitrostarch (see in this Vol) with the formula $C_{24}H_{32}O_{12}(ONO_2)_8$, and closely resembled a product previously prepd (1832) by Braconnot by treating starch with neat concd nitric acid
Ref: Daniel (1902), 459, under Nitramidon

Pyroxyle. A generic term applied to various kinds of NC prepd by the nitration of either cotton, wood, paper, jute or ramie
Ref: Daniel (1902), 665

Pyroxylées. Fr sporting powders, invented in the 19th century by Bruneau, contg NC 83 and Amm bichromate 17%. "Poudre J" and "Poudre S" were known by this name
Ref: Daniel (1902), 385 & 665

Pyroxylins. A group of Nitrocelluloses with N content ranging from 10% and less to about 12.65%. The lower N members (see also under Collodion Cotton in Vol **3**, C394-R) are used

for the prepn of celluloid, pharmaceutical products and lacquers. The higher N members find use in the prepn of Dynamites and smokeless powders (see under Pyrocollodion and Pyrocellulose in this Vol)

Pyroxylins may be divided as follows:
a) *Pyroxylin for Smokeless Powder.* This includes Pyrocollodion (about 12.44% N) and Pyrocellulose (12.6–12.7% N). It is nearly completely (about 99%) sol in eth-alc, acet, acetate esters, etc; partly sol in methanol;
b) *Collodion Cotton* (Soluble Pyroxylin or Varnish Cotton) – see under Collodion Cotton;
c) *Celluloid Pyroxylines.* Contain about 10.7% to 11.25% N, partially overlapping the Collodion Cotton range. It is used chiefly in the manuf of celluloid, plastics and some lacquers. It is prepd to give higher viscosities than Collodion Cotton. Sol in eth-alc, acet, acetic esters, methanol, and many other organic solvents;
d) Pyroxylins contg 10.0–10.7% N are sol in some organic solvents, especially ethanol. They are not used in industry; e) Pyroxylins contg less than 10% N are practically insol in organic solvents, and are not used in industry
Refs: 1) Daniel (1902), 765 2) Bebie (1943), 128 3) Davis (1943), 257 4) A. Pérez Ara (1945), 367 5) CondChemDict (1971), 621-L

Pyroxylite. An expl patented in Fr in 1887 by Antoine and Grunselle consisting of PA, Pb oxide and K dichromate. It was tested in 1888 by the CSE and found to be of no interest to the Fr Govt (Ref 1)
Refs: 1) L. Liouville, MP **2**, 648 (1884–89) 2) Daniel (1902), 665

Pyroxylol. Synonym for Pyroxylin

Pyruvic Acid (2-Oxopropanoic Acid, Acetylformic Acid, Pyroracemic Acid, Brenztraubensäure in Ger), $CH_3COCOOH$, mw 88.06, colorl liq, mp 11.8°, bp 165° decomps, d 1.267 g/cc at 15/4°. Miscible with w, alc & eth. Polymerizes and decomps on standing unless pure and kept in container with airtight closure. Can be prepd by distn of tartaric acid in the presence of K acid sulfate as a dehydrating agent. The distillate must be fractionated under reduced press
Refs: 1) Beil **3**, 608 & {1146} 2) Merck (1976), 7811-L

Pyruvic Acid Nitrophenylhydrazones; Salts. Ciusa and Musajo (Ref 2) prepd a number of mono-metallic salts of the o-, m- and p-nitrophenylhydrazones of the general formula $(O_2N)C_6H_4.NH.N:C.CH_3.COOM$, where M is a metal

Ragno (Ref 3) prepd a number of monometallic salts of 2,4-dinitrocompds of the general formula $(O_2N)_2C_6H_3.NH.N:C.CH_3.COOM$. They all proved to be more or less expl. The most expl was the Pb salt – it expld violently at about 240° when heated slowly in a capillary tube. Other salts did not expld when heated slowly, but simply decompd. They expld or deflagrated, however, when heated rapidly in a capillary or test tube. Most of the salts were insensitive to shock
Refs: 1) Beil – not found 2) R. Ciusa & L. Musajo, Gazz **60**, 486–92 (1930) & CA **25**, 277 (1931) 3) M. Ragno, Gazz **75**, 186–92 (1945) & CA **41**, 4126 (1947)

Pyruvonitrolic Acid. See under Acetylmethylnitrolic Acid in Vol **1**, A84-L

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