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Chemical Explosives and Rocket Propellants

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PART I. CHEMICAL EXPLOSIVES

INTRODUCTION

The average citizen in today's world gives little thought to the important role that commercial explosives play in our lives and how their use is linked to our standard of living and our way of life. Explosives provide the energy required to give us access to the vast resources of the earth for the advancement of civilization.

To maintain our standard of living in the United States, every day 187,000 tons of concrete are mixed, 35 million paper clips are purchased, 21 million photographs are taken, using large quantities of silver, 80 pounds of gold are used to fill 500,000 cavities, and 3.6 million light bulbs are purchased. It takes more than 40 different minerals to make a telephone, and 35 to make a color television. Even everyday products such as talcum powder, toothpaste, cosmetics, and medicines contain minerals, all of which must be mined using chemical explosives.[1]

Without explosives the steel industry and our entire transportation system would not be possible. The generation of electricity has been largely dependent on coal, and coal mining today is still the largest consumer of industrial explosives. Rock quarrying for road building and excavations for skyscrapers, tunnels, roads, pipelines, and utilities are direct beneficiaries of the labor-saving use of explosives.

COMMERCIAL EXPLOSIVES MARKET

The use of commercial explosives in the United States was fairly constant over the past decade, averaging between 2 to 3 million tons per year.

Figure 37.1 indicates explosives usage by year as reported by the U.S. Geological Survey

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*Consultant, Part I, Chemical Explosives. The author wishes to acknowledge that this section is an update of the corresponding material in the tenth edition authored by Boyd Hansen.

**Aerojet Propulsion Division. Part II, Rocket Propellants.

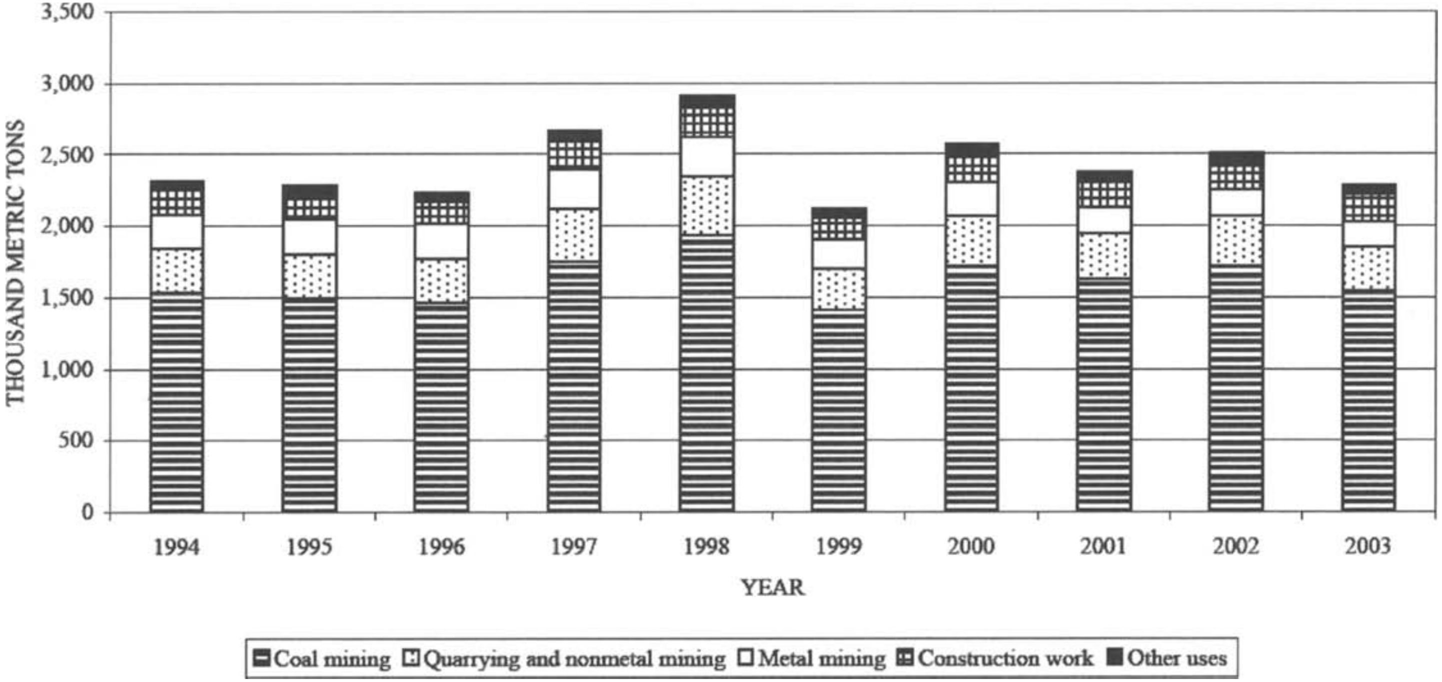


Fig. 37.1. Sales for consumption of U.S. industrial explosives from 1991 to 2000. (*Kramer, Deborah A., United States Geological Survey, Explosives Statistics and Information, Minerals Yearbook 2000, and the Institute of Makers of Explosives.*)

TABLE 37.1 Industrial Explosives and Blasting Agents Sold in the United States by State and Class (Metric Tons)

	2002				*2003*			
	Fixed High Explosives				*Fixed High Explosives*			
State	*Permissibles*	*Other High Explosives*	*Blasting Agents and Oxidizers*	*Total*	*Permissibles*	*Other High Explosives*	*Blasting Agents and Oxidizers*	*Total*
Indiana	3	1,130	220,000	221,000	38	1,070	204,000	205,000
Kentucky	780	1,990	312,000	315,000	439	1,410	264,000	266,000
Pennsylvania	81	1,810	117,000	119,000	71	1,490	127,000	128,000
Virginia	163	1,670	159,000	161,000	106	3,300	141,000	145,000
West Virginia	19	1,170	363,000	364,000	121	719	331,000	332,000
Wyoming	39	528	272,000	273,000	—	2,420	231,000	234,000
Others	270	29,799	1,025,141	1,055,544	291	25,095	953,198	978,351
Total	1,360	38,100	2,470,000	2,510,000	1,070	35,500	2,250,000	2,290,000

Note: Data rounded; may not add up to total shown.
Source: IME.

(USGS) and the Institute of Makers of Explosives (IME) from 1994 to 2003.[2,3] Figure 37.1 also separates the volumes by industry use. The open-pit coal mining industry continues to be the largest user, as it has been for many years. Table 37.1 shows the commercial explosive usage by seven leading states for 2002 and 2003.[2] In the year 2003, the four states consuming the most explosives (in decreasing order) were: West Virginia, Kentucky, Wyoming, and Indiana, all coal mining states. The coal market is also slowly making a shift from the eastern states to the western states with lower BTU, but more importantly, lower sulfur coal. Through the 1990s the sparsely populated state of Nevada ranked in the top ten states using commercial explosives. This reflected the growth of large volume gold mining operations in North America. Many of the smaller underground gold mines were transformed into large open-pit operations using efficiencies of scale to overcome the overall lower grade of ore, the same transformations that other metal mines had made decades before. Along with this change in mining style came a conversion from small diameter packaged explosives such as dynamite to large, bulk explosive loading systems using emulsions and ammonium nitrate/fuel oil (ANFO).

CHEMISTRY OF COMBUSTION AND EXPLOSION

For a simple understanding of explosives it is helpful to compare an explosive reaction with the more familiar combustion or burning reaction. Three components are needed to have a fire: fuel, oxygen, and a source of ignition. The process of combustion is basically anoxidation–reduction (redox) reactionbeween the fuel and oxygen from the air. Once initiated, this reaction becomes self-sustaining and produces large volumes of gases and heat. The heat given off further expands the gases and provides the stimulus for the reaction to continue.

The burning reaction is a relatively slow process, depending upon how finely divided the fuel is, that is, the intimacy of contact between the fuel and the oxygen in the air. Because burning is diffusion-controlled, the more intimately the fuel and oxygen are mixed, the faster they can react. Obviously, the smaller the particles of fuel, the faster the combustion can occur.

Another result of the fineness or particle size of the fuel is the completeness or efficiency of the reaction. In a complete combustion all the fuel elements are oxidized to their highest oxidation state. Thus, wood, being mainly cellulose, and gasoline, being generally a hydrocarbon (e.g., octane), produce primarily carbon dioxide and water vapor upon complete combustion. Once initiated these burning reactions give off heat energy, which sustains the reactions. Heat is released because the oxidized products of the reaction are lower in energy (more stable) than the reactants. The maximum potential energy release can be calculated from the respective heats of formation of the products and reactants. Actual heats of combustion can be measured experimentally by causing the reaction to occur in a bomb calorimeter. The calculated energy values for the above reactions are −3,857 cal/g for cellulose and −10,704 cal/g for octane, respectively.

In the case of an inefficient burn, some less stable or higher-energy products are formed so that the resultant heat energy given off is lower than that for complete combustion. In the above examples inefficient combustion could result from lack of oxygen accessibility, producing carbon monoxide or even carbon particles instead of carbon dioxide. A smoky flame is evidence of unburned carbon particles and results from inefficient combustion where fuel particles are so large or so dense that oxygen cannot diffuse to the burning surface fast enough. If this inefficiency is great enough, insufficient heat is given off to keep the reaction going, and the fire will die out.

All chemical explosive reactions involve similar redox reactions; so the above principles of combustion can help illustrate, in a very basic way, the chemistry involved in explosions. As in a fire, three components (fuel, oxidizer, ignition source) are needed for an explosion. Figure 37.2 shows an explosion triangle, which is similar to the fire triangle. In general, the products of an explosion are gases and heat although some solid oxidation products may be produced, depending upon the chemical explosive composition. As in normal combustion, the gases produced usually include carbon dioxide and water vapor plus other gases such as nitrogen, again depending upon the composition of the chemical explosive.

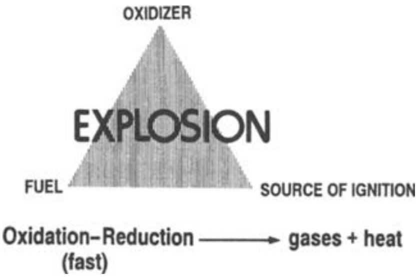


Fig. 37.2. An explosion triangle.

It should be noted that an explosion differs from ordinary combustion in two very significant ways. First, oxygen from the air is not a major reactant in the redox reactions of most explosives. The source of oxygen (or other reducible species) needed for reaction with the fuel—the oxidizer—may be part of the same molecule as the fuel or a separate intermixed material. Thus an explosive may be thought of as merely an intimate mixture of oxidizer and fuel. This degree of intimacy contributes to the second significant difference between an explosion and normal combustion—the speed with which the reaction occurs.

Explosives in which the oxidizer and fuel portions are part of the same molecule are called molecular explosives. Classical examples of molecular explosives are 2,4,6- trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and nitroglycerin (NG) or, more precisely glycerol trinitrate. The chemical structures of these explosives are shown in Fig. 37.3. As can be seen in the structures, the oxidizer portions of the explosives are the nitro (–NO_2) groups in TNT and the nitrate (–ONO_2) groups in PETN and NG. The fuel portions of all three explosives are the carbon and hydrogen (C and H) atoms. Comparison of the ratios of carbon to oxygen in these explosives (i.e., approximately 1 : 1 for TNT, approximately 1 : 2 for PETN, and 1 : 3 for NG) shows that TNT and PETN are deficient in oxygen; that is, there is insufficient oxygen present in the molecule to fully oxidize the carbon and hydrogen. Consequently, products such as carbon monoxide, solid carbon (soot), and hydrogen are produced, as well as carbon dioxide and water vapor. Prediction of the exact products of

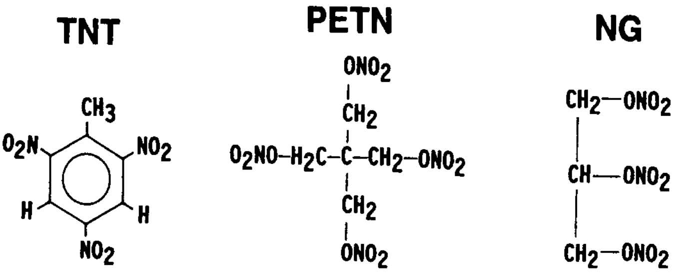


Fig. 37.3. Chemical structure of three molecular explosives.

explosion is complex, especially for the oxygen-deficient explosives, because the ratios of CO_2, CO, H_2O, and H_2 will vary, depending upon reaction conditions (explosive density, degree of confinement of the explosive, etc.).[4,5] The following equations show typical ideal reaction products along with calculated heats of reaction for these molecular explosives:

$$\underset{\text{TNT}}{C_7H_5N_3O_6} \rightarrow 1.5CO_2 + 0.5CO + 2.5H_2O + 1.5N_2 + 5C + 1290\ \text{cal/g}$$

$$\underset{\text{PETN}}{C_5H_8N_40_{12}} \rightarrow 4CO_2 + 4H_2O + 2N_2 + C + 1510\ \text{cal/g}$$

$$\underset{\text{NG}}{C_3H_5N_3O_9} \rightarrow 3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2 + 1480\ \text{cal/g}$$

Explosives in which the oxidizer and fuel portions come from different molecules are called composite explosives because they are a mixture of two or more chemicals. A classic industrial example is a mixture of solid ammonium nitrate (AN) and liquid fuel oil (FO). The common designation for this explosive is the acronym, ANFO. The oil used (typically #2 diesel fuel) is added in sufficient quantity to react with the available oxygen from the nitrate portion of AN. The redox reaction of ANFO is as follows:

$$\underset{\text{AN}}{3NH_4NO_3} + \underset{\text{FO}}{-CH_2-} \rightarrow CO_2 + 7H_2O + 3N_2 + 880\ \text{cal/g}$$

"Oxygen balance" (O.B.) is the term applied to quantify either the excess oxygen in an explosive compound or mixture (beyond what is needed for complete combustion of the fuel elements) or oxygen deficiency (compared to the amount required for complete combustion). It is expressed as either a percentage or a decimal fraction of the molecular weight of the oxygen in excess (+) or deficiency (−) divided by the molecular weight of the explosive or the ingredient being considered. Individual components of an explosive mixture have O.B. values that may be summed for the mixture. Shown below are the O.B. calculations for AN and FO:

$$\underset{\substack{\text{AN}\\ \text{Mol. wt.} = 80}}{NH_4NO_3} \rightarrow 2H_2O + N_2 + \underset{\text{Mol. wt.} = 32}{\tfrac{1}{2}O_2}$$

$$\text{O.B.} = \frac{+(1/2)(32)}{80} = +0.20$$

$$\underset{\substack{\text{FO}\\ \text{Mol. wt.} = \sim 14n}}{-(CH_2)_n} \rightarrow + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O$$

$$\text{O.B.} = \frac{-(3n/2)(32)}{14n} = -3.43$$

From the O.B. values, one can readily determine the ratio of ingredients to give a zero O.B. mixture for optimum efficiency and energy. Thus the weight ratio for ANFO is 94.5 parts of AN and 5.5 parts of FO ($94.5 \times 0.20 = 5.5 \times 3.43$).

For the molecular explosives shown previously, the respective oxygen balances are: TNT, −0.74; PETN, −0.10; and NG, +0.04. Thus, NG is nearly perfectly oxygen-balanced;

PETN is only slightly negative; but TNT is very negative, meaning significantly deficient in oxygen. Therefore, combinations of TNT and AN have been employed to provide additional oxygen for the excess fuel, as, for example, in the Amatols developed by the British in World War I.[6]

Modern commercial explosives react in a very rapid and characteristic manner referred to as a detonation. Detonation has been defined as a process in which a shock-induced supersonic combustion wave propagates through a reactive mixture or compound. This high pressure shock wave compresses the reactive material in contact with it resulting in rapid heating of the material, initiation of chemical reaction, and liberation of energy. This energy, in turn, continues to drive the shock wave. Pressure in a detonation shock wave may reach millions of pounds per square inch. The sudden pressure pulse shocks the explosive material as it passes through, causing a nearly instantaneous chemical reaction in the body of the explosive. Once initiated, molecular explosives tend to reach a steady-state reaction with a characteristic detonation velocity. Composite or mixture explosives also have steady-state detonation velocities, but these velocities are more variable than those of molecular explosives and are influenced by such factors as diameter of the charge, temperature, and confinement.

HISTORICAL DEVELOPMENT

The first known explosive material was black powder, a mixture of potassium nitrate (saltpeter), charcoal, and sulfur. As such it is a composite explosive whose properties are dependent upon how finely divided each of the ingredients is, and how intimately they are mixed. The exact origins of black powder are lost in antiquity. Publications referring to it seem about equally divided between those that attribute its origin to third- or fourth-century China[7,8] and those that place it closer to the 13th century, at about the time of Roger Bacon's written description in 1242.[9–13] Nevertheless, its use did not become very popular until the invention of the gun by Berthol Schwartz in the early 1300s; and its first recorded use in mining did not occur for over 300 years after that. First used for blasting in 1627, the production and application of black powder played a critical role in the rapid expansion of the United States in the early 19th century as canals were dug and railroads built to span the continent.

For over 200 years black powder was the only blasting agent known, but the 1800s brought a number of rapid developments that led to its demise, replacing it with safer and more powerful explosives. Table 37.2 presents a chronological summary of some of the significant discoveries of the 1800s. Credit for the first preparation of NG is generally ascribed to Ascanio Sobrero in Italy in 1846.

Swedish inventors Emmanuel Nobel and his son Alfred took an interest in this powerful liquid explosive and produced it commercially in 1862. However, its transportation and its handling were very hazardous, and eventually Alfred Nobel discovered that NG absorbed into a granular type of material (kieselguhr) was still explosive, but was much safer to handle and use than the straight liquid. This new invention, called "dynamite," was difficult to ignite by the usual methods used for pure NG. Therefore, also in 1867, Alfred Nobel devised the blasting cap using mercury fulminate. With this development dynamite became the foundation of the commercial explosives industry.

For military and gun applications black powder continued to be the only explosive of

TABLE 37.2 Nineteenth Century Explosive Discoveries

1800	Mercury fulminate
1846	Nitrocellulose
1846	Nitroglycerin
1847	Hexanitromannite
1862	Commercial production of nitroglycerin
1867	Dynamite
1867	Blasting cap
1867	Ammonium nitrate explosive patented
1875	Blasting gelatin and gelatin dynamite
1884	Smokeless powder
1886	Picric acid
1891	TNT
1894	PETN

choice as a propellant or bursting charge until the inventions of the late 1800s, when smokeless powder, based on nitrocellulose, proved to be a cleaner, safer, and more effective propellant than black powder. The synthesis of picric acid (2,4,6-trinitrophenol) followed by TNT and PETN gave solid, powerful, molecular explosives of more uniform performance for use in bombs and artillery shells. The main explosives used in World War I were TNT, Tetryl (2,4,6-trinitrophenylmethylnitramine), and Hexyl (hexanitrodiphenylamine), and in World War II they were TNT, PETN, and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane).[14]

In the industrial arena the production of black powder in the United States dropped precipitously after reaching a peak of 277 million lb in 1917.[15] By the mid-1960s it had ceased to be of commercial significance, but during the same time period dynamite production rose from 300 million lb to 600 million lb.

In 1947 a spectacular accident of catastrophic proportions ushered in the next revolution in explosives. Fertilizer-grade AN, in the form of prills (small spherical particles coated with paraffin to prevent caking), was being loaded into ships in Galveston Bay, Texas. Along with other cargo, one of these ships, the partially loaded *SS Grandcamp*, contained 2300 tons of this material. On the morning of April 16, soon after loading was resumed aboard the *Grandcamp*, a fire was discovered in one of the holds containing AN. Efforts to extinguish the fire were unsuccessful, and an hour later the bulk of the coated fertilizer detonated, killing 600 people and injuring 3000.[16]

This tragedy, along with several other large-scale accidents involving AN explosions, finally led researchers to the conclusion that inexpensive, readily available, fertilizer-grade AN could be used as the basis for modern industrial explosives.

Soon after the advent of porous AN prills, introduced in the early 1950s, investigators realized that these prills readily absorbed just the right amount of FO to produce an oxygen-balanced mixture that was both an inexpensive and effective blasting agent, in addition to being safe and simple to manufacture. This technology was widely adopted and soon constituted 85 percent of the industrial explosives produced in the United States.[17] With ANFO's cost and safety characteristics, it became practical for surface miners to drill larger boreholes and to utilize bulk ANFO delivery systems. Nevertheless ANFO had two significant limitations: AN is very water soluble, so wet boreholes readily deactivated the explosive; and ANFO's low density of 0.85 g/cc limited its bulk explosive strength. Cook[18] hit upon the idea of dissolving the AN in a small amount of hot water, mixing in fuels such as aluminum powder, sulfur, or charcoal, and adding a thickening agent to gel the mixture and hold the slurried ingredients in place. As this mixture cooled down, the AN salt crystals would precipitate, but the gel would preserve the close contact between the oxidizer and the fuels, resulting in a detonable explosive. Other oxidizers also could be added, and the density could be adjusted with chemical foaming agents to vary the bulk explosive strength of the product. With the addition of a cross-linking agent, the slurry or water gel could be converted to a semisolid material having some water resistance. The latest significant development in industrial explosives actually was invented only a few years after slurries.[19a,b] Water-in-oil emulsion explosives involve essentially the same ingredients that slurry composite explosives do, but in a different physical form. Emulsion explosives are discussed fully under the section titled "Explosives Manufacture and Use."

The main developments in military types of explosives since World War II have been trends toward the use of plastic bonded explosives (PBXs) and the development of insensitive high explosives. Driving these trends are desires for increased safety and improved economics in the process of replacing aging TNT-based munitions and bomb fills. PBXs involve the coating of fine particles of molecular explosives such as RDX and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) with polymeric binders and then pressing the resultant powder under vacuum to give a solid mass with the desired density. The final form or shape usually is obtained by machining. Explosives such as triaminotrinitrobenzene (TATB), nitroguanidine,[20] and hexanitrostilbene (HNS)[21] are of interest because of their high levels of shock insensitivity and thermal stability. The synthesis of many new, potentially explosive compounds is a very active and ongoing area of research,[22,23] but recently interest also has focused on composite explosives similar to those used by industry. Examples are EAK, a eutectic mixture of ethylenediamine dinitrate, AN, and potassium nitrate,[24] and nonaqueous hardened or cast emulsion-based mixtures.[25]

CLASSIFICATION OF EXPLOSIVES

The original classification of explosives separated them into two very general types: low and high, referring to the relative speeds of their chemical reactions and the relative pressures produced by these reactions. This classification still is used but is of limited utility because the only low explosives of any significance are black powder and smokeless powder. All other commercial and military explosives are high explosives.

High explosives are classified further according to their sensitivity level or ease of initiation. Actually sensitivity is more of a continuum than a series of discrete levels, but it is convenient to speak of primary, secondary, and tertiary high explosives. Primary explosives are the most sensitive, being readily initiated by heat, friction, impact, or spark. They are used only in very small quantities and usually in an initiator as part of an explosive train involving less sensitive materials, such as in a blasting cap. They are very dangerous materials to handle and must be manufactured with the utmost care, generally involving only remotely controlled operations. Mercury fulminate, used in Nobel's first blasting cap, is in this category, as is the more commonly used lead azide. On the other end of the spectrum are the tertiary explosives that are so insensitive that they generally are not considered explosive.

By far the largest grouping is secondary explosives, which includes all of the major military and industrial explosives. They are much less easily brought to detonation than primary explosives and are less hazardous to manufacture. Beyond that, however, generalizations are difficult because their sensitivity to initiation covers a very wide range. Generally, the military products tend to be more sensitive and the industrial products less sensitive, but all are potentially hazardous and should be handled and stored as prescribed by law. Table 37.3 lists some of the more prominent explosives of each type, along with a few of their properties.

For industrial applications, secondary explosives are subdivided according to their initiation sensitivity into two classes: Class 1.1 and Class 1.5. Class 1.1 explosives are sensitive to initiation by a blasting cap and usually are used in relatively small-diameter applications of 1–3-in. boreholes. Class 1.5 (blasting agents) are high explosives that are not initiated by a Standard # 8 electric blasting cap under test conditions defined by the U.S. Department of Transportation (DOT), and that pass other defined tests designed to show that the explosive is "so insensitive that there is very little probability of accidental initiation to explosion or of the transition from deflagration to detonation."[26] Being less sensitive, blasting agents are generally used in medium- and large-diameter boreholes and in bulk applications. Dynamites are always Class 1.1, but other composite explosives made from mixtures of oxidizers and fuels can be made either Class 1.1 or 1.5, depending upon the formulation and the density. Density plays a significant role in the performance of most explosives, and this is especially true for slurry and emulsion explosives where the density may be adjusted by air incorporation, foaming agents, or physical bulking agents, irrespective of the formulation. Blasting agent (class 1.5) classification is of interest because regulations governing transportation, use, and storage are less stringent for blasting agents than for Class 1.1 explosives. (Propellants and fireworks are classified by the DOT as Class 1.2 or 1.3 explosives, and blasting caps and detonating cord as Class 1.4.)

TABLE 37.3 Some Properties of Common Explosives

Common Name	*Symbol*	*Composition*	*Molecular Weight*	*Density (g/cc)*	*Detonation Velocity (km/sec)*	*Detonation Pressure (kilobars)*	*Explosive Energy (cal/g)*
Primary Explosives							
Mercury fulminate		$Hg(CNO)_2$	284.7	3.6	4.7	220	428
Lead azide		$Pb(N_3)_2$	291.3	4.0	5.1	250	366
Silver azide		AgN_3	149.9	5.1	6.8	—	452
Lead styphnate		$C_6H(NO_2)_3O_2Pb$	468.3	2.5	4.8	150	368
Mannitol hexanitrate (Nitromannite)	MHN	$C_6H_8(ONO_2)_6$	452.2	1.7	8.3	300	1,420
Diazodinitrophenol	DDNP	$C_6H_2N_4O_5$	210.1	1.5	6.6	160	820
Tetrazene		$C_2H_8N_{10}O$	188.2	1.5	—	—	658
Secondary Explosives							
Nitroglycerin	NG	$C_3H_5(ONO_2)_3$	227.1	1.6	7.6	253	1,480
Pentaerythritol tetranitrate	PETN	$C(CH_2ONO_2)_4$	316.2	1.6	7.9	300	1,510
Trinitrotoluene	TNT	$CH_3C_6H_2(NO_2)_3$	227.0	1.6	6.9	190	900
Ethyleneglycol dinitrate	EGDN	$C_2H_4(ONO_2)_2$	152.1	1.5	7.4		1,430
Cyclotrimethylenetrinitramine (Hexogen or Cyclonite)	RDX	$C_3H_6N_3(NO_2)_3$	222.1	1.6	8.0	347	1,320
Cyclotetramethylenetetranitramine (Octogen)	HMX	$C_4H_8N_4(NO_2)_4$	296.2	1.9	9.1	393	1,350
Trinitrophenylmethylnitramine (Tetryl)		$(NO_2)_3C_6H_2N(CH_3)NO_2$	287.2	1.4	7.6	251	950
Nitroguanidine	NQ	$CH_4N_3NO_2$	104.1	1.6	7.6	256	721
Nitromethane	NM	CH_3NO_2	61.0	1.1	6.2	125	1,188
Nitrocellulose	NC	Variable	—	1.4	6.4	210	950
Triaminotrinitrobenzene	TATB	$C_6H_6N_3(NO_2)_3$	258.2	1.8	7.9	315	829
Diaminotrinitrobenzene	DATB	$C_6H_5N_2(NO_2)_3$	243.2	1.6	7.5	259	993
Ethylenediamine dinitrate	EDDN	$C_2H_{10}N_4O_6$	186.1	1.5	6.8	—	948
Ethylenedinitramine (Haleite)	EDNA	$C_2H_6N_2(NO_2)_2$	150.1	1.5	7.6	266	1,080
Picric acid		$C_6H_3O(NO_2)_3$	229.1	1.7	7.4	265	1,000
Ammonium picrate (Explosive D)		$C_6H_6NO(NO_2)_3$	246.1	1.6	6.9	—	800
Picramide		$C_6H_4N(NO_2)_3$	228.1	1.7	7.3	—	1,070
Hexanitrostilbene	HNS	$[C_6H_3C(NO_2)_3]_2$	450.2	1.7	7.1	200	1,005

TACOT-Z		$C_{12}H_4N_8O_8$	388.2	1.6	7.2	181	980
Azobishexanitrobiphenyl	ABH	$C_{24}H_6N_{14}O_{24}$	874.4	1.8	7.6	—	
Dinitrotoluene	DNT	$CH_3C_6H_3(NO_2)_2$	182.1	1.5	5.0	—	700
Composition B		49/50/1 TNT/RDX/wax	—	1.7	8.0	294	1,100
Pentolite		50/50 TNT/PETN	—	1.6	7.7	245	1,100
Amatol		50/50 TNT/AN	—	1.6	6.5	—	950
Dynamite		Variable NG and various oxidizers and fuels	—	0.8–1.6	1.8–7.6	30–160	675–1,090
Prilled AN–Fuel Oil	ANFO	94/6 AN/FO	—	0.8–0.9	1.5–4.0 (depends on diameter)	—	880
Slurries or water gels		Variable mixtures of oxidizers, fuels, and water	—	0.9–1.4	3.5–5.0	—	600–1,200
Emulsions		Variable solutions of oxidizers in water and fuels	—	0.9–1.4	4.5–6.0	—	700–1,100
Heavy ANFO		50–75% AN with 50–25% emulsion	—	1.1–1.3	4.0–4.5	—	755–815
Tertiary Explosives							
Mononitrotoluene	MNT	$CH_3C_6H_4NO_2$	137.1	1.2			
Ammonium perchlorate	AP	NH_4ClO_4	117.5	1.9	3.4	187	488
Ammonium nitrate	AN	NH_4NO_3	80.1	1.4	3.2	—	346

STRUCTURAL CHARACTERISTICS OF EXPLOSIVES

The number of potentially explosive compounds is virtually unlimited. A listing by the U.S. Bureau of Alcohol, Tobacco and Firearms of explosive materials under federal regulation[27] numbered 225, and many of the items listed were broad, general categories. The ten-volume *Encyclopedia of Explosives and Related Items* compiled by the U.S. Army Picatinny Arsenal over a 25-year period contains several thousand entries. New organic molecular explosives are being synthesized continually; composite explosives, such as current commercial products that are mixtures of oxidizers and fuels, present an infinite number of possible combinations. The complexity of trying to comprehensively list the chemical structures of explosives is shown by a 1977 reference that listed 13 separate categories just for primary explosives.[28] However, the majority of the most important explosives can be grouped into a few classes sharing common structural features that are of value to researchers in understanding and predicting explosive properties.

The following seven categories,[29a,b] updated to include the relatively recent fluoroderivatives,[22] appear to be the most encompassing. Many explosives may contain more than one category, but not every compound that contains one of these chemical groups is necessarily an explosive.

1. $-\mathrm{N{=}O}$
2. $-\mathrm{N{-}N}-$, $-\mathrm{N{=}N}-$, and $-\mathrm{N \equiv N}$
3. $-\mathrm{C \equiv N}-$ and $-\mathrm{C \equiv N}$
4. $-\mathrm{C \equiv C}-$
5. $-\mathrm{Cl{=}O}$
6. $-\mathrm{N{-}X}$, where $\mathrm{X} = \mathrm{Cl, F, I}$
7. $-\mathrm{O{-}O}-$

Category 1 is by far the largest. It includes nitro groups, both aliphatic and aromatic; nitrate esters; nitrate salts; nitramines; and nitrosamines. Nearly all of the explosives listed in Table 37.3 fall into this category. Prominent examples are: nitromethane, an aliphatic nitro compound; TNT, an aromatic nitro compound; NG and PETN, nitrate esters; EDDN and ammonium nitrate, nitrate salts; and RDX and HMX, nitramines. Category 2 represents the hydrazine, azo, diazo, and azide compounds, both organic and inorganic. Hydrazine, tetrazene, and lead azide are examples of this group. Category 3 is represented by the explosives mercury fulminate and cyanogen, respectively. Acetylene and metallic acetylide salts constitute category 4. Category 5 consists mainly of inorganic and organic ammonium salts of chloric and perchloric acid, but would also include various chlorine oxides. Category 6 is generalized to include most of the amine halogens, nitrogen triiodide being a classic example. Also, considerable new synthetic work has focused on inserting the energetic difluoroamine groups into various organic molecules to form explosives that fall into this category. Category 7 includes organic peroxides and ozonides as well as hydrogen peroxide itself.

Commercial industrial explosives such as dynamites, slurries, and emulsions are included in these categories because their major components, nitrate esters and nitrate and perchlorate salts, are listed. However, mixtures of fuels and oxygen or other gases that may be explosive at certain ratios are not covered, including the liquid oxygen explosives that saw limited application earlier in the 20th century.

EXPLOSIVES MANUFACTURING AND USE

Details of the synthesis and larger-scale production of a number of molecular explosives including dynamites are given in the four-volume series by Urbanski (*Chemistry and Technology of Explosives*, Pergamon Press. 1964–84) and in various military books such as *Engineering Design Handbook: Explosive Series*. Formulations of commercial slurries and emulsions generally are consideredproprietary and are described mainly in the patent literature. Some specific examples of prominent explosives with general preparation methods are given below.

TNT (2,4,6-Trinitrotoluene)

TNT is no longer manufactured commercially in the United States, but is manufactured in significant quantities at several government plants because it is still an important military explosive. It is produced commercially in Canada and other countries and is imported into the United States for use in cast boosters to initiate industrial blasting agents. In a relatively straightforward process, TNT is made by the direct trinitration of toluene with nitric acid. Most modern processes are set up for continuous production in a series of nitrators and separators with the nitrating acid flowing countercurrently. This procedure avoids having to isolate the intermediate mono- and dinitration products and may also employ continuous purification and crystallization, being carried out simultaneously with production.

Mixed nitric and sulfuric acids sometimes are used with the addition of SO_3 or oleum. The sulfuric acid or oleum helps drive the reaction to completion by removing the water produced by nitration and by dehydrating nitric acid to form the more reactive nitronium ion (NO_2^+). Because toluene is not very soluble in the acid, powerful agitation is required. The spent acid is removed in successive separation steps, and the sulfuric acid is reused after the addition of more nitric acid. The molten TNT product is purified with multiple water and sodium sulfate washes, which produce significant quantities of "yellow water" and "red water" waste streams, respectively, that must be properly handled to avoid environmental problems. The low melting point of TNT (80–82°C) is ideal for melt casting, and TNT usually is employed as a mixture with other higher-melting explosives such as PETN, RDX, HMX, and tetryl. This feature and the excellent chemical stability of TNT have made it the most popular and widely used military explosive in the world.

RDX and HMX

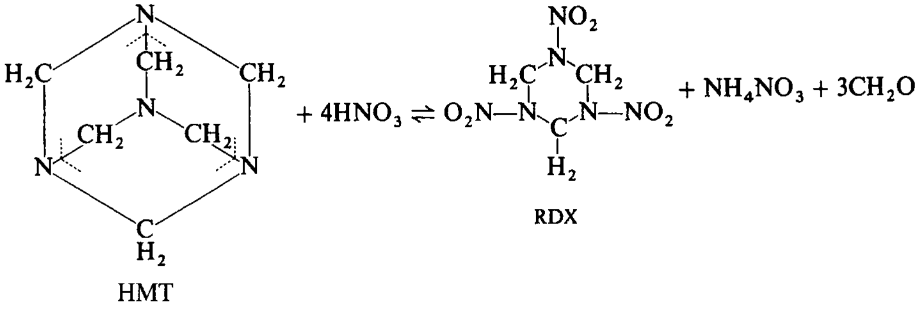
Both RDX and HMX are cyclic nitramines made by nitrolysis of hexamethylene tetramine (HMT). Their good thermal stabilities, high melting points (>200°C), and high energy properties make these crystalline compounds popular as projectile and bomb fills and for use in cast boosters and flexible, sheet explosives. HMX has superior detonation properties and a higher melting point than RDX, but it is more difficult and more expensive to manufacture. Reaction 1 shows the formation of RDX by the action of nitric acid on HMT. Schematically, RDX formation can be pictured as nitration of the three "outside" nitrogen atoms of HMT (in more accurate, three-dimensional representations all four nitrogens are equivalent) with removal of the "inside" nitrogen and methylene ($-CH_2-$) groups. AN (NH_4NO_3) and formaldehyde (CH_2O) are produced as by-products but can be used to form more RDX with the addition of acetic anhydride, as shown in Reaction 2. In actual practice these two reactions are run simultaneously, as shown in the combined reaction to produce approximately two moles of RDX for each mole of HMT.

HMX was discovered as an impurity produced in the RDX reaction. It is composed of an eight-membered ring rather than the six-membered ring of RDX. The latter is more readily formed than the eight-membered ring, but with adjustment of reaction conditions (lower temperature and different ingredient ratios), HMX formation can be favored. Schematically its formation can be pictured by nitration of all four nitrogens in hexamethylene tetramine and removal of two methylene groups as indicated in Reaction 3. To obtain pure HMX the RDX "impurity" must be removed by alkaline hydrolysis or by differential solubility in acetone.

HNS (2,2′,4,4′,6,6′-Hexanitrostilbene)

This is a relatively new explosive having been prepared unequivocally for the first time in the early 1960s.[30a,b] It is of interest primarily

Reaction 1



Reaction 2

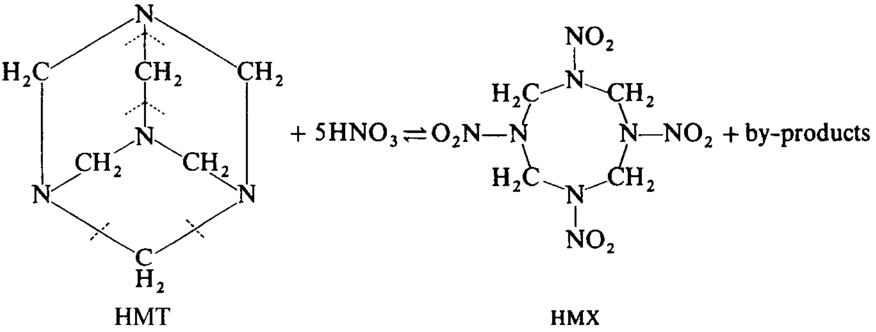
$$3CH_2O + 3NH_4NO_3 + 6(CH_3CO)_2O \rightleftharpoons (CH_2{\cdot}N{\cdot}NO_2)_3 + 12CH_3COOH$$

Formaldehyde AN Acetic anhydride RDX Acetic acid

Combined Reaction

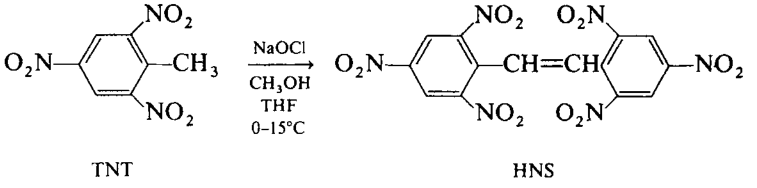
$$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2 \rightleftharpoons 2(CH_2{\cdot}N{\cdot}NO_2)_3 + 12CH_3COOH$$

Reaction 3



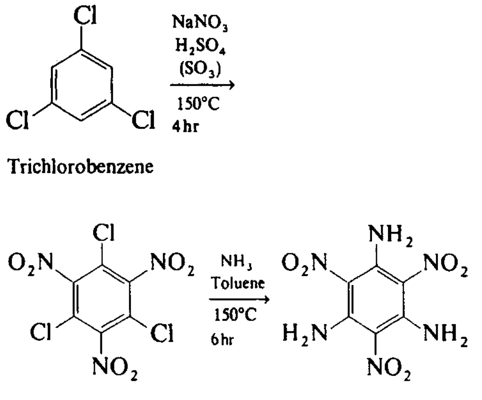
for two reasons: (1) its high melting point (316°C) and excellent thermal stability, and (2) its unique crystal-habit-modifying effects on cast TNT. The former makes HNS useful in certain military and space applications as well as in hot, very deep wells, and the second property is used to improve TNT castings. It can be manufactured continuously by oxidative coupling of TNT as shown below.

This relatively simple process from readily available TNT and household bleach (5% NaOCl solution) has been shown to involve a series of intermediate steps that give HNS in only low to moderate yields (30–45%) with many by-products. Although it also involves the use of expensive organic solvents that must be recovered, this synthesis is used commercially.[31,32] Studies to improve this process constitute an active area of research.



TATB (1,3,5-Triamino-2,4,6-trinitrobenzene)

This highly symmetrical explosive molecule has even higher thermal stability than HNS (greater than 400°C) and has become of special interest in the last two decades because of its extreme insensitivity.[33,34a,b] Because its accidental initiation is highly unlikely, TATB has been used in nuclear warheads and is being explored in plastic bonded systems for a number of military and space applications.[20] Currently it is manufactured in large-scale batch processes that are little changed from its original synthesis over 100 years ago. The two-step process involves trinitration of trichlorobenzene followed by amination to displace the chlorine groups as shown below.



Trichlorobenzene

Trinitrotrichlorobenzene

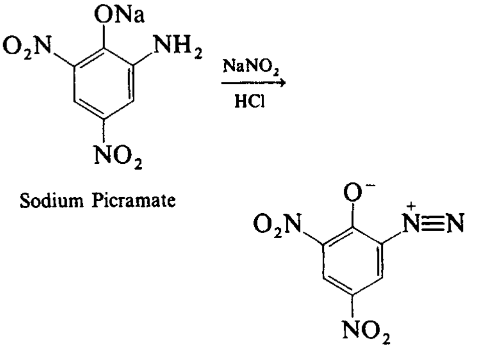
TATB

Both steps require high temperature and considerable reaction time but give 80–90 percent yields. The major problem areas are chloride impurities in the final product and the excessively fine particle size of the final product. Because TATB is highly insoluble in most solvents, it is difficult to purify the product or to change its particle size by recrystallization. Also the starting material is expensive and not very readily available.

More recently a similar synthetic procedure starting with 3,5-dichloranisole was reported.[35]

DDNP (2-Diazo-4,6-dinitrophenol)

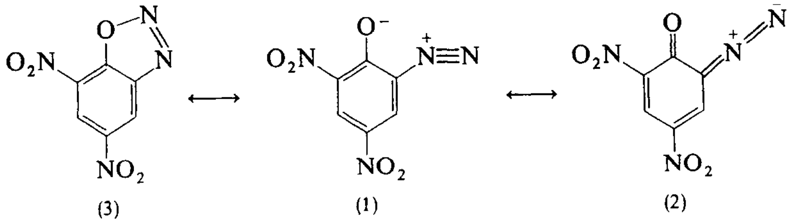
This yellow-to-brown crystalline material (melting point 188°C) is a primary explosive used as the initiator charge in electric blasting caps as an alternative to lead azide. It is less stable than lead azide but much more stable than lead styphnate, and is a stronger explosive than either of them because it does not contain any metal atoms. DDNP is also characterized as not being subject to dead pressing (tested at pressures as high as 130,000 psi). It was the first diazo compound discovered (1858) and was commercially prepared in 1928. It is manufactured in a single-step, batch process by diazotizing a slurry of sodium picramate in water.



Sodium Picramate

DDNP

The structure shown is convenient for visualization purposes, but DDNP actually exists in several tautomeric forms with form (2) apparently predominating.



(3)

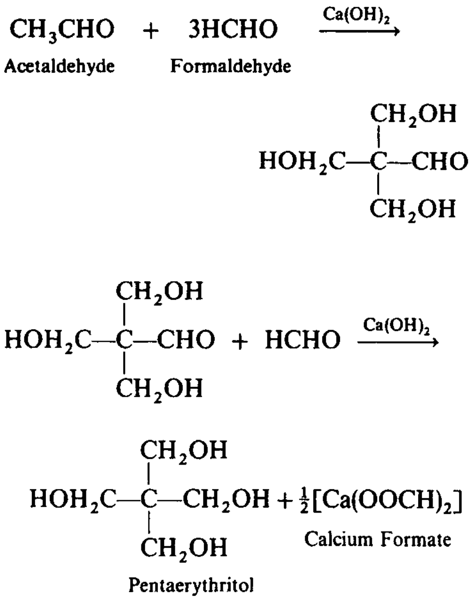
(1)

(2)

The sodium picramate starting material is itself explosive, but is commercially available as a chemical intermediate. It can be made by the reduction of picric acid with reducing agents such as sodium sulfide. The key to making useful DDNP is to control the rate of diazotization so that relatively large, rounded crystals are formed instead of needles or platelets that do not flow or pack well.

PETN (Pentaerythritol Tetranitrate)

Although known as an explosive since 1894, PETN was used very little until after World War I when the ingredients to make the starting material became commercially available. The symmetrical, solid alcohol starting material, pentaerythritol, is made from acetaldehyde and formaldehyde, which react by aldol condensation under basic catalysis followed by a crossed Cannizzaro disproportionation to produce the alcohol and formate salt. Although the reaction takes place in a single mixture, it is shown below in two steps for clarity.



$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Formaldehyde}}{3HCHO} \xrightarrow{Ca(OH)_2} HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO$$

$$HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO + HCHO \xrightarrow{Ca(OH)_2} \underset{\text{Pentaerythritol}}{HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH} + \underset{\text{Calcium Formate}}{\tfrac{1}{2}[Ca(OOCH)_2]}$$

For PETN manufacture the pentaerythritol starting material can be readily purchased as a commodity chemical from commercial suppliers. The nitration is relatively simple, involving only nitric acid (96–98%) and the solid alcohol added slowly with mixing and cooling. PETN is not very soluble in nitric acid or water and is readily filtered directly from the acid or after dilution of the acid with water. Water washing and recrystallization from acetone–water mixtures give the desired particle size ranges and the desired purity. PETN can be made either batchwise or continuously for large-scale production.

Pure PETN is a white, crystalline solid with a melting point of 141.3°C. Because of its symmetry it is said to have higher chemical stability than all other nitrate esters.[36] Relatively insensitive to friction or spark initiation, PETN is easily initiated by an explosive shock and has been described overall as one of the most sensitive, non-initiating, military explosives.[37] As with most explosives, the detonation velocity of PETN varies with the bulk density of the explosive. Most military applications of PETN have been converted to RDX because of its greater thermal stability. However, in industry PETN is widely used as the major component in cast boosters for initiating blasting agents, as the explosive core in detonating cord, and as the base load in detonators and blasting caps. For safety in handling, PETN is shipped in cloth bags immersed in water–alcohol mixtures and dried just before use.

NG (Nitroglycerin or Glyercol Trinitrate)

This nitrate ester is one of only a very few liquid molecular explosives that are manufactured commercially. It is a clear, oily liquid that freezes when pure at 13°C. As seen in the historical section, the first practical use of NG was in dynamites, where it is still used today more than 100 years later. It also is used as a component in multibased propellants and as a medicine to treat certain coronary ailments. This latter usage is attributed to NG's ability to be rapidly absorbed by skin contact or inhalation into the blood, where it acts as a vasodilator. (At high exposure levels such as in dynamite manufacture and handling, this property is responsible for the infamous powder headache.) NG is undoubtedly the most sensitive explosive manufactured in relatively large quantities. Its sensitivity to initiation by shock, friction, and impact is very close to that of primary explosives, and extreme safety precautions are taken during manufacture. Pure glycerin is nitrated in very concentrated nitric and sulfuric acid mixtures (typically a 40/60 ratio), separated from excess acid, and washed with water, sodium carbonate solution, and water again until free from traces of acid or base. Pure NG is stable below 50°C, but storage is not recommended. It is transported over short distances only as an emulsion in water or dissolved in an organic solvent such as acetone. Traditionally it has been made in large batch processes, but safety improvements have led to the use of several types of continuous nitrators that minimize the reaction times and quantities of explosives involved. Because of its sensitivity, NG is utilized only when desensitized with other liquids or absorbent solids or compounded with nitrocellulose.

Dynamite

Dynamite is not a single molecular compound but a mixture of explosive and nonexplosive materials formulated in cylindrical paper or cardboard cartridges for a number of different blasting applications. Originally Nobel simply absorbed NG into kieselguhr, an inert diatomaceous material, but later he replaced that with active ingredients—finely divided fuels and oxidizers called dopes. Thus, energy is derived not only from the NG, but also from the reaction of oxidizers such as sodium nitrate with the combustibles.

The manufacture of dynamite involves mixing carefully weighed proportions of NG and various dopes to the desired consistency and then loading preformed paper shells through automatic equipment. Because dynamites represent the most sensitive commercial products produced today, stringent safety precautions such as the use of nonsparking and very-little-metal equipment, good housekeeping practices, limited personnel exposure, and barricaded separations between processing stations are necessary. Today, the "NG" used in dynamite is actually a mixture of EGDN and NG (formed by nitrating mixtures of the two alcohols), in which NG is usually the minor component. Table 37.4 lists the common general types of dynamites with their distinguishing features. The straight dynamites and gelatins largely have been replaced by the ammonia dynamites and ammonia gelatins for better economy and safety characteristics.

TABLE 37.4 General Types of Dynamite

1. Straight dynamite	Granular texture with NG as the major source of energy.
2. Ammonia dynamite ("extra" dynamite)	AN replacing part of the NG and sodium nitrate of the straight dynamite.
3. Straight gelatin dynamite	Small amount of nitrocellulose added to produce soft to tough rubbery gel.
4. Ammonia gelatin dynamite ("extra" gelatin)	AN replacing part of the NG and sodium nitrate of the straight gelatin.
5. Semigelatin dynamite	Combination of types 2 and 4 with in-between properties.
6. Permissible dynamite	Ammonia dynamite or gelatin with added flame retardant.

Packaged Explosives

The use of NG-based dynamite continued to decline during the 1990's throughout the world. For example, by 1995 there was only one dynamite manufacturing plant left in North America, and in 2000 the dynamite production at this plant had dropped to less than half the amount produced in 1990. The reasons for the declining use of dynamite are its unpopular properties of sensitivity to accidental initiation and the headache-causing fumes. Both bulk and packaged emulsions have been slowly replacing dynamite since about 1980.

Packaged emulsions are basically made with the same manufacturing equipment as the bulk emulsions (see next section). The fuel

Fig. 37.4. Commercial packaged emulsion cartridges.

component usually contains waxes and other thickeners to give the emulsions a thick, putty-like consistency, and the oxidizer solution often contains both AN and a second oxidizer salt to produce optimum after-blast fumes. After manufacture, the thick emulsion is extruded into packaging material, normally a plastic film. The final product is then clipped together with metal clips forming firm, sausage-like chubs. Some packaged emulsions are also available in paper cartridges, designed to simulate dynamite packaging. Figure 37.4 shows some commercial packaged emulsion cartridges in both plastic and paper wrappings.

To obtain reliable detonability in small diameters, the density of packaged emulsions must be maintained at a relatively low value, typically 1.10–1.20 g/cc. On the other hand, some dynamites are available with densities in excess of 1.40 g/cc. These higher density and energy dynamites have been the most difficult to replace with emulsions and are the primary dynamite products currently in production.

Ammonium Nitrate and ANFO

AN continues to be the most widely used component of commercial explosives. It is used in nearly all of the packaged and bulk explosives on the market. The manufacturing process is described in Chapter 29.

Ammonia is basically the main raw material needed to manufacture AN. Some of the AN manufacturers make their own ammonia and some purchase it on the open market. It is obvious that the cost of manufacturing AN will depend on the price of ammonia and, even more basically, natural gas from which it is made. The volatility of ammonia prices is shown by the fact that in 1992 it cost $95 per ton and in 1995 the cost was $207 per ton.[38]

There are many producers of AN in North America making both AN solution and explosive grade AN prills. The AN solution is used in the manufacture of packaged and bulk emulsion and water gel explosives, and explosive-grade AN prills are used to make ANFO. ANFO, the acronym for a mixture of AN and FO is the single most commonly used chemical explosive. (ANFO is an example of a *composite* explosive as described in an earlier section, "Chemistry of Combustion and Explosions".) These low density AN prills are made by a specialized process, in which internal voids are created making the prills porous and able to absorb the required 5.5–6 percent FO.

ANFO alone represents about three fourths of the current volume of commercial explosives in use today around the world. Because of this, ANFO is commonly used as a reference when defining and comparing explosive properties. Some of these important explosive properties include density, detonation velocity, and energy release.

The crystal density of AN is about 1.72 g/cc, and the particle density of explosive-grade AN prills ranges from 1.40 to 1.45 g/cc depending upon the manufacturing process. This difference in crystal and particle density reveals the volume of pores or voids created by the specialized prilling process. The porosity of AN prills is the property desired in the manufacture of ANFO, since this determines how much FO can be absorbed. This intimate mixture of AN with FO is critical in the efficient detonability of ANFO. The AN prill particle density and inherent void-space value also become important when predicting and calculating the densities of ANFO blends with water-gel and emulsion explosives.

The bulk density of ANFO ranges from 0.80 to 0.87 g/cc. So, clearly about half of the ANFO is air or void space. All explosives require a certain amount of entrained void space in order to detonate properly. These void spaces also play a major role in the detonation reaction by creating "hot spots" under adiabatic compression in the detonation front.[39] The amount of void space in any given explosive and the resultant change in density have a significant impact on the detonation properties like detonation velocity, sensitivity, and even energy release.

Generally speaking, the detonation velocity of an explosive will increase with density until a failure point is reached. This failure point is commonly referred to as the critical density of that particular explosive. The density at that point is so high and the void space so low that the detonation cannot be sustained and failure occurs.

Other important parameters that affect the detonation velocity and performance of ANFO are charge diameter and confinement. The detonation velocity of ANFO will increase by about 300 m/s when the charge confinement is changed from a PVC tube to a Schedule 40 steel pipe. A summary of test data on ANFO velocity versus confinement and diameter is shown in Fig. 37.5.

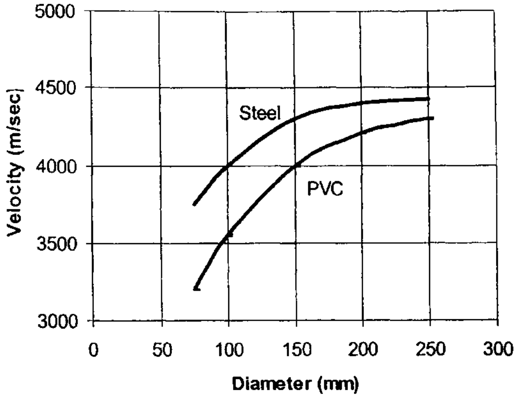


Fig. 37.5. Detonation velocity of ANFO versus diameter and confinement.

The basic chemical reaction of ANFO can be described with the following equation:

$$3NH_4NO_3 + CH_2 \rightarrow CO_2 + 7H_2O + 3N_2 + 880\ \text{cal/g}$$

Using CH_2 to represent FO is generally accepted, but it really is an oversimplification, since it is a mixture of hydrocarbons. The heat energy release of 880 cal/g is the theoretical maximum value based upon the heats of formation of the reactants and products. Of course, all of the products of detonation are gases at the detonation temperature of about 2700°K.

The theoretical work energy that is released from an explosive reaction can be calculated using a variety of equations of state and computer programs.[40] Explosive energy can also be measured by a variety of techniques including underwater detonation of limited size charges with concurrent measurements of the shock and bubble energies.[41] Each explosive manufacturer has an energy measurement and equation of state that is used to calculate and report their product properties. This often leads to confusion and controversy when explosive consumers try to compare product lines when given only technical information sheets. Since theoretical calculations must of necessity be based on a number of assumptions, the only valid comparisons are done in the field with product testing and detailed evaluation of results.

Bulk Emulsions

During the past decade the commercial use of bulk emulsion explosives continued to increase. Bulk emulsion products began to significantly replace packaged products in underground mining and in quarry operations. Also, bulk emulsion and ANFO blends became very popular in large volume open-pit mining operations. Emulsions are made by combining an oxidizer solution and a fuel solution using a high-shear mixing process. The oxidizer solution is normally 90–95 percent by weight of the emulsion. It contains AN, water, and sometimes a second oxidizer salt, that is, sodium or calcium nitrate. The solution must be kept quite hot, since the water is minimized for increased energy, and the crystallization temperature is typically 50–70°C. The fuel solution contains liquid organic fuels, such as FO and/or mineral oils, and one or more emulsifiers. An emulsifier is a surface active chemical that has both polar and nonpolar ends of the molecule. In the high-shear manufacturing process, the oxidizer solution is broken up into small droplets, each of which is coated with a layer of fuel solution. The droplets in this metastable water-in-oil emulsion are basically held together with the emulsifier molecules, which migrate to the surface of the dispersed droplets. In today's explosives industry, much of the research work is directed towards developing better and more efficient emulsifier molecules that will improve the storage life and handling characteristics of the bulk and packaged emulsions. The emulsifiers currently used in commercial explosives range from relatively simple fatty acid esters with molecular weights of 300–400 to the more complex polymeric emulsifiers having molecular weights in excess of 2000.

Figure 37.6 shows a photomicrograph of an emulsion explosive at 400 power with the typical distribution of the fuel-coated oxidizer solution droplets (normally 1–5 μm in diameter). Figure 37.7 shows a bulk emulsion exiting a loading hose and displaying the soft ice cream-like texture typical of bulk emulsions. The viscosities of bulk emulsions can range from nearly as thin as 90 weight oil to as thick as mayonnaise, depending upon the application requirements. Emulsion viscosity increases with product cooling, but most emulsions continue to remain stable at temperatures below 0°C, which is considerably below the crystallization temperature of the oxidizer solution. The oxidizer solution droplets in the emulsion are therefore held in a supersaturated state. Over time, the surface layers created by the emulsifier molecules can be broken, and the oxidizer solution droplets are free to form crystals. At this point the emulsion begins to "break down" and lose some of the desirable properties. For this reason the

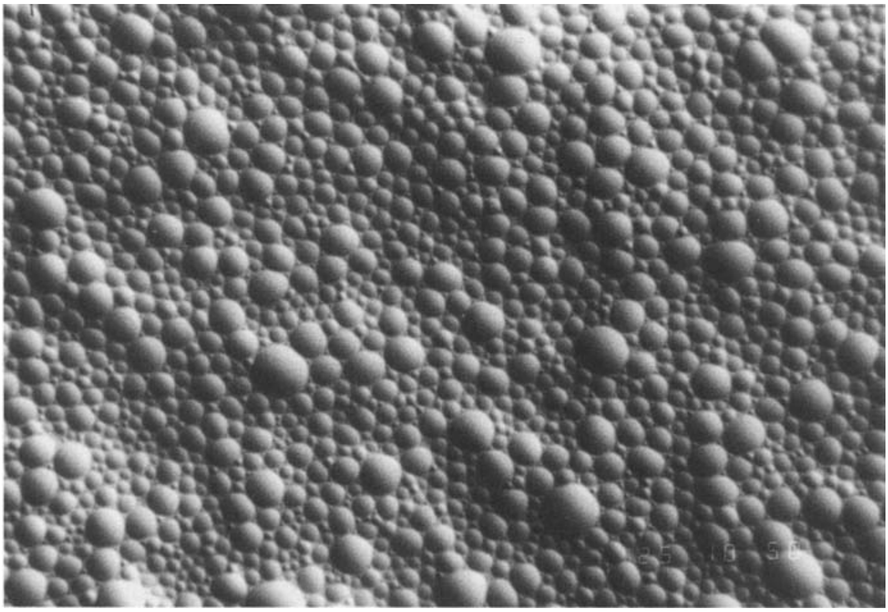


Fig. 37.6. Photomicrograph of a bulk emulsion.

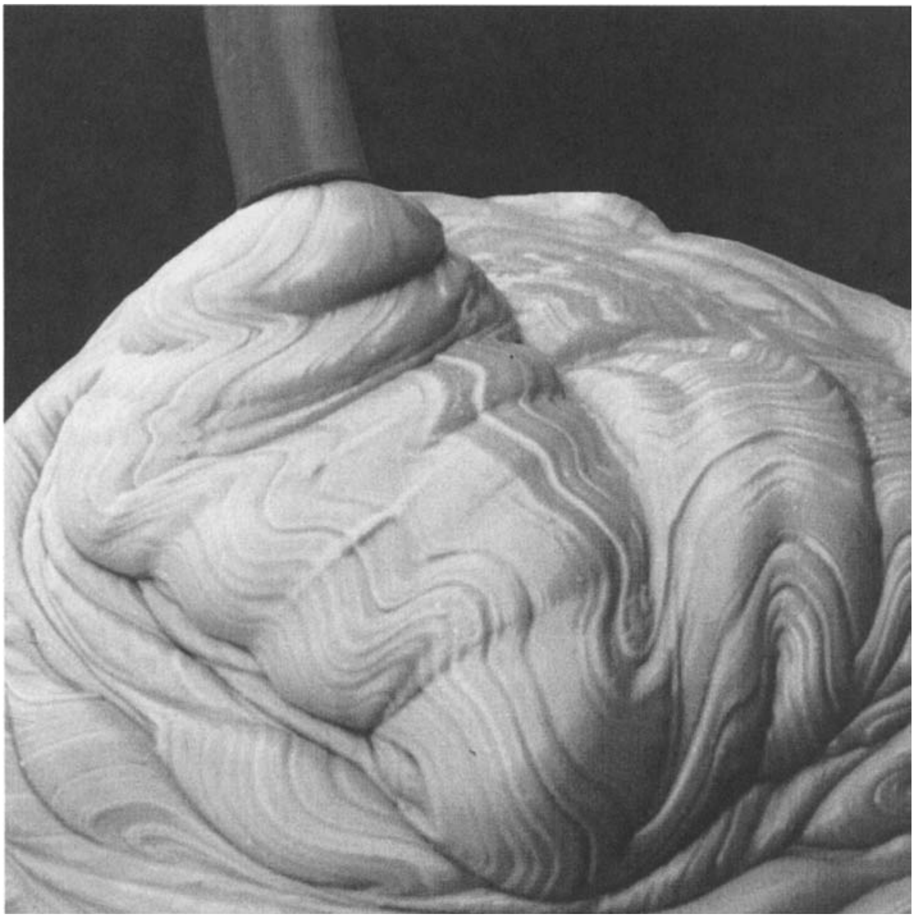


Fig. 37.7. Bulk emulsion exiting a loading hose.

emulsion composition must be optimized for a particular application in terms of its product stability and usable storage life.

The intimate mixing of oxidizer and fuel in emulsions give these explosives much higher detonation velocities when compared to ANFO. For example, in 150 mm diameter PVC ANFO has a velocity of about 4000 m/sec, and a sensitized emulsion would have a velocity closer to 6000 m/sec at a density of 1.20–1.25 g/cc. Also, the layer of oil surrounding each oxidizer solution droplet protects the emulsion from extraneous water intrusion and subsequent deterioration of the explosive. Many studies have shown that when mining operations use emulsion explosives rather than ANFO, which has basically no water resistance, the amount of nitrate salts in mine ground water is reduced considerably. This can be a very important factor in today's environmentally conscious mining and explosives industry.

Bulk emulsions are generally nondetonable per se and must be sensitized with some type of density control medium to become usable blasting agents. That is, voids, creating "hot spots," are required to sustain the detonation front. The two most commonly used density control methods are hollow solid microspheres or gas bubbles created by an in-situ chemical reaction. Both glass and plastic hollow microspheres are commercially available and used by explosives manufacturers. The in-situ chemical gassing techniques require considerably more expertise and generally utilize proprietary technology.

In the past decade the use of sensitized bulk emulsions has increased considerably in underground mining. Much of this has been due to the development of innovative loading equipment and techniques. One example of this is shown in Fig. 37.8 which shows a small-volume pressure vessel that can be used for development and tunnel rounds utilizing horizontally drilled boreholes. The bulk emulsion blasting agent is pressurized inside the vessel and literally squeezed through the loading hose into the boreholes. A continuous column of explosives is assured by inserting the loading hose to the back of the hole and extracting it as the product is loaded. Much more complex underground loading units are available for loading bulk emulsion into boreholes drilled at any angle to the horizontal from straight up to straight down. The emulsion explosives used in these specialized loading units were specifically designed for underground use over twenty years ago, and have been successfully used in underground mining operations around the world. The fuel and oxidizer contents are carefully balanced, and this, combined with the excellent water resistance and detonation efficiency, results in the near elimination of after-blast toxic fumes, such as CO, NO, and NO_2. The fume characteristics of this product have been shown to be considerably superior to either dynamite or ANFO. For example, a series of tests in an underground chamber in Sweden compared the after-blast fumes of this emulsion to ANFO. The CO was reduced from 11 to less than 6 L/kg of explosive, and the NO plus NO_2 was reduced from about 7 to less than 1 L/kg of explosive.[42]

Many open-pit quarries also use bulk emulsions for their blasting operations. As the size of the quarry increases, the size of the explosive loading trucks also must increase. Truck payloads can range from 5000 to 30,000 lb of product. Figure 37.9 shows an emulsion pumper truck in a quarry in south Florida. These particular trucks, with a payload of about 20,000 lb, are specially designed for a site-mixed system, in which each truck is an emulsion manufacturing unit. Combining nonexplosive raw materials directly on the truck maximizes safety and minimizes requirement for explosive storage. This particular bulk emulsion is manufactured at a rate between 300 and 500 lb/min and sensitized to the desired density with a chemical gassing system as it is loaded into the boreholes. Figure 37.10 shows a Florida blast in progress. Note the ejection of cardboard tubes from some holes. These tubes must be used in most areas to keep the boreholes from collapsing in the layered, coral limestone formation.

Many of the large volume metal and coal mining operations around the world have both

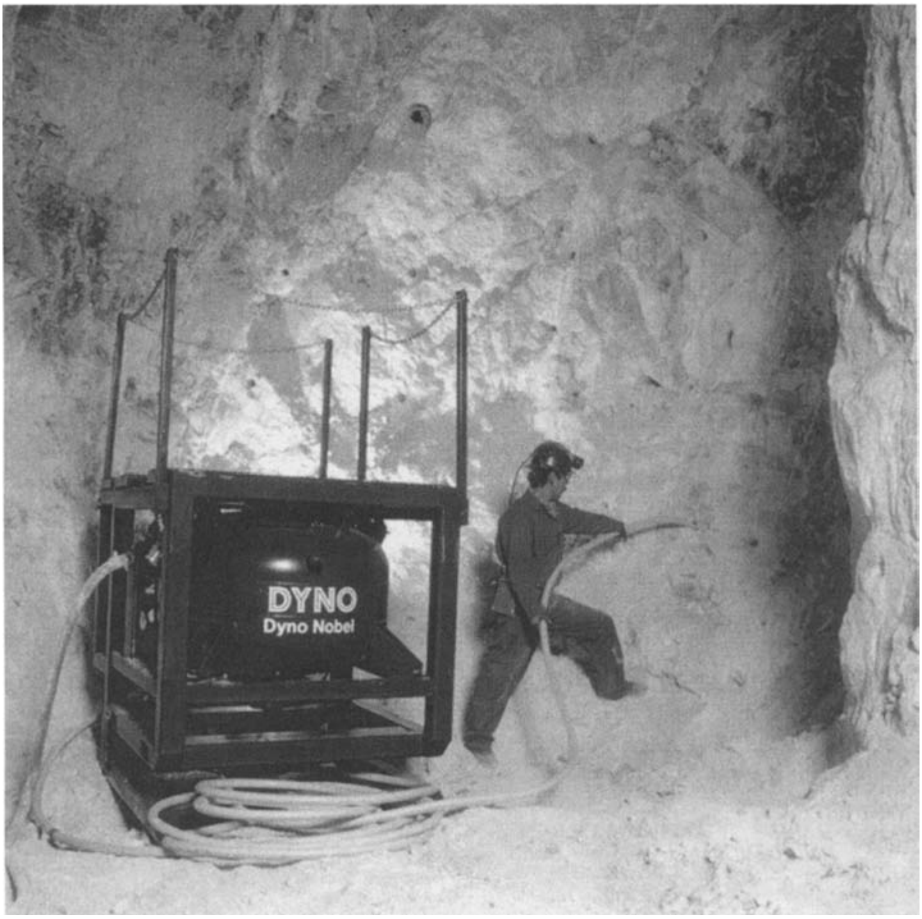


Fig. 37.8. Underground pressure vessel loader for bulk emulsion. (*Courtesy Dyno Nobel*)

bulk emulsion and AN prills stored either on site or nearby so that any combination of these two products can be used. Figure 37.11 shows a typical explosive staging area in a large open-pit coal mine in Wyoming. The explosive truck in the foreground has compartments on board for emulsion, AN prills, and FO, so any combination of products ranging from straight emulsion to straight ANFO can be loaded. The truck has a capacity of about 50,000 lb and can deliver product to the boreholes at up to a ton per minute. Each borehole can contain as much as 5 tons of explosive, and some of the blast patterns can contain as much as 10 million total pounds.

The emulsion/ANFO explosive blend selection to be used in any given mining application depends upon many factors. Typically, ANFO is the least expensive product, but it also has the lowest density and no water resistance. As emulsion is added to ANFO it begins to fit into the interstitial voids between the solid particles and coat the AN prills increasing the density, detonation velocity, and water resistance. The density increases nearly linearly with percent emulsion from about 0.85 g/cc with ANFO to about 1.32 g/cc with a 50/50 blend. This range of emulsion/ANFO blends is commonly referred to as Heavy ANFO. As the density increases, the amount of explosive that can be loaded into each borehole increases, and either drill patterns based on ANFO can be spread out or better blasting results can be obtained.

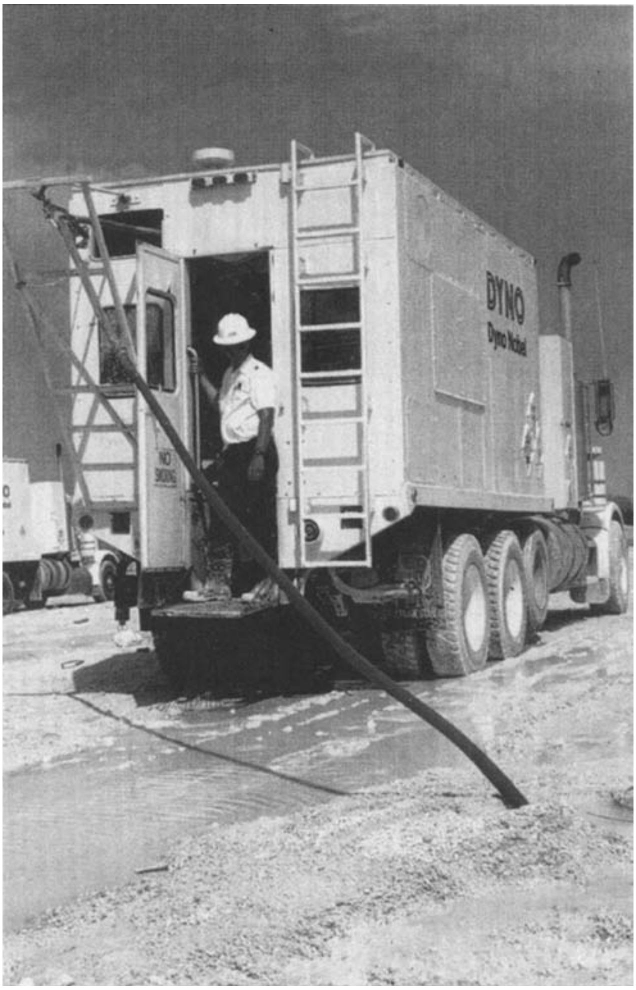


Fig. 37.9. Bulk emulsion loading truck in a Florida quarry.

It is commonly accepted in the explosive and mining industry that at least 40–50 percent emulsion is required to protect the Heavy ANFO blend from borehole water intrusion. Pumped explosive blends with 60–80 percent emulsion can even be used when severe water conditions are encountered. These products can be pumped through a loading hose, which can be lowered to the bottom of the borehole and displace the water during loading. Trucks similar to that shown in Fig. 37.9 can be used for these products. Most Heavy ANFO products are more simply mixed and loaded through an auger into the top of boreholes. For Heavy ANFO products the holes must be either dry or dewatered using pumps.

The basic chemical composition of a typical all-AN oxidizer emulsion explosive would be: AN plus about 15 percent water plus about 5 percent fuels. The fuels may contain fuel oil, mineral oils, and emulsifiers, the majority of which can generally be described as CH_2 hydrocarbon chains. Therefore, a very simplified chemical reaction for a basic emulsion is similar to that for ANFO shown above.

By adding 15 percent water to the ANFO reaction described earlier, the theoretical heat energy release is reduced from 880 to 680 cal/g. The difference is the energy price

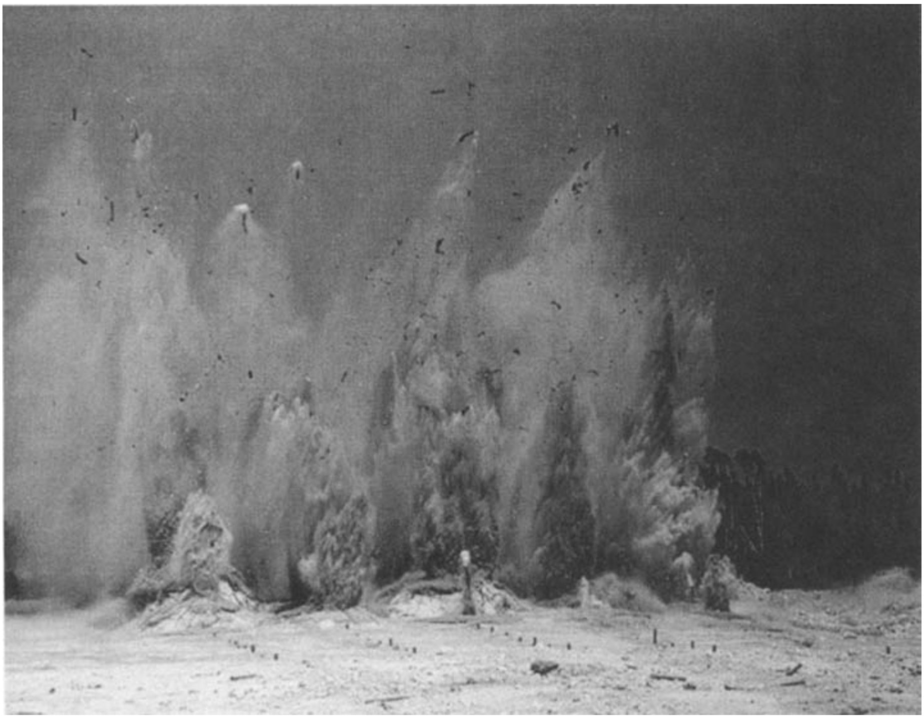


Fig. 37.10. Florida quarry blast in progress.

paid for using water and converting it to steam in the detonation reaction. The advantages and disadvantages of using ANFO or emulsions begin to become clear. ANFO is easily mixed and is probably the least expensive form of explosive energy, but it has no water resistance and has a relatively low loading density. Emulsions are considerably more complicated to formulate and manufacture, but they have excellent water resistance and more flexibility in terms of density, velocity, and energy to match rock types and blasting applications.

INITIATION SYSTEMS

The first reliable initiation system for commercial explosives could probably be traced back to Alfred Nobel's invention of the blasting cap in 1864. This, combined with his subsequent invention of dynamite about three years later, basically started the modern era of blasting. In the century that followed, the initiation systems became more and more sophisticated and safe. Short and long-period delay electric blasting caps were perfected and detonating cord was developed. Detonating cord is a flexible cord made of cloth or plastic with a core load of high explosives, usually PETN. Strings or circuits of detonating cord could be used to initiate several explosive charges with only one blasting cap.

Prior to about 1950 most of the commercial explosives in the market were reliably detonable with just a blasting cap or detonating cord as the initiator. Then came the advent of ANFO and later water-gels, invented by Melvin A. Cook in 1957. These explosive products were considerably less sensitive than dynamites and required larger "booster" charges for reliable detonation. At first, a high density and high velocity dynamite was used as the booster charge, and later TNT-based cast boosters came into the market. These cast boosters continue to be used today in nearly all large mining operations. Cast TNT by itself is not reliably detonable with a blasting cap or detonating cord, and so 40–60 percent

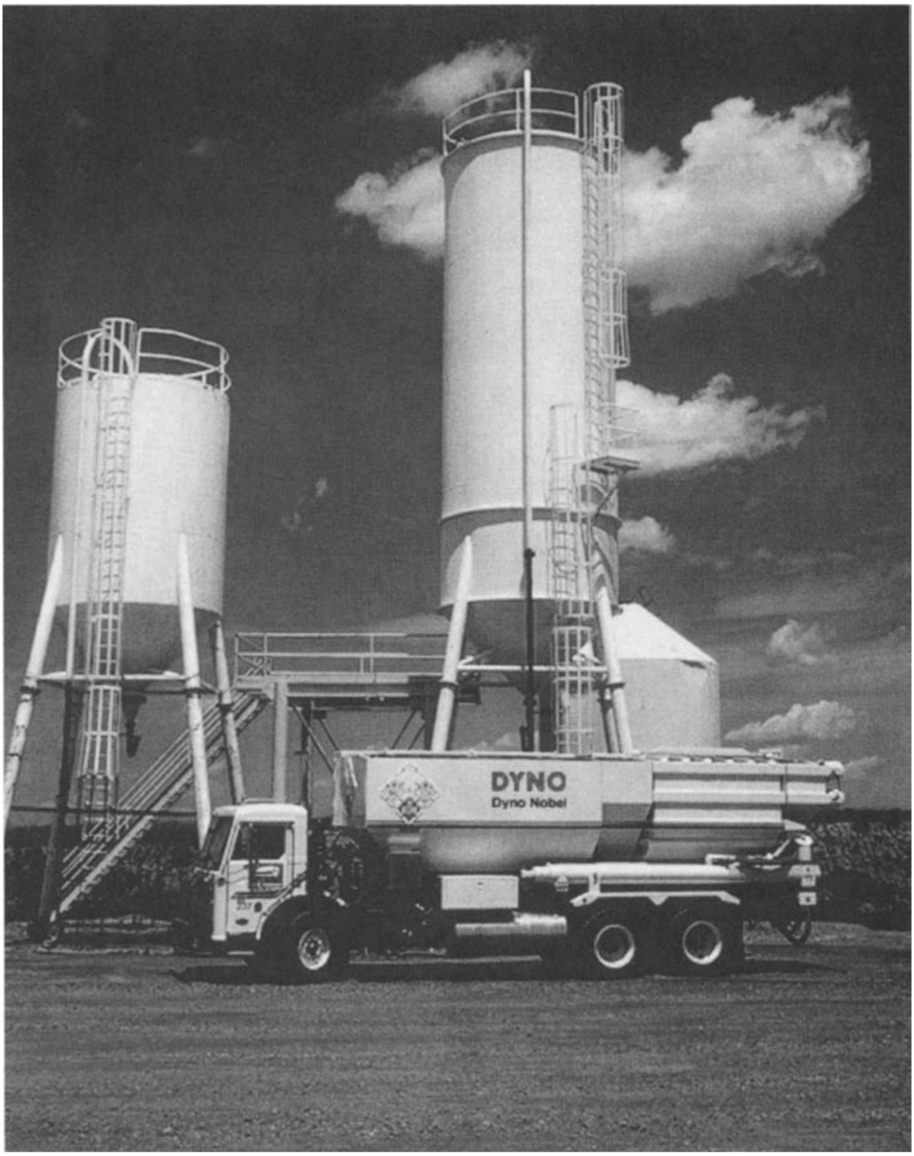


Fig. 37.11. Typical bulk explosives staging area in a large open-pit mine.

PETN is normally added to the TNT melt and subsequent cast. The combination of TNT and PETN is called Pentolite. TNT has a melting point of about 80°C, which makes it an excellent base explosive for casting into forms. The military has used this concept for decades for filling bomb casings. Once the TNT has melted, other material can be added to give the final cast explosive composition the desired properties. In the case of Pentolite cast boosters the added material is finely divided PETN. Commercial cast boosters are available in a variety of sizes from about 10–800 g as shown in Fig. 37.12.

This very brief history relates the development in the commercial explosives industry of an explosive loading and initiation system that emphasized safety. An entire pattern of boreholes can now be loaded with an insensitive blasting agent primed with cast boosters

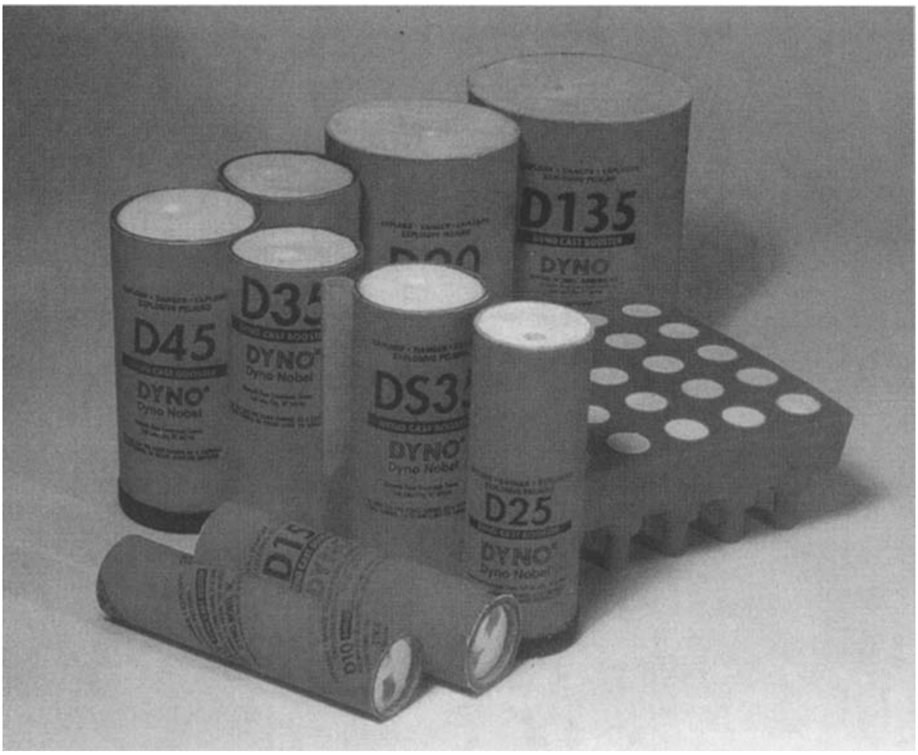


Fig. 37.12. Some commercial cast boosters.

on detonating cord down lines. The down lines can then later be tied to surface detonating cord line, and the entire blast initiated with just one blasting cap after the blast pattern has been completely cleared of personnel. Delay elements were also developed that could be placed between holes to control the borehole firing sequence for maximum blast movement and rock fragmentation.

Non-Electric Initiation

In 1967 Per-Anders Persson of Nitro Nobel AB in Sweden (now part of Dyno Nobel Europe) invented a non-electric initiation system, designated Nonel® that has revolutionized this aspect of the explosives Industry. The Nonel system consists of an extruded hollow plastic tube that contains an internal coating of a mixture of powdered molecular explosive and aluminum. The plastic tube is inserted into and attached to a specially designed detonator or blasting cap. The Nonel tubing can be initiated by a number of starter devices, one of which uses a shotgun shell primer. The explosive/aluminum mixture explodes down the inside of the tube at about 2000 m/sec and initiates the blasting cap. The tubing is about 3 mm outside diameter and 1 mm inside diameter, and the explosive core load is only about 18 mg/m, not even enough to rupture the tubing. The Nonel product is not susceptible to the hazard associated with electric blasting caps wherein premature initiation by extraneous electric sources can occur. Figure 37.13 is a photograph of both an electric blasting cap with the two electrical wires and a typical Nonel unit with the plastic tubing.

The 1990s saw a large increase in the use of Nonel products around the world to replace both electric blasting caps and detonating cord down lines. It has long been known that detonating cord down lines disrupt and partially react with blasting agents causing some degree of energy loss. Also, the use of surface detonating cords to initiate

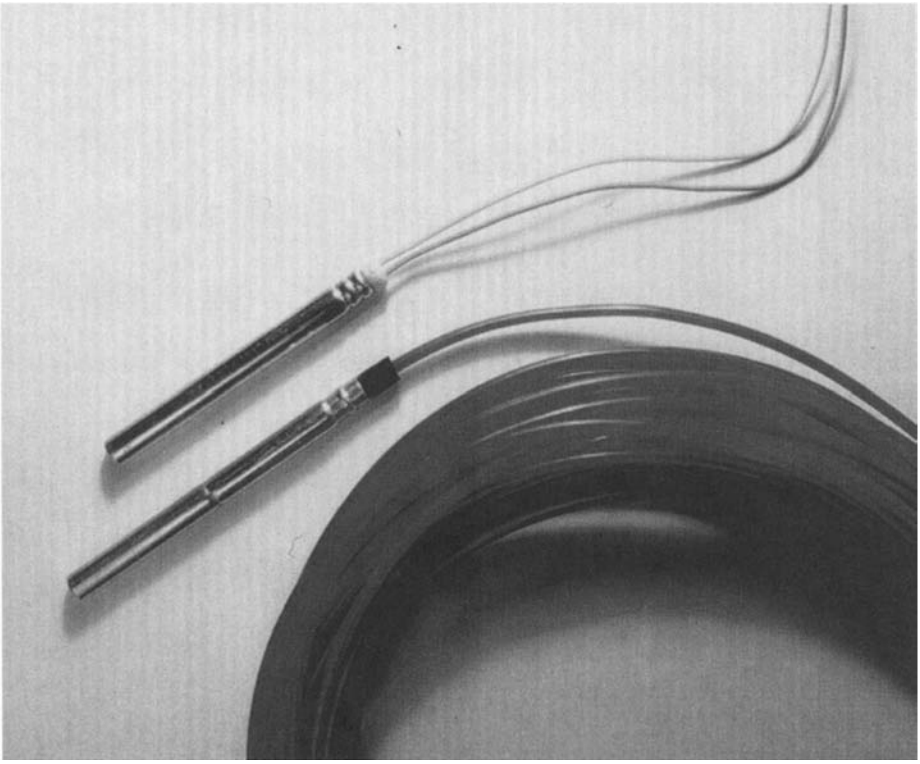


Fig. 37.13. An electric blasting cap showing electrical wires, typical Nonel unit with plastic tubing.

blasts can lead to noise complaints. As a result, long-lead Nonels were developed to replace the detonating cord in boreholes. As delay elements were perfected for the Nonel blasting caps, their application and use grew even further and especially in underground mining where a large percentage of blasting caps is used.

Detonator manufacturers are now perfecting initiation systems using electronic blasting caps containing programmable delay circuitry and remote initiation features. The manufacturing cost of these units is currently relatively high, but as the science progresses these electronic detonators will likely be a wave of the future.

PART II. ROCKET PROPELLANTS

A rocket is a device that uses the expulsion of internally generated gases as a source of motive power. The gases used for propelling the rocket are generated by chemical reaction of a fuel and an oxidizer. The force that acts against a rocket as gases are expelled is called thrust. Because rockets carry their own fuel and oxidizer and do not rely on air, the thrust from reaction (combustion) of the propellant chemicals will act in a vacuum. Thus, rockets, unlike internal combustion engines, are capable of providing power in space as well as in the earth's atmosphere.

The use of rockets has been traced to 13th century China, but it was not until the development of the liquid-fueled V-2 in Germany during World War II that a practical long-range missile using rocket propulsion was achieved. Work during the early 20th century by such pioneers as Konstantin Tsiolkovsky in Russia, Robert Goddard in the United States, and Hermann Oberth in Germany provided the basis for the successful German effort and the spectacular space exploration studies that followed. The launching into orbit of the *Sputnik* satellite from the Soviet Union in 1957 was the initial

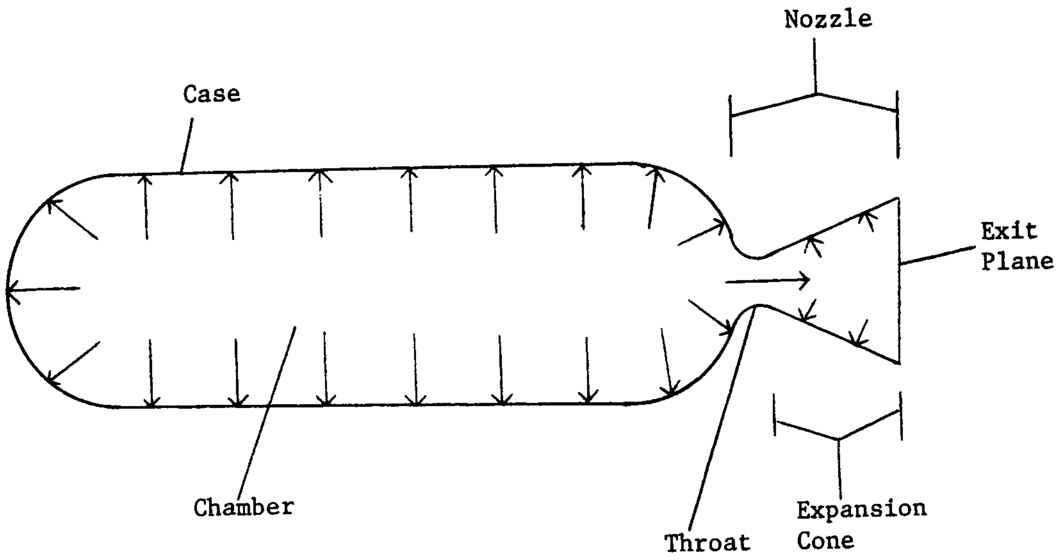


Fig. 37.14. Schematic drawing of a simple rocket.

event in a huge expansion of rocket development efforts in recent years. These developments have resulted in rockets used for three principal applications:

- space exploration and satellite launching
- strategic missiles
- tactical missiles

Space exploration efforts have been very well publicized in recent years. These efforts have included such notable developments, in addition to Sputnik, as the launching of manned rockets (with the first astronauts Yuri Gagarin in the Soviet Union and Alan Shepard in the United Sates), the Apollo missions to the moon (with Neil Armstrong's momentous first step), the Russian, American, and International space stations, the U.S. space shuttle program, and the exploration of the solar system by such spacecraft as the Russian Venera and the U.S. Pioneer, Mariner, and Voyager. Perhaps less well publicized, but of great commercial and strategic importance, has been the launching of satellites for purposes of communication, mapping, and surveillance. Launch vehicles for the U.S. space program have included the Atlas Agena, Delta, Juno, Saturn, Scout, Thor, and Titan rockets.

The space exploration efforts were paralleled in the United States and the Soviet Union by the development of rocket-powered missiles for strategic military use. Such U.S. systems as the Air Force Minuteman, Peacekeeper, and Small ICBM and the Navy submarine-launched Polaris and Trident are widely deployed.

The use of missiles for tactical military applications has also been an area of major development since World War II. Among the first such applications were the JATO (rocket assisted takeoff) units used to provide power to boost launching of airplanes. Tactical missiles have become an important component of weaponry and include U.S. rockets such as the Navy Sidewinder and Standard Missile, the Army Hawk and Hellfire, and the Air Force Sparrow, AMRAAM, and Phoenix.

PRINCIPLES OF ROCKET PROPULSION

The flight of rockets is based on the thrust achieved by expelling gases from the aft end of the missile; this provides a forward impetus. A schematic diagram of a simple rocket is shown in Fig. 37.14. Combustion of the propellant causes pressurization of the chamber by hot gases; the pressure from the gases is counterbalanced by the strength of the chamber. At a narrow opening, the throat, gases are allowed to escape, providing thrust. If there were no expansion cones, and gases were expelled at the throat, the force, F, acting to propel the rocket would be:

$$F = A_t P_c$$

where A_t is the area of the throat and P_c is the chamber pressure. When an expansion cone is present, a new term called the thrust coefficient, C_f, enters the equation:

$$F = A_t P_c C_f$$

The value of C_f depends on the ratio of the chamber pressure to the pressure at the exit plane, and on the ratio of the throat area to the exit plane area. The optimum performance of a rocket results when the pressure at the exit plane, P_e, is equal to the pressure of the surrounding atmosphere (which is one atmosphere for firings at sea level and zero atmospheres in space).

Because thrust is dependent on motor design and the rate of propellant combustion, it is not a convenient measure of propellant effectiveness. A parameter that is used to compare effectiveness is the specific impulse, I_{sp}, which is equivalent to the force divided by the mass flow rate of the propellant:

$$I_{sp} = \frac{Ft}{W} = \int \frac{\mathrm{F}}{\dot{\mathrm{w}}}$$

where $\dot{w}$ is the weight flow rate of the propellant, W is the total weight of the propellant, and t is the time. Because the impulse is dependent on a variety of parameters, it is customary to use the standard specific impulse, I^{o}_{sps}, which is the value of the specific impulse for an ideal rocket motor fired at 1000 psi, exhausting to 14.7 psi, with no heat loss, and with a nozzle of 15° half-angle. Frequently, measured or delivered impulse, I_{spd} values from motor firings will be converted to I^{o}_{sps} for comparison with previous firings and with expectations. The ratio of delivered to predicted impulse is termed the efficiency. In engineering units, specific impulse is given in (pounds-force * seconds)/pound-mass. A thorough yet succinct discussion of the physics and thermodynamics of rocket propulsion is found in Sutton.[43]

The prediction of rocket propellant specific impulse, as well as impulse under other conditions, may be reliably accomplished by calculation using as input the chemical composition, the heat of formation, and the density of the component propellant chemicals. Not only impulse but also the composition of exhaust species (and of species in the combustion chamber and the throat) may be calculated if the thermodynamic properties of the chemical species involved are known or can be estimated. The present standard computer code for such calculations is that described by Gordon and McBride.[44] Theoretical performance predictions using such programs are widely used to guide propellant formulation efforts and to predict rocket propellant performance; however, verification of actual performance is necessary.

TYPES OF PROPELLANTS

The two principal types of rocket propellant in general use are solid propellants and liquid propellants. Solid propellants are chemical compositions that burn on exposed surfaces to produce gases for rocket power. Liquid propellants rely on pumping or pressurized flow of stored liquids to the combustion chamber. The choice between solid and liquid propellants for a specific application depends on a variety of considerations; to date, many of the strategic missiles and most of the tactical missiles rely on solid propellants because of the lower cost of the rocket and the greater storability of the propellant. On the other hand, large space vehicles and rockets fired for maneuvering in space use liquid propellants, in part because of the ready controllability of liquid systems. Less widely used are hybrid rockets, which use solid fuel and liquid or gas-phase oxidizer. If a single chemical compound (e.g., nitromethane) containing both oxidizing and reducing functions in the same molecule is employed to power a rocket, it is called a monopropellant. If two chemicals combine to provide the propulsion, they form a bipropellant system.

SOLID PROPELLANTS

A solid propellant rocket motor is quite simple in concept, although in practice a complete motor is more complex. As shown in Fig. 37.15, the rocket propellant is contained within a case, which may be metal or a reinforced high-performance composite. Frequently, the case is internally shielded by a bonded layer of insulation. The insulation is coated with a liner that bonds the propellant to the insulation. The integrity of the propellant-to-liner bond is of utmost importance; failure at this interface during a motor firing can result in a sudden increase in the area of propellant surface exposed to combustion, with potentially catastrophic results.

The bore or perforation of the propellant grain is a major factor in determining the ballistic performance of a rocket. In the simplest instance, the grain has no perforation, and the burning is restricted to the end of the grain; the resulting end-burning rockets have a relatively long burning duration with low thrust. More commonly, a perforation extends through the grain (center-perforated) and may have a cylindrical, star, cross-shaped, wagon-wheel, or other more complex profile. The configuration of the grain is used to control the burning behavior of the propellant; the more surface area there is exposed, the more rapidly propellant will be consumed, affecting performance over time. The length of time a rocket motor will burn is governed not only by the perforation geometry, but also by the web thickness of the propellant (distance from perforation to liner), the burning rate of the particular rocket propellant, and the throat diameter of the nozzle. The pressure–time curve resulting from motor burning may be neutral (a single pressure is achieved and maintained throughout the burn), progressive, or regressive. Progressive burning leads to acceleration, whereas regressive burning gives lower pressure as the firing progresses. Tactical solid propellant motors frequently are manufactured with two types of propellant: a rapid-burning boost propellant to provide initial acceleration and a slower-burning sustain propellant to complete the desired flight profile. The trajectory of missiles as a function of propellant properties, grain configuration, and missile design may be reliably predicted or simulated by sophisticated computer calculations. A typical tactical solid propellant-based missile is shown in Fig. 37.16.

Single and Double-Base Propellants. Early solid rocket propellants were based on processing methods similar to that used in the rubber industry, with propellants extruded into the desired grain configuration. Propellants

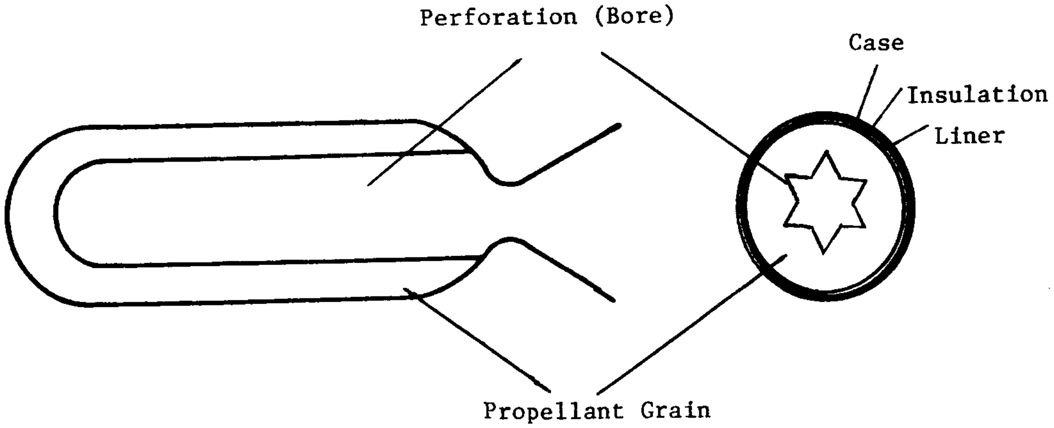


Fig. 37.15. A solid propellant rocket motor.

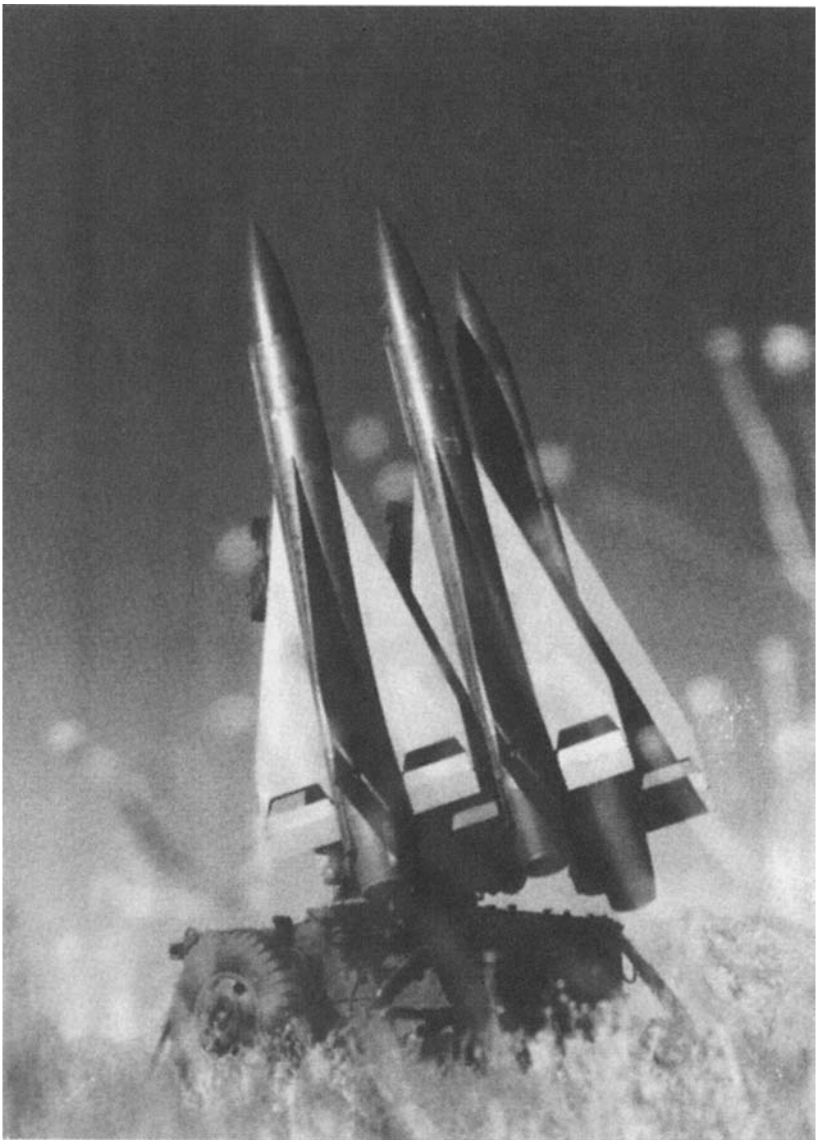


Fig. 37.16. Solid propellant-based HAWK tactical missile.

that have been successfully manufactured by this technique include nitrocellulose (single-base) and nitrocellulose-nitratoester (double-base) materials.* Double-base propellants contain both nitrocellulose and NG as the principal components; additionally, chemicals such as stabilizers, plasticizers, and burning rate modifiers may be added as appropriate. Other nitratoesters also may be in double-base systems. Extruded propellants usually are limited to small grain diameters (<<12 in.) by the size of the equipment required for extrusion, or by the difficulties of solvent removal if a solvent-based process is employed.

A processing advantage is achieved with the castable double-base systems; a rocket chamber is filled with particulate nitrocellulose

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*Triple-base propellants have also been produced, having double-base composition plus nitroguanidine, added as a combustion coolant or as a ballistic modifier.

TABLE 37.5 Properties of Oxidizers Used in Solid Propellants

Material	*Formula*	*Molecular Weight*	*Density, g/cm^3*	*Heat of Formation ΔH_f° at 298 K, cal/100 g*	*g Atom Oxygen/100 g*
AP	NH_4ClO_4	117.4	1.95	−60.21	3.404
AN	$N_2H_4O_3$	80.0	1.725	−109.12	3.748
NaN	$NaNO_3$	85.0	2.26	−131.23	3.530
KP	$KClO_4$	138.6	2.53	−74.49	2.887
RDX	$C_3H_6N_6O_6$	222.1	1.82	+6.61	2.701
HMX	$C_4H_8N_8O_8$	296.2	1.90	+6.05	2.701

(casting powder), which then is treated with NG-containing lacquers or a mixture of nitratoesters. The nitrocellulose is swollen by the nitratoester to give the final propellant, a tough material with relatively low elasticity.

Double-base propellants may be formulated to include fuels such as aluminum metal, oxidizers such as ammonium perchlorate (AP), or energetic materials such as the high energy-density nitramines RDX or HMX. The resulting compositions are termed *composite-modified double-base (CMDB) propellants.* A further modification, the addition of a polymer that is curable with a low molecular weight curing agent, allows formulation of propellants with much improved mechanical properties over the temperature range of usage. Such propellants are termed elastomer-modified composite double-base (EMCDB) propellants, and are currently among the most energetic and highest-performance propellant formulations.

Composite Propellants

In recent years, the great majority of solid rockets have utilized composite propellants. Most composite propellants are based on a solid oxidizer and a curable liquid polymeric binder. The binder also serves as fuel. Optionally, metallic fuels such as aluminum or boron may also be used.[45] The propellant components are mixed together, and then the binder is cured to give the tough, flexible, elastomeric (rubbery thermoset) solid propellant required for modern missile use. An excellent source of information on the formulation of solid propellants is a report by Oberth.[46]

Oxidizer. The major component, by weight and volume, of composite solid propellants is the oxidizer. By far, the most important oxidizer used is AP, a crystalline solid material ground to exacting particle size distributions. This chemical possesses the desirable properties of high density, good thermal stability, and oxygen availability, and relatively low reactivity and cost. Properties of AP and several other materials that are used as oxidizers are summarized in Table 37.5.

AN has been considered as an oxidizer for many applications; but its principal use to date is in gas generator propellants, where generation of gases is required to provide initial motor pressurization or to power turbines. Widespread use of AN has been hindered by a propensity of the compound to undergo numerous crystalline phase transitions, some involving a large (4%) volume change of the oxidizer, with concomitant oxidizer particle and binder degradation, upon warming or cooling. Phase-stabilized AN (PSAN), which avoids this difficulty, has been developed but for various reasons has not yet found widespread use. An area of potential application for AN is insensitive minimum smoke propellants, which better meet military criteria of handling and storage safety. Another alternative solid propellant oxygen source, sodium nitrate, has been demonstrated as a cooxidizer—scavenger propellants. These propellants contain sufficient alkali metal (sodium) in the formulation to react with the chlorine generated during combustion of the major oxidizer, AP. Sodium chloride, rather than hydrochloric acid, is produced in the exhaust stream as the final chloride-containing reaction product. The benefit of scavenging the chloride ion is lowered exhaust toxicity; however, a substantial loss of propellant impulse results.

The energetic nitramines, RDX and HMX, provide excellent impulse and nonsmoky exhaust, but their use gives propellants that may detonate when subjected to shock or impact. The possibility of unwanted violent burning or detonation of propellants during transport or storage has resulted in recent emphasis on the development of insensitive (reduced hazard) rocket propellants for tactical applications. Special attention are required in using these energetic materials.[47]

A number of other materials have received attention as potential oxidizers for propellant use, but to date have found little actual use. They include hydroxylammonium nitrate (HAN), hydroxylammonium perchlorate (HAP), hydrazinium nitrate (HN), hydrazinium perchlorate (HP), and hexanitroisowurtzitane (CL-20).

Metallic Fuels. In rocket applications where exhaust smoke is not a major concern, the use of metallic fuels adds considerable impulse to the composition. By far, the most common metal in use as a solid propellant fuel is finely divided aluminum, because of a combination of several desirable properties:

- low equivalent weight
- high heat of formation of its oxide
- low reactivity
- relatively high density
- low volatility
- low cost
- low exhaust product toxicity

An interesting comparison of some properties of metals with respect to their use as solid propellant fuels is available.[48]

Although theoretical considerations indicate that boron and beryllium might be preferred to aluminum, practical considerations dictate otherwise. Some of the theoretical advantage of boron is lost because of the volatility of the oxide, and because boron is oxidized to a mixture of oxidation states, not cleanly to the trivalent oxide. The use of beryllium is, in general, not possible today because of the high toxicity of the metal and its exhaust products. Aluminum is preferred to magnesium because of its lower equivalent weight and reactivity; aluminum metal powder normally has a thin oxide coating that diminishes its reactivity until combustion temperatures are reached.

Binder. The binder of a composite solid propellant serves the dual function of providing a matrix to hold the oxidizer and the metal fuel, and of serving as a fuel itself—although its total makeup in modern formulations may only be 8–10 wt percent. The binder of the propellant usually is considered to consist of the polymer, the curing agent, and the plasticizer—and can arguably include soluble stabilizers, as well.

In early years, natural rubber, asphalt, polysulfide-based organic polymers (Thiokol rubber), and acrylate polymers were employed as binders, but polymers based on polybutadiene, polypropylene, polyethylene, or polyesters have largely supplanted them. The two most important types of prepolymers used in present propellants are those terminated with cure-reactive carboxyl or with hydroxyl functional groups. These functional groups are used to react with curing agents (cross-linkers), as shown in Fig. 37.17, to provide the high molecular weight polymer networks that function as propellant binders. In general, the lower molecular weight prepolymer introduced into the propellant formulation is di- or polyfunctional so that the polymer resulting from reaction with a curing agent has a degree of cross-linking sufficient to lend a desirable degree of rigidity to the flexible propellant. The most common prepolymers in recent propellant use are the hydroxy-terminated polybutadienes; in the previous generation, *carboxy*-terminated polybutadienes were employed. For example, the binder used in the space shuttle solid booster propellant is based on PBAN, a carboxy-terminated terpolymer of butadiene, acrylic acid, and acrylonitrile. Hydroxy-terminated polyethers also are used, particularly in high-performance propellants. Hydroxy-terminated prepolymers, which are cured with linear or branched isocyanates to

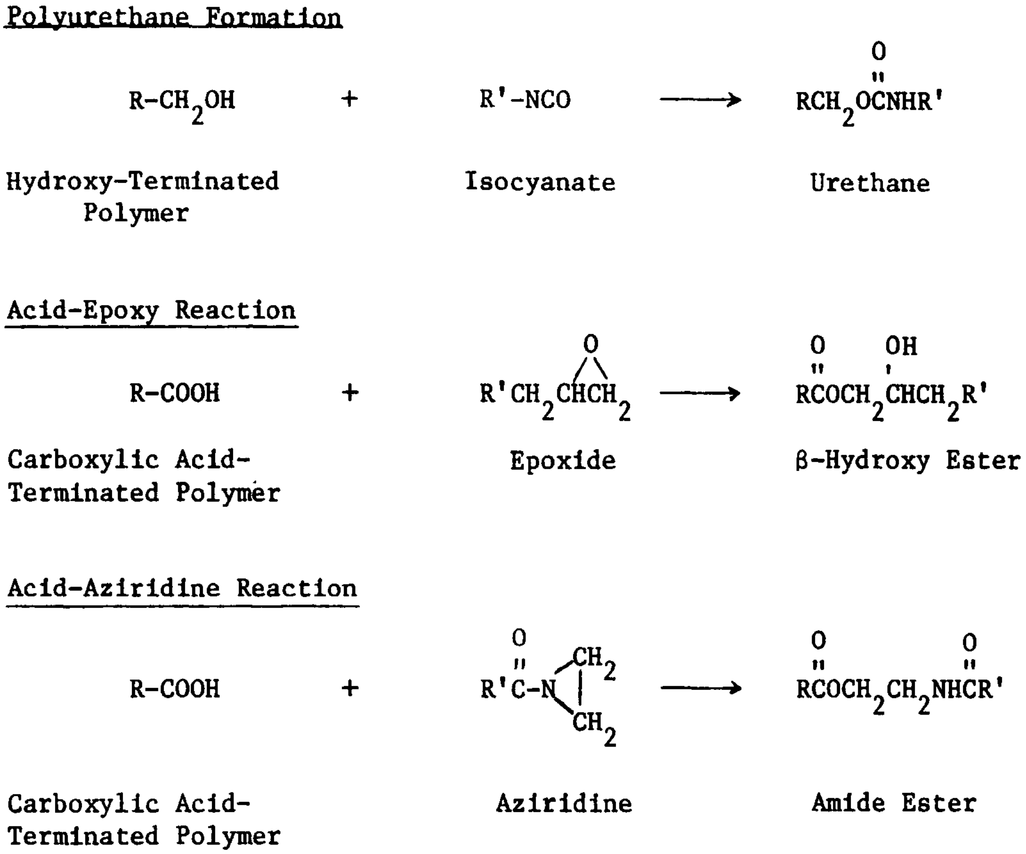

Fig. 37.17. Curing reactions used in present propellants. Each reactant is di- or polyfunctional, so that high molecular weight polymers are formed as the propellant binder.

give polyurethanes, offer advantages over carboxylic acid-terminated prepolymers:

- lower mix viscosity
- faster, lower temperature cure
- lower susceptibility to side reactions
- higher oxidizer and metal fuel solids loading

New prepolymers based on 3,3-bis (azidomethyl) oxetane (BAMO) and 3-nitratomethyl- 3-methyloxetane (NMMO) are used in advanced pintle-controllable solid rocket motor applications. These polymers yield favorable propellant energy with the combination of nitrato esters and ammonium nitrate, and allow solid propellant designs to compete with liquid propellants in arenas of energy management, approaching true start–stop–restart operation.

Plasticizer. In general, propellant formulations include plasticizers, which are nonreactive liquid diluents used to improve processing and mechanical properties (particularly the low temperature properties) of the propellant. Plasticizers such as high-boiling esters (e.g., dioctyl adipate) or low molecular weight isobutene oligomers are frequently used. In energetic formulations, nitratoester plasticizer blends, such as NG with BTTN, DEGDN, EGDN, and others, are used not only to improve processing and low temperature properties but also to improve impulse and to serve as oxidizers. In such formulations, high plasticizer/polymer weight ratios ($2–3^+$) are frequently used. The nitratoester plasticizers are not miscible with the butadiene-based polymers, hence use of telechelic hydroxy-prepolymers based on ethylene-oxide or propylene-oxide repeat units are required. Because of this, high solids loadings much above 75–80 wt percent are not practical. By comparison, propellants based on (poly)butadiene prepolymers and their appropriate plasticizers can achieve solids loadings of

Fig. 37.18. The solid booster rockets for the space shuttle are one of the most widely publicized applications of solid rocket propellants.

90 wt percent or higher, while simultaneously retaining high mechanical integrity for over 20 years' service life expectation, a wondrous achievement!

Other Propellant Chemicals. In addition to the binder, oxidizer, and fuel, a solid propellant may have a variety of other chemicals added (usually in small amounts) for specific purposes. These include:

- aging stabilizers or sequestrants
- processing aids
- bonding agents
- cross-linking agents
- burning rate modifiers
- signature-modifying agents
- cure catalysts
- cure catalyst scavengers
- combustion stability enhancers

The final propellant composition is a result of the interaction of a considerable number of chemicals, each of which is important and is selected either for one characteristic or for several reasons. The ultimate purpose of the formulation is to give a propellant whose properties are reproducible from batch to batch and from motor to motor, and are adequate for the intended use as shown, for example, in Fig. 37.18.

Classification of Propellents Based on Exhaust Properties. Based on the exhaust properties, solid propellants can be classified as smoky, reduced smoke, minimum smoke, or minimum signature propellants. The description of these categories are listed as follows:

Smoky. Propellants containing metals (such as aluminum) give exhaust with particulate matter (such as aluminum oxide) which is visible in the exhaust stream as smoke. Solid exhaust products such as aluminum oxide are called primary smoke. Smoky propellants formulated to reduce hydrogen chloride (HCl) emissions to less than one percent of the exhaust gas mixture are termed clean propellants.

Reduced Smoke. Propellants without metals or primary smoke, but containing oxidizers such as AP which gives HCl gas as a principal combustion product, are called reduced smoke propellants. If HCl is exhausted in atmospheres of high or moderate humidity, water droplets will coalesce about the HCl molecules, resulting in a visible exhaust trail of what is called secondary smoke. In atmospheres of low humidity, the exhaust plume of reduced smoke propellants is not visible.

Minimum Smoke. Propellants with no metals, and having exhaust free of nucleating species such as HCl, are termed minimum smoke propellants.

Minimum Signature. Propellants whose exhaust characteristics are tailored to give not only minimum smoke properties, but also to have low visible, ultraviolet, or infrared emissions are termed minimum signature propellants. Minimum signature propellants are of interest from the standpoints of launch site and missile detectability and from considerations of through-plume guidance.

Propellant Use Criteria. To function properly in its intended use, a propellant must satisfy a large number of criteria, as discussed in the following paragraphs.

Performance. The composition must have adequate specific impulse and volumetric impulse to perform its mission. Volumetric impulse is the product of impulse *and* density (or density raised to a fractional power).

Mechanical Properties. The important propellant properties include the tensile strength, strain capability (elongation), modulus of elasticity, and strain endurance. The propellant is formulated so that it will be sufficiently flexible to withstand the stresses of acceleration and temperature changes without cracking, yet be sufficiently rigid so as not to slump or deform upon standing or undergoing temperature changes. Bonding agents, which improve the interaction between polymer and filler (oxidizer), are frequently employed to improve mechanical properties.

Bond Properties. The strength of the propellant-to-liner-to-insulation bond must be sufficient to maintain its integrity under the stresses mentioned above.

Ballistic Properties. Important parameters in this regard are the burning rate, the pressure dependence of the burning rate, and the temperature dependence of the burning rate. The burning rate is adjusted using the oxidizer particle size and combustion-modifying additives as variables. With AP oxidizer, finer oxidizer particles give faster burning rates. Finely divided iron oxide is a catalyst frequently employed to accelerate the burning rate of AP propellants. In general, low sensitivity of the burning rate to changes in pressure or temperature is mandatory. Burning rates and ballistic properties are measured in progressively larger motor firings as development of a propellant proceeds.

Combustion Stability. Although burning without acoustic oscillations is partly a motor design concern, the propellant may be modified by the addition of refractory particles to dampen such vibrations. If uncorrected, pressure oscillations from combustion instability may be large enough to destroy a motor during firing.

Aging and Service Life. Propellants must be storable for at least as long as the intended service life of the missile system without undergoing degradation or change of ballistic or mechanical properties. Usually the service life is estimated by extrapolation from properties measured for sample aged at elevated temperatures. This accelerated aging is presumed to speed processes that would take place at lower (storage) temperatures. Stabilizers selected to enhance the aging capability are usual components of propellant compositions; the stabilizer choice depends on the polymer, plasticizer, and oxidizer types.

Processibility and Castability. In order to be introduced into a rocket motor, a castable propellant composition must be blended until all components are evenly dispersed. The resulting composition must be sufficiently fluid that it may be cast into the motor without creating voids or bubbles in the propellant and yet be sufficiently viscous that dense particles (oxidizer, aluminum) do not settle, or less dense materials (polymer) rise to the surface. Certain chemicals can significantly improve the processibility of propellants when added in small amounts.

Potlife and Cure. In addition to achieving a castable viscosity, it is necessary that the liquid (uncured) propellant remain fluid for a sufficient amount of time to be transported, cast, and cleaned up, with allowance for possible delays, before it solidifies appreciably. Following cast, the composition must be cured to a solid, preferably at temperatures close to the intended storage temperature. The balancing of potlife and cure rate frequently requires careful adjustment of cure catalyst levels, catalyst scavengers, mix temperature, and cure temperature.

Hazard Properties. It must be verified that the propellant is sufficiently insensitive to shock, electrostatic discharge, friction, thermal decomposition, or self-heating (in larger quantities) that it does not represent an unwarranted hazard in its intended use. Rocket propellants are energetic compositions and must be formulated so that chance stimulus will not initiate violent reaction.

Ignitability. Conditions for ignition in the desired application must be defined, and the propellant formulated so that it may be reliably ignited under these conditions.

All of the above factors must be carefully studied and optimized before a solid propellant can be considered adequate for its intended use.

Composite Propellant Manufacture. In a typical batch processing sequence for a modern polyurethane-cure composite propellant, a submix is prepared first. The submix contains the liquid prepolymer, plasticizers, liquid or powder-form stabilizers, and usually a (liquid) bonding agent; it is slurried with aluminum powder to give a premix. The premix is added to a moderate-shear slurry mixer, and AP oxidizer is added in several portions with intervening mixing which may include heating rate profiles and interim vacuum degas steps. Following addition of the oxidizer, the composition is mixed under high vacuum for a defined period. Vacuum is released, and the curing agent and cure catalyst(s) are added. After a final vacuum mix, the propellant is ready for casting. Frequently, the propellant is cast into an evacuated motor; the use of vacuum increases the casting rate and lessens the possibility of air entrapment and possible void formation in the cured grain. The cast motor then is placed in a cure oven (typically held at a temperature in the range of 110–160°F) until the propellant slurry has cured to the desired hardness. At many points in the process, samples may be taken and analyzed to ensure motor quality and integrity.

Although most solid propellants are manufactured in a vertical mixer batch process, a continuous mixing process has been used successfully in the production of the first stage A-3 Polaris propellant and in the NASA 260 inch demonstration motor program. The use of a continuous mixing process, in which propellant chemicals are metered into a helical kneader, offers considerable benefit in terms of safety and cost for large-volume propellant production.

Liquid Propellants

Energetic materials which support rocket propulsion via chemical and thermodynamic changes in *engines*, as opposed to rocket *motors*, distinguish the liquid propellant mission versus applications of solid propellants. Liquid propellants encompass liquid-phase materials in the unreacted state, and are controlled by pressure- or pump-fed liquid rocket engine (LRE) components. Most commonly, liquid propellant rocket systems derive their propulsive energy from the combustion of a liquid fuel and a liquid oxidizer in a combustion chamber. Additionally, new liquid fuel or oxidizer blends, fuel and oxidizer gels, plus solid/liquid propellant hybrid systems are of increasing interest when combined with advances in high strength, low weight, high temperature materials, fast actuation components, or reduced toxicity requirements.

Liquid propellants can be categorized by their type of storage (cryogenic propellants vs. storable propellants) or by their function in the chemical propulsion system (oxidizers, fuels, bipropellants, or monopropellants). In common, is their physical state—usually liquid phase—from tankage to the injector within the combustion chamber. In addition, selected liquid propellants, either oxidizer, fuel, or both may be gelled as a neat material or as a heterogeneous gel mixture. These gelled propellants may contain suspended solid material such as metal fuel powder, together with polymeric or other particulate gel additives, for rheology tailoring or performance enhancement, usually with military applications in mind.

Chemical *bipropellants* include conventional fuel + oxidizer LRE designs that use either *cryogenic* (less than $-150°C/-238°F$) propellant fluids or *storable* fuels and oxidizers, the latter not requiring extensive facility cooling or refrigeration launch support. Typical *bipropellants* include LO_2/LH_2 (cryogenic) or dinitrogen tetroxide/hydrazine (storable). *Monopropellants* may be classified separately as either fuels or oxidizers. Their decomposition via heterogeneous catalysts (such as iridium on alumina support in the case of hydrazine monopropellant, or silver-plated catalyst screens for hydrogen peroxide decomposition) either provides the propulsive thrust or functions as gas generators.

Gel propellants can be considered as a separate category of liquid propellant technology. They provide a unique application of solid propellant processing techniques and materials to the liquid propellant LRE designs, which maximize on some of the advantages of both liquid and solid propellant systems. Gel propellants are thixotropic (shear thinning) liquids by nature of various gelling additives, either polymeric in nature, or as high surface area powders, or both, and flow readily under pressure. A key requirement of gel bipropellants is *rheology matching* the viscosity vs. shear rate and flow dependencies of both the fuel and oxidizer gel, such that optimum combustion requirements are met over the entire temperature range of operation—no easy feat. Of benefit in gel systems are their improved safety in handling, for spills of either gelled fuels or oxidizers are easily contained. Advanced applications in gel propellants utilize energetic, insensitive, nanoparticulate gellants and fillers together with reduced toxicity fuel or oxidizer liquids. The application of these combined technologies expands the capability and performance of many conventional currently deployed solid- and liquid-propellant military and civil applications.

Of current intense study is the category of "green", or environmentally benign, propellants—most notably liquid hydrocarbon fuels with liquid/gaseous oxygen or highly concentrated hydrogen peroxide—in studies in this country and abroad. The economic, environmental, and toxicological advantages abound when considering long-term effects of manufacturing, transporting, storing, deploying, or disposing highly toxic storable propellants based on hydrazine and nitric acid chemistry. Increased use of high performance "green" propellant alternatives can only benefit the efficient utilization of space, while at the same time improving the quality of land, water, and air resources in the ever-shrinking global community.

Applications. To date, the liquid propellant systems used in chemical propulsion range from a small trajectory control thruster with only 0.2 lbf (0.89 N) thrust for orbital station-keeping to large booster rocket engines with over 1.0 million lbf (4.44 MN) thrust. Bipropellant propulsion systems are the most extensively used type today for

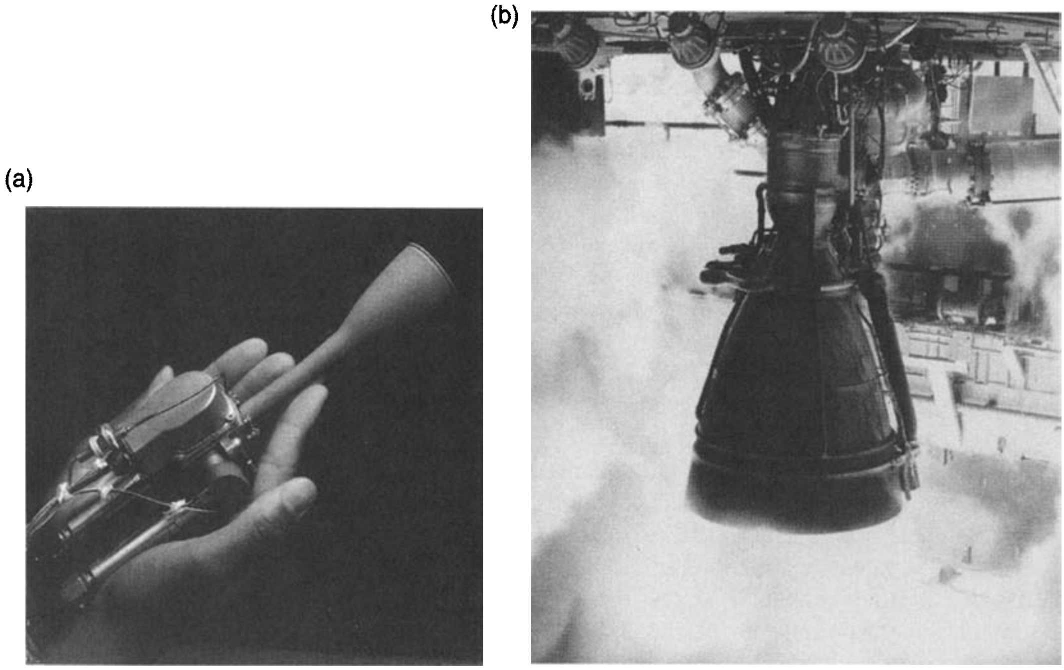

Fig. 37.19. (a) Small thruster used in Milstar and (b) high thrust-to-weight liquid oxygen/kerosene engines for commercial launch vehicles. (*Courtesy Aerojet Propulsion*)

applications in main combustion chambers and gas generators as shown in Fig. 37.19. The monopropellant propulsion system is widely used in low temperature gas generators and auxiliary rockets for trajectory or orbital adjustment.

A major difference between liquid propellants and solid propellants used in chemical propulsion systems is the ease of use or controllability. The solid propellants are cast as a solid propellant grain. The burning rate is dependent on the propellant formulation and the configuration design of the solid propellant grain in addition to the chamber pressure and grain temperature. The combustion process is continuous, and a quench and reignition combustion process may be difficult. For the liquid bipropellant system, the liquid fuel and the liquid oxidizer are stored in separate tanks and fed separately to the combustion chamber. The propellants are fed either by means of pumps or by pressurization with an inert gas. A controller generally is used to control the flow rate of the liquid propellants in the system. Ignition and reignition combustion generally is employed to fit the mission requirements and objectives.

Small-orifice injectors are used to atomize and mix the liquid propellants in appropriate proportions. The propellants enter the thrust chamber through the injection manifold and burn inside the thrust chamber. A typical liquid bipropellant rocket engine is shown in Fig. 37.20.

Physical Properties. General physical properties, including freezing point, normal boiling point, critical temperature, critical pressure, specific gravity, heat of formation, and heat of vaporization, of some conventional or promising liquid propellants are listed in Table 37.6. Of the temperature-dependent physical properties, such as heat capacity, thermal conductivity, viscosity, and specific gravity, only the specific gravity is included in Table 37.6. Generally, cryogenic propellants are listed at their normal boiling point, whereas the storable propellants are evaluated at 68°F (293 K). Detailed information on the physical properties of the liquid propellants can be found in Vander Wall et al.[49] To obtain a wide

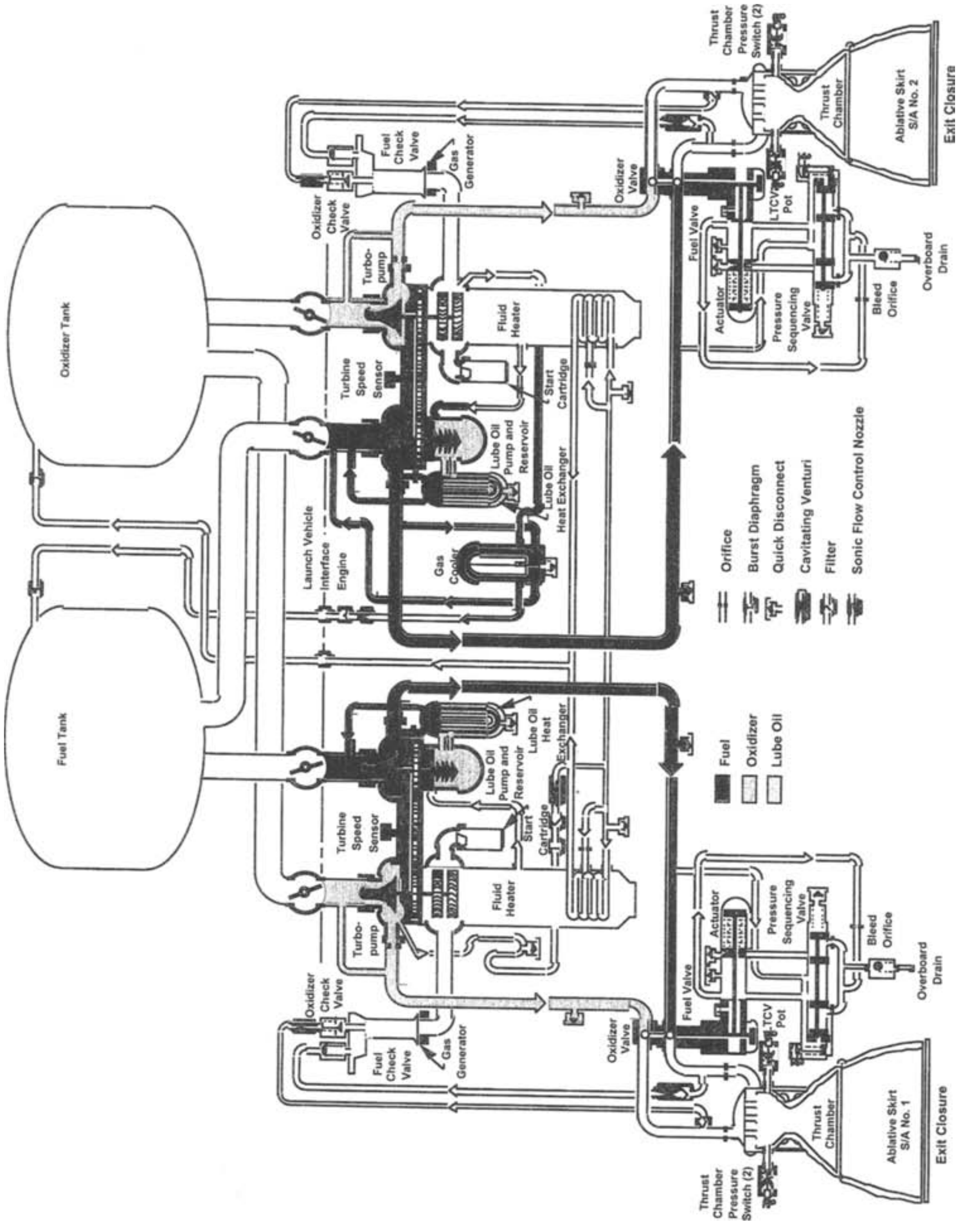

Fig. 37.20. Engine schematic for the Titan IV Stage I (LR87-AJ-II). *(Courtesy Aerojet Propulsion)*

TABLE 37.6 Properties of Common Liquid Propellants

Propellant	*Molecular Weight*	*Freezing Point (°F)*	*Boiling Point (°F)*	*Critical Temp. (°F)*	*Critical Press. (psia)*	*Specific Gravity*	*Heat of Formation (cal/mole at 298.16 K)*	*Heat of Vapor. (BTU/lb: NBP)*
LO_2	32.0	−362	−297	−182.0	730.6	1.14[a]	−2,896	91.62
F_2	38.0	−365	−307	−201	808.5	1.50[a]	−3,056	71.5
N_2O_4	92.011	11.75	70.4	316.8	1,441.3	1.45[b]	−4.7	178.2
ClF_5	130.445	−153.4	7.3	289.4	771	1.795[b]	−60,500	76.04
H_2O_2	34.016	31.2	302.4	855	3,146	1.38[b]	−44,750	76.04
H_2	2.016	−434.8	−423.3	−399.9	188	0.071[a]	−1,895	195.3
N_2H_4	32.045	34.75	237.6	716	2,131	1.008[b]	12,054	583
MMH	46.072	−62.3	189.8	594	1,195	0.879[b]	13,106	377
UDMH	60.099	−70.94	144.18	482	867	0.785[b]	12,339	250.6
A-50 (50% N_2H_4–50% UDMH)	41.802	22.0	158	633	1,731	0.905[b]	12,310	346.5
RP-1(H/C = 2.0)	172.0	−55	422	758	340	0.807[b]	−6,222	125
H_2O	18.016	32	212	705.4	3,206.2	1.0[b]	−68,317	970.3

[a] Evaluated at NBP; [b] Evaluated at 68°F (293.4 K).

operating range and a large payload capacity, the desired physical properties are:

- low freezing point
- low temperature variability
- low vapor pressure
- high specific gravity
- high heats of formation and vaporization

Because liquid propellants may also be used to cool the thrust chamber assembly, good heat transfer properties, such as high heat of vaporization, high thermal conductivity, high specific heat, and high boiling point, are desirable.

Liquid Oxidizers. Liquid oxidizers can be categorized as either storable or cryogenic. Many different types of liquid oxidizers have been used in chemical propulsion systems. In general, cryogenics such as liquid oxygen, fluorine, or fluorinated compounds give a high specific impulse. Several storable oxidizers such as nitrogen tetroxide (N_2O_4), inhibited red fuming nitric acid (IRFNA), or chlorine pentafluoride (ClF_5) have been used for their advantages in storage. A brief description of the commonly used oxidizers is given below.

Cryogenics. Liquid oxygen, the most important and extensively used liquid oxidizer, is used primarily with liquid hydrogen to give a very high specific impulse (usually near or over 400 lbf-sec/lbm). Major applications of the liquid oxygen and liquid hydrogen bipropellant system include the space shuttle main engine and the Saturn second stage engine (J-2). Liquid oxygen is also widely used with hydrocarbon fuels in the booster engine of heavy lift launch vehicles such as the Russian Energia. Although liquid oxygen can be used with storable fuels, such as hydrazine or monomethylhydrazine (MMH), this bipropellant combination engine is still in the development stage, mainly because of the difficulty of chamber cooling and combustion stability.

Both the freezing point (−362°F, 54.5 K) and the boiling point (−297°F, 90 K) of liquid oxygen are low, permitting a wide range of operation. Liquid oxygen is highly reactive with most organic materials in a rapidly pressurized confinement region of rocket combustion chambers. Except for the relatively high evaporation rate, the handling and storage problems for liquid oxygen are minimal. Although liquid oxygen is not considered corrosive and toxic, the surfaces that will be in contact with the liquid oxygen must be kept extremely free of any contamination because of its reactivity. The low boiling point also can cause problems due to low temperature embrittlement. In order to minimize oxidation problems, metals such as copper are used.

Storage tanks and transfer lines of liquid oxygen systems must be well insulated to prevent the condensation of moisture or air with subsequent ice formation on the outside. Vacuum jackets, formed plastics, and alternate layers of aluminum foil and glass-fiber mats have been used successfully.

Liquid fluorine and fluorine compounds (F_2, OF_2, or NF_3) are also cryogenic oxidizers. Although fluorine offers specific impulse and density advantages, extreme toxicity and corrosiveness have prevented the practical application of fluorine and fluorinated compounds in chemical rocket design. In addition, with fluorine the handling problems are significant because fluorine has the highest electronegativity, hence reactivity, of any of the elements—plus a very low boiling point (85 K), necessitating extensive facility support requirements.

Storable. Nitrogen tetroxide and IRFNA are the most important and most extensively used storable liquid oxidizers. A high density yellow-brown liquid, nitrogen tetroxide is very stable at room temperature, existing as an equilibrium with NO_2 ($N_2O_4 \leftarrow \leftarrow 2NO_2$), with the degree of dissociation varying directly with temperature and indirectly with pressure. At atmospheric pressure and room temperature N_2O_4 contains approximately 15 wt. % NO_2, but at 303°F (423 K) it is essentially completely dissociated into nitrogen dioxide. Upon cooling, nitrogen tetroxide dimer is re-formed. It is used as the oxidizer for the Titan first and second stage rocket engines, Delta second stage rocket engine, for the orbital maneuvering engines of the space shuttle, plus finds use in divert and attitude control (DACS) military and civil applications.

The freezing temperature of nitrogen tetroxide (11.75°F, 262 K) is relatively high, so care must be taken to avoid freezing (causing flow blockage) whenever it is used. For this reason, nitric oxide (NO) may be added (applications with as much as 30 wt. % NO, as mixed oxides of nitrogen (MON), have been noted) to the nitrogen tetroxide to depress the freezing point, improving space-storability of this oxidizer. Additionally, with 1–3 wt. % NO, storability in titanium tanks is greatly improved, due to reduced stress corrosion over time. Nitrogen tetroxide itself is not corrosive if pure, that is, if the moisture content is very low. Carbon steels, aluminum, stainless steel, nickel, and Inconel can be used with it. However, when the moisture content increases above about 0.2 wt. %, the nitrogen tetroxide becomes increasingly corrosive, and 300-series stainless steel should be used.

IRFNA consists of concentrated nitric acid (HNO_3) that contains dissolved nitrogen dioxide and a small amount of fluoride ion, as hydrofluric acid (HF).

The addition of HF provides the fluoride ion, which reacts with the metal containers, forming a metal fluoride coating and reducing the corrosiveness significantly. As with nitrogen tetroxide, IRFNA is mainly used with hydrazine-type fuels in bipropellant systems. Because nitric acid ignites spontaneously with aniline and amines (hypergolicity), care must be taken in handling and storing the IRFNA. However, this is an advantage in systems where extinguishment and reignition are desired.

MON and high density acid (HDA) are variants of storable oxidizers based on dinitrogen tetroxide. The MON propellants consist of N_2O_4 and NO, as noted earlier, and HDA is a mixture of nitric acid and N_2O_4. Both HDA and MON behave similarly to IRFNA.

Other liquid oxidizers, such as concentrated (usually >70 wt. %) hydrogen peroxide (H_2O_2), chlorine trifluoride (ClF_3), and ClF_5 are used as rocket propellants for special applications. ClF_3 and ClF_5 can be highly corrosive to metals. Other interhalogen compounds such as ClO_3F, ClF_3O, or BrF_5 can also be considered as alternatives. Rocket-grade hydrogen peroxide, recently available in quantity at concentrations over 98 wt. % via the anthroquinone process, is gaining widespread respect as a “green” propellant option. However, hydrogen peroxide has serious shortcomings in its incompatibility with a wide range of possible contaminants, which have resulted in catastrophic failure of lines and tanks in extended storage scenarios. Booster

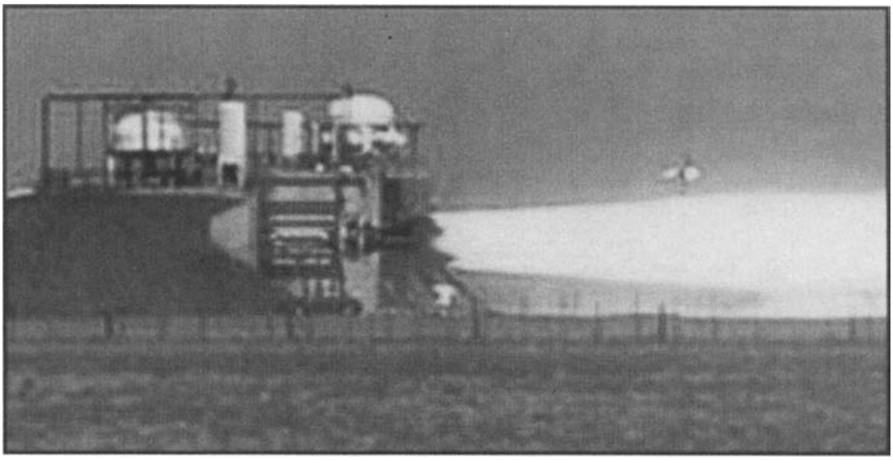

Fig. 37.21. A 200-f (60-m) long flame shoots out from the Beal Aerospace second stage engine during a test firing March 4, 2000. The engine is supposed to produce 810,000 lb of vacuum thrust, using hydrogen peroxide and kerosene propellants. (*Photo courtesy of Beal Aerospace.*)

applications have demonstrated, in static test firings, capabilities for high-performance heavy lift launch vehicles using H_2O_2/kerosene propellants as shown in Fig. 37.21.

Liquid Fuels

Cryogenic. Liquid hydrogen, the most important and widely used liquid fuel, is used mainly with liquid oxygen to give high performance, as mentioned above. Liquid hydrogen has excellent heat transfer characteristics: high heat of vaporization, high specific heat, and high thermal conductivity. It is a very good choice to cool the thrust chamber assembly when it is used in a regeneratively cooled system. However, the low boiling point (−434.8°F, 14 K) and low density of liquid hydrogen make it difficult to handle and store. The low fuel density means that a very large and bulky fuel tank is required; this is considered a disadvantage when a high ratio of payload to vehicle dry weight is desired. Liquid hydrogen has been found to react with metals, causing embrittlement of such metals as nickel. Copper is the best and most widely used material for liquid hydrogen in rocket engine applications.

As with liquid oxygen, storage tanks and transfer lines of liquid hydrogen systems must be well insulated, to prevent the evaporation of hydrogen or condensation of moisture or air with subsequent ice formation on the outside. Vacuum jackets, formed plastics, or glass-fiber mats mixed with aluminum foil can minimize the problems.

Molecular hydrogen exists in two forms: *ortho*-hydrogen (nuclei of the two atoms spinning in the same direction) and *para*-hydrogen (nuclei of the two atoms spinning in opposite directions). These two forms are in equilibrium with each other, and at room temperature the equilibrium mixture contains 75 percent of the *ortho* form and 25 percent of the *para* form. Upon cooling to the normal boiling point (−425°F, 20.4 K), the equilibrium is shifted. At this temperature, the *ortho* form will convert slowly to the *para* form. The equilibrium concentration of *para*-hydrogen at this temperature is 99.8 percent. (The shift of the ortho–para equilibrium produces energy that causes a liquid hydrogen storage problem.) Therefore, *para*-hydrogen generally is used as liquid fuel for rocket engine applications. Modern liquefiers can produce liquid hydrogen that is more than 99 percent *para*-hydrogen.[50]

Liquid methane (CH_4), another kind of cryogenic fuel used in testing and experiment, generally is used with liquid oxygen in a bipropellant system. It has the advantage of a considerably higher density than that of hydrogen (the specific gravity for methane is 0.4507 at (−258.7°F, 111.7 k) the normal boiling point). To date no operational rocket engine utilizes liquid methane as the fuel; all liquid oxygen/liquid methane engines are still in the development stage.

Storable. Together with liquid hydrocarbons, hydrazine-type fuels are the most important storable liquid propellants. They include hydrazine (N_2H_4), MMH, unsymmetrical dimethylhydrazine (UDMH), Aerozine-50 (50% N_2H_4 and 50% UDMH), and various blends of these fuels with other amine-based components. All hydrazine-type fuels are toxic to some degree, as are their breakdown products in the environment (especially, as in the case of dilute UDMH with nitrates and nitrites, forming carcinogenic and highly water soluble *nitrosodimethylamine*, or *NDMA*). The most notable hydrocarbon storable fuels include kerosene-based liquid propellants (RP-1, JP-8, and others).

A colorless liquid, hydrazine is stable to shock, heat, and cold. The freezing point of hydrazine (34.75°F, 274.9 K) is the highest of commonly used hydrazine-type fuels. Because it starts to decompose at 320°F (433 K) with no catalysts present, it is undesirable for use as the coolant for regenerative cooling of the thrust chamber. Different blends of hydrazine and MMH have been tested to improve heat transfer properties. Hydrazine is generally compatible with stainless steel, nickel, or aluminum. (See Chapter 22 for more information on hydrazine.)

UDMH is neither shock- nor heat-sensitive, and it is a stable liquid even at high temperature. A key advantage is its low freezing point (−71°F). Furthermore, it is compatible with nickel, Monel, and stainless steel. UDMH is often used as rocket propellant mixed with hydrazine in various proportions. A 50/50 mixture with hydrazine, Aerozine-50, is used for the current Delta II Stage 2. Anecdotally, the Titan IV vehicle fly-out (last flight) occurred in October 2005 with vehicle B-26, a "black" mission with a satellite for the National Reconnaissance office (NRO) engines.

MMH fuel is generally used with nitrogen tetroxide (N_2O_4) oxidizer in small spacecraft rocket engines such as orbital maneuvering or altitude control engines. Compared to hydrazine, MMH has better shock resistance and better heat transfer properties as a coolant. However, the specific impulse for MMH/N_2O_4 engines is slightly lower than that for hydrazine/N_2O_4 bipropellant engines. Like hydrazine, MMH is compatible with stainless steel, nickel, aluminum, Teflon, and Kel-F.

In general, the hydrazine-type fuels do not have very good heat transfer properties. Therefore, in the latest development of a high-pressure bipropellant system using N_2O_4 and hydrazine-type fuels, the oxidizer N_2O_4 has been used as a regenerative coolant instead of the fuel itself.

Monopropellants. Simplicity and low cost are the major reasons why monopropellant rocket engines are considered for development and deployment. The specific impulse for monopropellant engines generally is much lower than that for bipropellant engines (in the range of 200 lbf-sec/lbm for monopropellant vs. 280–400 lbf-sec/lbm for bipropellant). Hydrazine is the most important and widely used monopropellant in small trajectory correction or altitude control rockets. In an effort to lower the freezing point for improved storability, many hydrazine blends have been studied.[51]

Hydrogen peroxide has been used as a monopropellant, especially in various-concentration solutions with water. It was used as a rocket propellant in the X-15 research aircraft. Current use of rocket-grade hydrogen peroxide, or "high-test" peroxide (HTP—generally greater than 90% concentration in water) as a monopropellant is in the developmental stages, mostly for station-keeping on orbit, or as an oxidizer-compatible pressurant gas source.[52,53] Long-term storability of highly concentrated hydrogen peroxide is still problematic, although recent advances in oriented crystalline polymers and other novel composites show great promise in lightweight yet compatible tankage materials.

Gelled Propellants. As with powdered metallic fuels in solid composite propellants, early interest in gelled liquid propellants focused on gelation as a means of incorporating high-energy solids into liquid propellants to achieve high specific impulse and density. Storable hydrazine-type fuels such as hydrazine and MMH have received most of the attention in gelation development. During the development of Titan IIA*, a stable suspension of aluminum powder in gelled hydrazine (called Alumazine) was developed and tested extensively. Later the needs for such a vehicle disappeared, leaving the gelation technology to languish for lack of other applications.

In the early 1980s, an increasing focus on improving the safety and handling characteristics of storable liquid propellants revived the interest in developing gelled liquid propellants. Although gelation technology for both cryogenic and storable liquid propellants has been developed, most of the activities have concentrated on storable propellants, especially in liquid fuels. Comprehensive reviews covering all gelled fuels development activities can be found in references 54 and 55. A brief description of the gelled fuels and oxidizers is given below.

Gelled Fuel. Gelled fuels generally have consisted of metallic powders such as aluminum or boron, or carbon black plus other polymeric gelants, suspended in MMH or an MMH-blend fuel. These gels are typically applied to tactical missile applications. The gelled fuels without metal additives have drawn added interest as propellants with minimum or reduced exhaust signatures and relatively high specific impulse.

Gelled fuels have essentially the same toxicities as their ungelled counterparts because gelation does not significantly change their compositions or equilibrium vapor pressure. However, the rates of vaporization are decreased significantly, reducing the toxic exposure hazards. Gelled fuels, such as gelled MMH, are hypergolic but can burn only upon direct contact of the fuel gel with oxidizer; the fire hazards are greatly reduced with respect to both intensity and extent. Compatibility of the gelled fuels generally is the same as those of the ungelled fuels as regards materials of tankage.[56] There is evidence, however, that selected fillers or gel loadings in MMH have caused inordinate off-gas and pressure increase over time with these tactical fuel gels; ongoing studies are underway to identify and minimize this potential incompatibility in storage.

Gelled Oxidizers. Development work on gelled oxidizers was started during the 1960s, but virtually no effort was expended on them during the 1970s. Development work was revived in the 1980s as interest in gels was awakened because of their improved safety and handling characteristics. Gelled oxidizers include nitrogen tetroxide, MON, red fuming nitric acids (RFNA), and IRFNA. The gelling agents used for the oxidizers include powdered lithium nitrate ($LiNO_3$), lithium fluoride (LiF), plastisol nitrocellulose (PNC), and colloidal silica. The early work on these gels can be found in references 57 and 58. For tactical applications with minimum exhaust signatures, gelled IRFNA and ClFs are the primary gel oxidizers.

Like the gelled fuels, the toxicity of gelled oxidizers is not reduced, but the handling and safety hazards of storage are greatly improved. Gelled IRFNA is considered to be compatible with aluminum. Recent efforts have shown that it can be stored for at least as long as the non-gelled IFRNA. Studies at UAH in this country (sponsored by the U.S. Army Missile Command) and University of Nottingham (sponsored by the United Kingdom's Royal Ordnance) have identified mechanisms and additives to increase storability of gelled IRFNA and analogs; their deployment, however, is yet to be seen.

ADVANCED MONOPROPELLANT STUDIES

HAN, ADN, AN, HNF, HTP: Monopropellants (and oxidizer) Alphabet Soup Studies of hydrazine-family replacements, in this context including hydrazine, methylhydrazine, and unsymmetrical dimethylhydrazine, are increasingly justified based on decreasing toxic limit exposures and associated higher cost for storage and deployments of these

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*Titan I utilized kerosene and LOX as propellant; the Titan II ICBM development required earth-storable propellant selection.

propellants as both mono- and bi-propellants.[59] As monopropellant, hydrazine has increased competition from water-based ionic liquid blends that to a large degree include hydroxylammonium nitrate (HAN, NH_3OHNO_3), ammonium dinitramide (ADN, $NH_4N(NO_2)_2$), or ammonium nitrate (AN, NH_4NO_3), and to a lesser degree includes hydrazinium nitrate (HN, $N_2H_5NO_3$), hydrazinium nitroformate (HNF, $N_2H_5C(NO_2)_3$), or perhaps hydrogen peroxide (HTP, H_2O_2).[60–64] Blends of these compounds, with or without ionic or molecular fuels, have been studied for their applicability as gun propellants or monopropellants to varying degrees, without significant fielded deployments as of this date of writing. The predominant issues that prevent wider acceptance of these propellants include high combustion temperatures (on the order of 2000^+ °C versus 1100°C for hydrazine), reliable performance with heterogeneous catalysts (typically iridium on alumina support), and their storability and compatibility with typical materials of construction.

In a series of gas-generating compositions also having utility as monopropellants, U.S. Navy investigators report the PERSOL, OXSOL, PERHAN-family water-based blends using $H_2O_2/AN/H_2O$, $H_2O_2/HN/H_2O$ (PERSOLs), $HN/AN/H_2O$ (OXSOLs), or $H_2O_2/HAN/H_2O$ (PERHANs).[65–68] The versatility of these blends offer not only reduced toxicity as compared to hydrazine replacement monopropellants, but also as oxidizers in bipropellant or hybrid propulsion systems. Alternative applications may even include breathable gas generation or use as an oxygen source for welding. These ternary blends are unique also in their low freezing points (as low as -50°C) and relatively high densities (1.3–1.6g/cc or greater) which make them attractive as improved performance options regardless of their reduced toxicity potential. However, as in the case for HTP or HAN use elsewhere, storage stabilities and potential incompatibilities due to fume-off when inadvertently contaminated by decomposition catalysts may make their use problematic. Work in government and industry labs is ongoing in these areas in search of risk mitigation for use of these advanced mono- and bipropellant materials.

BIPROPELLANT APPLICATIONS

The ongoing search for reduced toxicity and improved performance in both mono- and bipropellants is driven by cost factors and infrastructure concerns as noted above, but also in programs such as the U.S. national effort *Integrated High Payoff Rocket Propulsion Technology* (IHPRPT)[69] multiphased goals. In our context of propellants and their ingredients, the IHPRPT goals are to double the performance of rocket propulsion systems over the current state of the art, and to decrease the cost of access to space for both commercial and military sectors. Predominant among the applications for these high-payoff improvements in propellants, the boost and orbit transfer segment is a major beneficiary, with spacecraft and tactical (i.e., defense) segments receiving a lesser benefit.

BIPROPELLANT FUELS

With many of the oxidizers discussed above in terms of use as monopropellants, blends with ionic and molecular fuels are noted to improve their performance, at the expense of hazards ratings or storage instabilities. Examples of ionic fuels intended for use as blends in monopropellants include tris(ethanol)ammonium nitrate (TEAN), $NH(C_2H_4OH)_3NO_3$, or hydroxyethylhydrazinium nitrate (HEHN), $NH_2NHCH_2CH_2OH$. Although these high-energy chemicals do show reduced toxicological activity in some studies,[70] it would be considered premature to class many of the hydrazine-derivatized compounds as nontoxic.

The list of molecular fuels that can be combined with these emerging oxidants for use in mono- and bipropellant applications are extremely long—examples include urea, glycine, glycerol, methanol, ethanol, amines, organoazides, and more—but in general are hallmarked by their miscibility, gas-generating potential (high nitrogen content), and by improvement to densities and standard enthalpies in their respective blends as fuels with conventional or advanced oxidizers. Fundamental studies on combustion stability, hypergolicity, and associated ignition delay

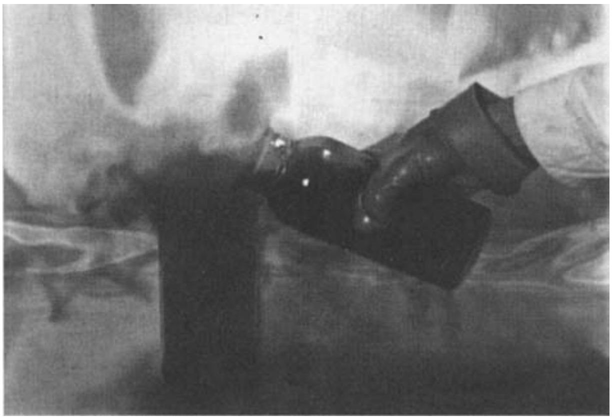
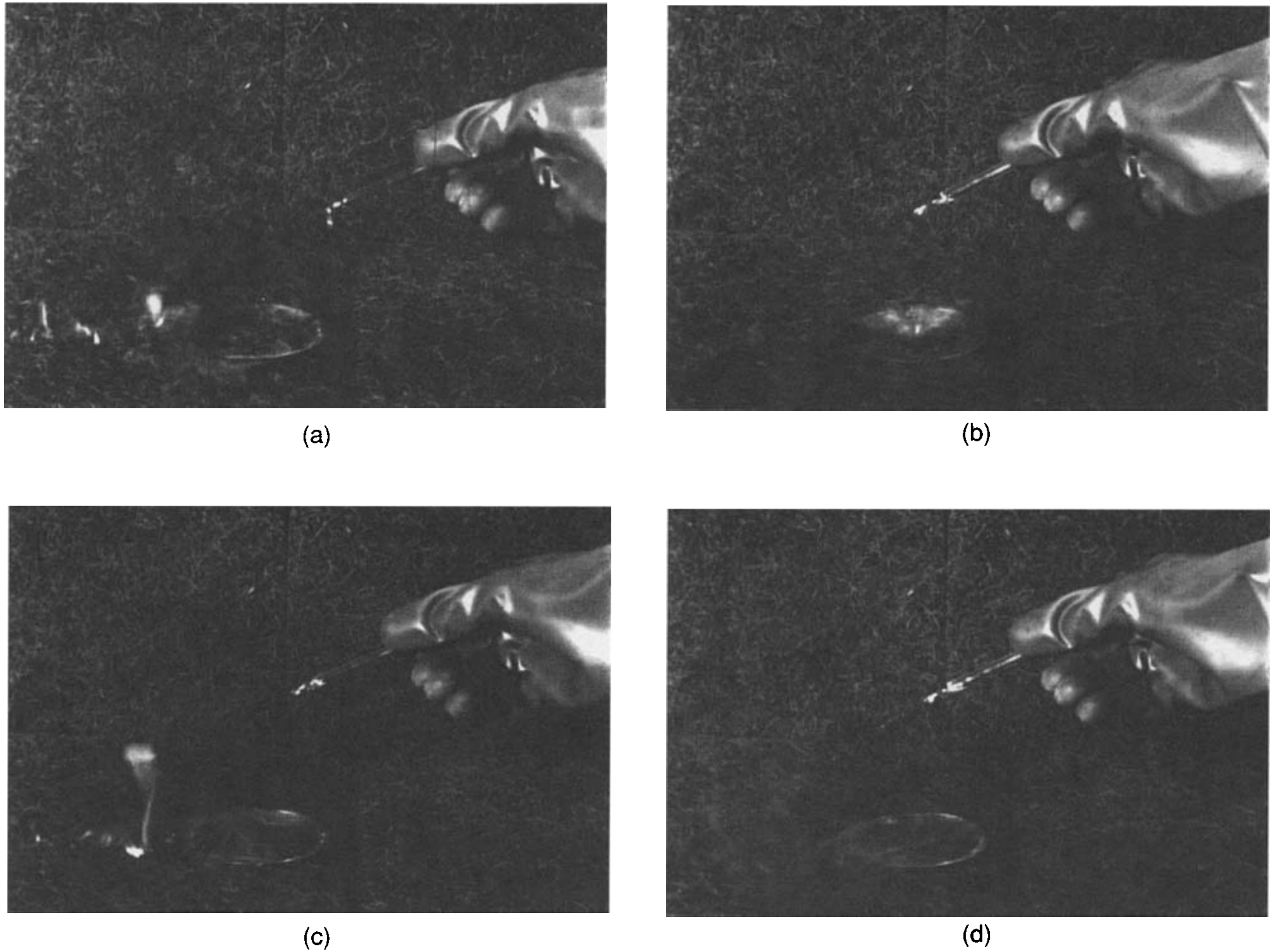


Fig. 37.22. Nitrogen Tetroxide Liquid Oxidizer Handling Demonstration, circa 1960s. Note the large volume of evolved NO_2 vapor (this oxidizer is near the boiling point at room temperature), a hazard concern in exposures to personnel.

reactivity between fuel and oxidizer streams in various injector and combustion chamber designs are underway in government and commercial labs at this time.

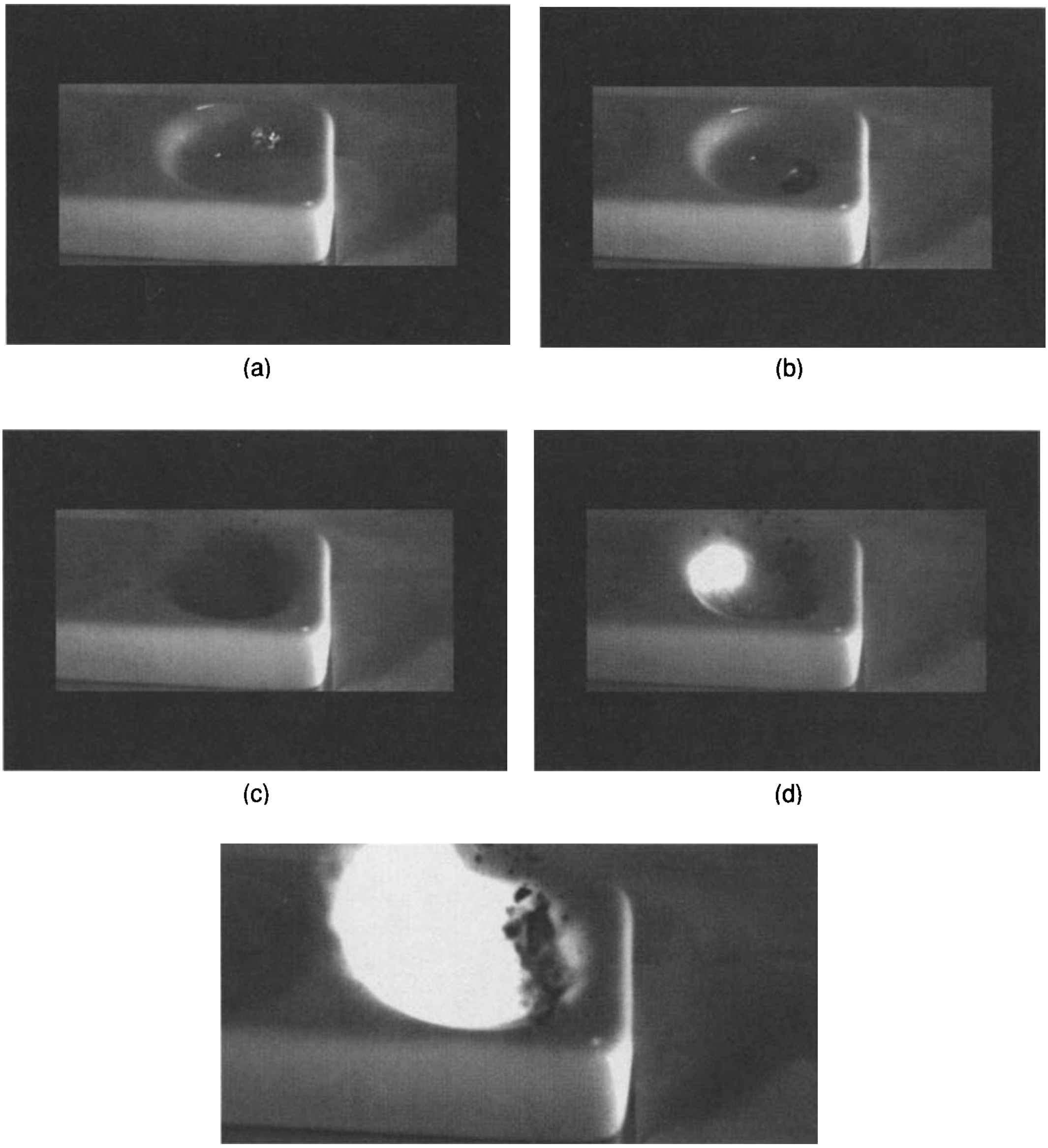
IGNITION DELAY

Arguably the most significant performance detractor to replacements of hydrazine-type fuels is the slower hypergolic reaction time observed for low-toxicity replacement fuels with nitric acid oxidizers, resulting in "hard-start" pressure spike phenomenon on engine startup that in some cases may be critically drastic. Recent studies[71,72] that reinvestigate the ignition phenomenon between new fuels and oxidizers take advantage of improvements in high-speed digital photography and fast-response data acquisition, analyzed by powerful standalone desktop computers commonly available to investigators both in the United States and abroad, invariably show the fast, efficient ignition event between hydrazine and nitrogen tetroxide (or MMH-IRFNA using a low-temperature storable bipropellant example). As a benchmark, either using quick-screen techniques of drop-on-drop testing and frame-by-frame analysis of high-speed video (see Figures 37.23 to 37.24), or studies involving the pressure transients in liquid rocket engine combustion chambers, most investigators would agree that conventional hydrazine-family fuels with nitric acid-type oxidizers will react in 10 milliseconds or less, and in some cases are shown to be an order of magnitude less under optimum conditions. University, industry, and government work involving identification of factors that affect ignition delay in amine fuels show 3° amines <2°, 1° amines when tested in drop-on-drop screening with liquid IRFNA.[73–77] Other trends are: higher amine content shows shorter ignition delay, as does less steric hindrance at the amine nitrogen, higher amine basicity, and multiple tertiary amine groups, shortens ignition delay. In aromatic amines, primary amine functionality tends to show shorter ignition delay than secondary/tertiary amine aromatics. Surprisingly, volatility of various amine compounds did not contribute to hypergolicity, whereas factors such as low temperature or low pressures have been seen to detract from hypergolicity and increase ignition delays. Proprietary designs of chambers and injectors for bipropellant rocket engines have also been studied in recent years for optimums for characteristics of mix and ignition—which most often shows much reduced delays as opposed to drop-on-drop screening tests—such that competitive advantage may be demonstrated for low-cost and high-performance (and fast response) applications.



(a) (b) (c) (d)

Fig. 37.23. A four-sequence 1960s demonstration of liquid Aerozine 50 fuel (50:50 hydrazine:unsymmetrical dimethylhydrazine) eyedropper quantities falling onto nitrogen tetroxide liquid oxidizer. Reaction is not dramatic in this testing, but is almost explosively violent when combined in typical liquid rocket engine combustion chambers.



(a) (b)

(c) (d)

(e)

Fig. 37.24. Modern drop-on-drop hypergol screening tests here show a sequence of high speed digital photos (~2 milliseconds between frames) with advanced low-toxicity liquid fuel falling into fuming nitric acid liquid oxidizer. When compared to similar tests with alkylhydrazine fuels, these are much more visibly dramatic, but here have about twice the ignition delay.

Ignition delay phenomena of hypergolic propellants are complex and understanding is incomplete for not only the mechanistic aspects of conventional bipropellants, but also advanced amine-type reduced toxicity fuels for use with nitric acid-type oxidizers. Both liquid-phase and gas-phase reactions play a part, along with physical effects of mixing, localized temperature, and pressures surrounding the impinging streams, plus intermolecular effects among the interacting fuel–oxidizer combinations, in short, an almost overwhelming set of phenomena that may contribute to significantly affect the ignition and sustained combustion phenomenon for advanced hydrazine-family replacement fuels.

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