

Don H. Cranney and Walter B. Sudweeks

Introduction

The average citizen in today's world gives little thought to the important role that commercial explosives play in their 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. In 2010, the Mineral Information Institute estimated that the average baby born in America will need the following quantities of minerals, metals, and fuels in their lifetime: copper—932 lb; salt—31,779 lb; clays—12,121 lb; zinc—544 lb; stone, sand, and gravel—1,100,000 lb; petroleum—72,499 gal; lead—777 lb; other minerals and metals—43,822 lb; natural gas—5.93 million ft³; cement—41,181 lb; iron ore—14,530 lb; bauxite (aluminum)—4,040 lb; coal—542,968 lb; phosphate rock—15,152 lb; and gold—1.383 troy oz [1]. Availability of all of these materials, which total 2.9 million lb/individual, depends on the use of explosives.

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 cement production, excavations for skyscrapers, tunnels, roads, pipelines, and utilities are direct beneficiaries of the labor-saving use of explosives. Exploration for oil and gas involves the use of explosives in seismic studies to map underground strata to find structures that may have these resources present. Our food supply depends on the use of phosphate based fertilizers. Significantly, the industrialization cycle being

experienced in several areas of the world, such as in China and other parts of Southeast Asia, is greatly ramping up the use of explosives worldwide to supply the needed materials for the massive building and infrastructure improvements.

Commercial Explosives Market

The use of commercial explosives in the United States over the last 10 years shows some cyclical behavior that basically follows the economic cycles. This is illustrated in Fig. 37.1, which indicates explosives usage by year as reported by the U.S. Geological Survey (USGS) [2] from 2000 to 2009. The data compiled in this figure show fairly level explosives sales for the years 2000 through 2004, hovering around 2.5 million metric tons/year. The years 2005 through 2008 show a distinct step up to volumes over three million metric tons consistent with the world wide commodities boom period and the booming U.S. economy during that period. This was followed by a sharp drop to below 2.5 million tons as the world wide recession of 2008/2009 sharply dropped explosives demand. 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 the ten leading states for 2008 and 2009 [3]. These ten states represent 75% of the total explosive use in the U.S. In the year 2009 (the latest statics available at the time of this update), the four states consuming the most explosives (in decreasing order) were: Wyoming, West Virginia, Kentucky, and Indiana; all coal mining states. These states alone accounted for over 50% of the total U.S. market. The coal market continues a shift from the eastern states to the western states with lower BTU, but more importantly, lower sulfur coal. This trend is congruent with the shift to large open-pit mining operations, both in the west and in other regions, in order to increase production and competitiveness. The dramatic effect of the economic downturn was indicated

D.H. Cranney (✉)
Senior R& D Mgr./Global Explosives Team, Dyno Nobel Inc., 10535
South Featherwood Drive, South Jordan, UT 84095, USA
e-mail: don.cranney@am.dynonobel.com; don.patc@comcast.net

W.B. Sudweeks
Retired 680 East 3230, Utah 84043, North Lehi

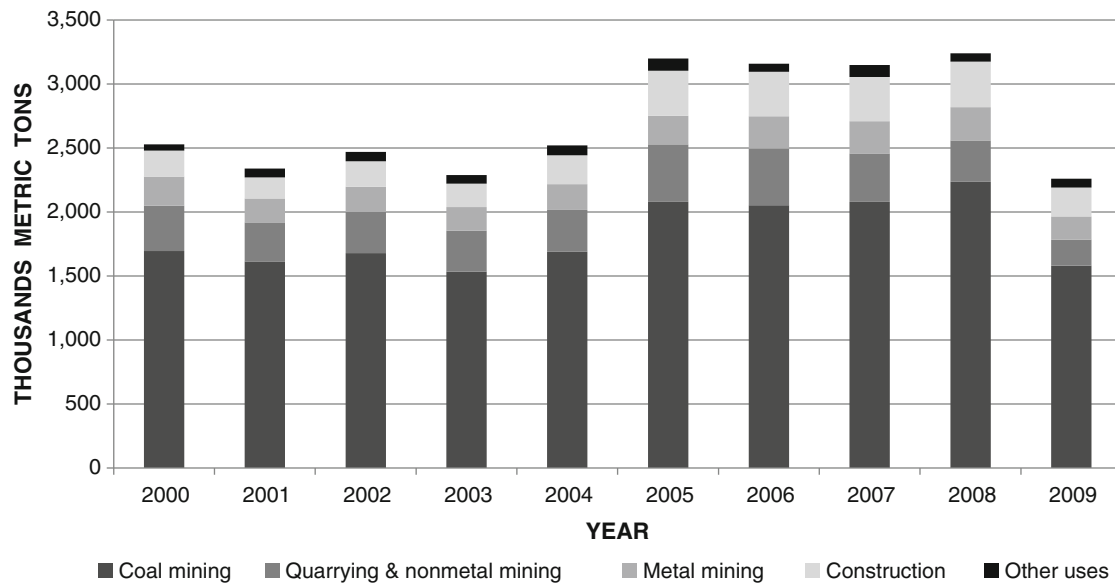


Fig. 37.1 Total sales of U.S. Industrial Explosives from 2000 to 2009. Relative volumes within major market segments indicated (Compiled from United States Geological Survey [2])

Table 37.1 Industrial explosives and blasting agents sold for consumption in the United States, by state and class^a

| State | 2008 | | | | 2009 | | | |
|--------------------------|-----------------------|---------------|-------------------------------|------------------|-----------------------|---------------|-------------------------------|------------------|
| | Fixed high explosives | | Blasting agents and oxidizers | Total | Fixed high explosives | | Blasting agents and oxidizers | Total |
| | Permissibles | Other | | | Permissibles | Other | | |
| Wyoming | – | 517 | 675,000 | 377,000 | 29 | 240 | 377,000 | 378,000 |
| West Virginia | 290 | 1,240 | 423,000 | 348,000 | 154 | 758 | 348,000 | 349,000 |
| Kentucky | 308 | 2,010 | 386,000 | 292,000 | 206 | 1,330 | 292,000 | 293,000 |
| Indiana | – | 975 | 187,000 | 189,000 | 70 | 980 | 189,000 | 190,000 |
| Virginia | 348 | 945 | 166,000 | 114,000 | 299 | 1,560 | 114,000 | 116,000 |
| Alabama | 25 | 301 | 87,300 | 95,900 | 14 | 257 | 95,900 | 96,200 |
| Pennsylvania | 64 | 1,290 | 102,000 | 90,400 | 36 | 1,390 | 90,400 | 91,800 |
| Utah | 19 | 321 | 94,800 | 64,100 | 43 | 219 | 64,100 | 64,400 |
| Texas | ⁽³⁾ | 1,470 | 118,000 | 62,700 | 18 | 699 | 62,700 | 63,500 |
| Montana | – | 1,880 | 73,500 | 55,200 | – | 2,010 | 55,200 | 57,200 |
| <i>Total</i> | <i>1,053</i> | <i>10,950</i> | <i>2,312,600</i> | <i>1,688,300</i> | <i>869</i> | <i>9,444</i> | <i>1,688,300</i> | <i>1,699,100</i> |
| <i>Total, all states</i> | <i>1,200</i> | <i>35,800</i> | <i>3,380,000</i> | <i>2,240,000</i> | <i>1,610</i> | <i>23,700</i> | <i>2,240,000</i> | <i>2,270,000</i> |

Source: Apodaca [3]

Data Source: Institute of Makers of Explosives

^aData are rounded to no more than three significant digits

⁽³⁾Less than 1/2 unit

by the drop of Nevada from the 6th position in the leading explosives consumers in 2008 to the 20th position in 2009 (not shown in Table 37.1). This was due to the slump in gold mining, which at the time of this update is recovering strongly. Other metal and commodity mines are also in a positive upswing, while construction and quarry (aggregate) operations remain in a slump.

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 common fire: fuel, oxygen from the air, and a source of

ignition. The process of combustion is basically an oxidation—reduction (redox) reaction between the fuel and oxygen. Once initiated, this reaction can become self-sustaining, producing large volumes of gases and heat. The heat given off further expands the gases and provides the stimulus for the reaction to continue by heating and igniting surrounding fuels.

The basic burning reaction is a relatively slow, diffusion-controlled process that occurs within the flames or near the surface of glowing embers. The size of the fire depends upon how much fuel is involved and on the rate of the combustion reaction. The rate of the combustion reaction depends on how finely divided the fuel is and how rapidly the oxygen reaches the flame, that is, the intimacy of contact between the fuel and the oxygen in the air. Burning rate is greatly increased when convection of the air, natural (wind) or man-made (fanning the flame), joins diffusion in supplying oxygen to the flame.

Another result of an intimate mixture of the fuel and air is the completeness or efficiency of the reaction. In a complete combustion all the fuel elements are oxidized to their highest oxidation state. Thus, burning of wood, being mainly cellulose and gasoline being generally a hydrocarbon (e.g., octane), produces 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 in a lower energy state (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.

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 accessible oxygen, 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 a fire triangle. In general, the products of an explosion are gases and heat, although some solid oxidation products may be

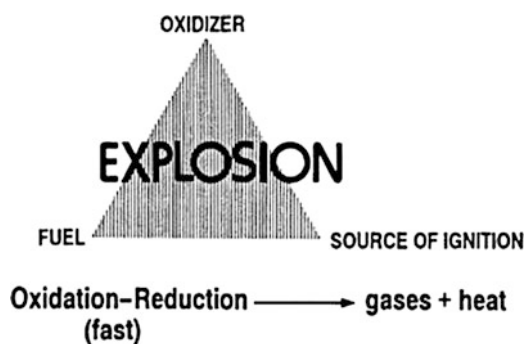


Fig. 37.2 An explosion triangle

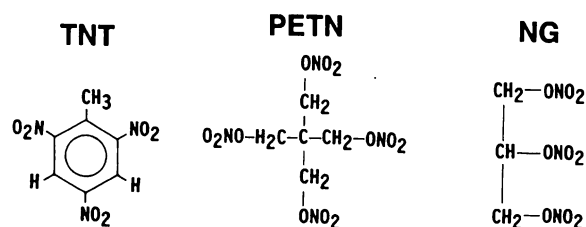


Fig. 37.3 Chemical structure of three molecular explosives

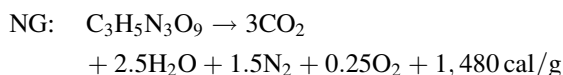
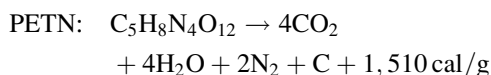
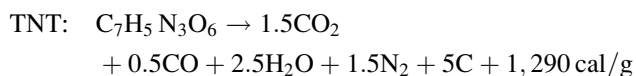
produced, depending upon the chemical explosive composition. As in normal combustion, the gases produced usually include carbon dioxide and water vapor plus other gases such as nitrogen, again depending upon the composition of the chemical explosive.

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 high degree of intimacy contributes to the second significant difference between an explosion and normal combustion—the speed with which the reaction occurs.

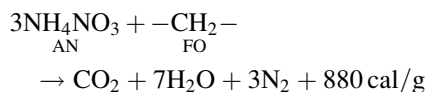
Explosives in which the oxidizer and fuel portions are part of the same molecule are called molecular explosives. Classical examples of molecular explosives are 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and nitroglycerin (NG) or, more precisely, glycerol trinitrate. The chemical 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 ($-\text{NO}_2$) groups in TNT and the nitrate ($-\text{ONO}_2$) 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

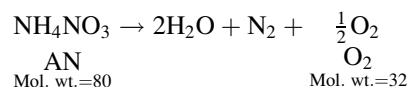
TNT, approximately 1:2 for PETN, and 1:3 for NG) shows that TNT and PETN are deficient in oxygen; that is, there is insufficient oxygen present in the molecule to fully oxidize the carbon and hydrogen. Consequently, products such as carbon monoxide, solid carbon (soot), and hydrogen are produced, as well as carbon dioxide and water vapor. Prediction of the exact products of explosion is complex, especially for the oxygen-deficient explosives, because the amounts of CO₂, CO, H₂O, and H₂ will vary as will a host of trace products such as residual hydrocarbons, 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:



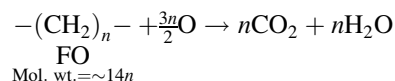
Explosives in which the oxidizer and fuel portions come from different molecules are called composite explosives because they are a mixture of two or more chemicals. A classic industrial example is a mixture of solid ammonium nitrate (AN) and liquid fuel oil (FO). The common designation for this explosive 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:



“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:



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



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

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 combustion-induced, supersonic shock wave propagates through a reactive mixture or compound. This high pressure shock wave compresses and interacts with the reactive material it contacts, resulting in very rapid heating of the material, initiation of chemical reaction, and liberation of energy. This energy, in turn, continues to drive the shock wave, thereby sustaining the detonation. Pressure in a detonation shock wave may reach millions of pounds per square inch. 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, density, 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

Table 37.2 Nineteenth century explosive discoveries

| | |
|------|--|
| 1800 | Mercury fulminate |
| 1831 | Safety Fuse |
| 1846 | Nitrocellulose |
| 1846 | Nitroglycerin |
| 1847 | Hexanitromannite |
| 1862 | Commercial production of nitroglycerin |
| 1866 | Dynamite |
| 1867 | Blasting cap, fuse initiated |
| 1867 | Ammonium nitrate explosive patented |
| 1875 | Blasting gelatin and gelatin dynamite |
| 1884 | Smokeless powder |
| 1886 | Picric acid |
| 1891 | 2,4,6-Trinitrotoluene (TNT) |
| 1894 | Pentaerythritol tetranitrate (PETN) |

closer to the thirteenth 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 nineteenth 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 fuse initiated 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 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-trinitrophenylmethyl nitramine),

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 in the explosives industry, but during the same time period dynamite production rose from 300 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, TX. Along with other cargo, one of these ships, the partially loaded SS Grandcamp, contained 2,300 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 3,000 [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 could readily absorb 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% 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 could be converted to a semisolid material, generally called a water gel, having some water resistance. The latest significant development in industrial explosives actually was invented only a few years after slurries [19, 20]. 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 Manufacturing 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 [21], and hexanitrostilbene (HNS) [22] are of interest because of their high levels of shock insensitivity and thermal stability. The development of new, explosive compounds and compositions is an ongoing area of research [23, 24], including interest in composite explosives similar to those used by industry. Examples are EAK, a eutectic mixture of ethylenediamine dinitrate, AN, and potassium nitrate [25], and nonaqueous hardened or cast emulsion-based mixtures [26].

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 (historically known as 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” [27]. 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 commercial, composite explosives such as slurries and emulsions where the density may be adjusted by air incorporation, foaming agents or physical bulking agents, irrespective of the formulation. The Class 1.5 explosives (blasting agents) are of interest because regulations governing transportation, use, and storage are less stringent 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.)

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 [28] 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

Table 37.3 Some properties of common explosives

| Common name | Symbol | Composition | Molecular weight | Density (g/cc) | Detonation velocity (km/s) | Detonation pressure (kbar) | 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 ₆ H(NO ₂) ₃ O ₂ Pb | 468.3 | 2.5 | 4.8 | 150 | 368 |
| Mannitol hexanitrate (nitromannite) | MHN | C ₆ H ₈ (ONO ₂) ₆ | 452.2 | 1.7 | 8.3 | 300 | 1,420 |
| Diazodinitrophenol | DDNP | C ₆ H ₂ N ₄ O ₅ | 210.1 | 1.5 | 6.6 | 160 | 820 |
| Tetrazene | | C ₂ H ₈ N ₁₀ O | 188.2 | 1.5 | – | – | 658 |
| Secondary explosives | | | | | | | |
| Nitroglycerin | NG | C ₃ H ₅ (ONO ₂) ₃ | 227.1 | 1.6 | 7.6 | 253 | 1,480 |
| Pentaerythritol tetranitrate | PETN | C(CH ₂ ONO ₂) ₄ | 316.2 | 1.6 | 7.9 | 300 | 1,510 |
| Trinitrotoluene | TNT | CH ₃ C ₆ H ₂ (NO ₂) ₃ | 227.0 | 1.6 | 6.9 | 190 | 900 |
| Ethylene glycol dinitrate | EGDN | C ₂ H ₄ (ONO ₂) ₂ | 152.1 | 1.5 | 7.4 | – | 1,430 |
| Cyclotrimethylenetrinitramine (hexogen or cyclonite) | RDX | C ₃ H ₆ N ₃ (NO ₂) ₃ | 222.1 | 1.6 | 8.0 | 347 | 1,320 |
| Cyclotetramethylenetetranitramine (octogen) | HMX | C ₄ H ₈ N ₄ (NO ₂) ₄ | 296.2 | 1.9 | 9.1 | 393 | 1,350 |
| Trinitrophenylmethyl nitramine (tetryl) | | (NO ₂) ₃ C ₆ H ₂ N(CH ₃)NO ₂ | 287.2 | 1.4 | 7.6 | 251 | 950 |
| Nitroguanidine | NQ | CH ₄ N ₃ NO ₂ | 104.1 | 1.6 | 7.6 | 256 | 721 |
| Nitromethane | NM | CH ₃ NO ₂ | 61.0 | 1.1 | 6.2 | 125 | 1,188 |
| Nitrocellulose | NC | Variable | – | 1.4 | 6.4 | 210 | 950 |
| Triaminotrinitrobenzene | TATB | C ₆ H ₆ N ₃ (NO ₂) ₃ | 258.2 | 1.8 | 7.9 | 315 | 829 |
| Diaminotrinitrobenzene | DATB | C ₆ H ₅ N ₂ (NO ₂) ₃ | 243.2 | 1.6 | 7.5 | 259 | 993 |
| Ethylenediamine dinitrate | EDDN | C ₂ H ₁₀ N ₄ O ₆ | 186.1 | 1.5 | 6.8 | – | 948 |
| Ethylenedinitramine (haleite) | EDNA | C ₂ H ₆ N ₂ (NO ₂) ₂ | 150.1 | 1.5 | 7.6 | 266 | 1,080 |
| Picric acid | | C ₆ H ₃ O(NO ₂) ₃ | 229.1 | 1.7 | 7.4 | 265 | 1,000 |
| Ammonium picrate (explosive D) | | C ₆ H ₆ NO(NO ₂) ₃ | 246.1 | 1.6 | 6.9 | – | 800 |
| Picramide | | C ₆ H ₆ N(NO ₂) ₃ | 228.1 | 1.7 | 7.3 | – | 1,070 |
| Hexanitrostilbene | HNS | [C ₆ H ₃ C(NO ₂) ₃] ₂ | 450.2 | 1.7 | 7.1 | 200 | 1,005 |
| TACOT-Z | | C ₁₂ H ₄ N ₈ O ₈ | 388.2 | 1.6 | 7.2 | 181 | 980 |
| Azobis hexanitro biphenyl | ABH | C ₂₄ H ₆ N ₁₄ O ₂₄ | 874.4 | 1.8 | 7.6 | – | – |
| Dinitrotoluene | DNT | CH ₃ C ₆ H ₃ (NO ₂) ₂ | 182.1 | 1.5 | 5.0 | – | 700 |
| Composition B | | 49/50/1 TNT/PDX/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 | 4.0–4.5 | 755–815 |
| Tertiary explosives | | | | | | | |
| Mononitrotoluene | MNT | CH ₃ C ₆ H ₄ NO ₂ | 137.1 | 1.2 | – | – | – |
| Ammonium perchlorate | AP | NH ₄ ClO ₄ | 117.5 | 1.9 | 3.4 | 187 | 488 |
| Ammonium nitrate | AN | NH ₄ NO ₃ | 80.1 | 1.4 | 3.2 | – | 346 |

Picatinny Arsenal over a 25-year period contains several thousand entries. New organic molecular explosives are still being synthesized; 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 [29]. 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 [30, 31], updated to include the relatively recent fluoroderivatives [23], 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.

- NO
- N-N-, -NN-, and -N≡N
- C≡N- and -C≡N
- C≡C-
- ClO
- N-X, where X = Cl, F, I
- 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 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 twentieth 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, 1964–1984) and in various military books such as *Engineering Design Handbook: Explosive Series*. Formulations of commercial slurries and emulsions generally are considered proprietary and are described mainly in the patent literature. Some specific examples of prominent explosives with general preparation methods are given below.

TNT

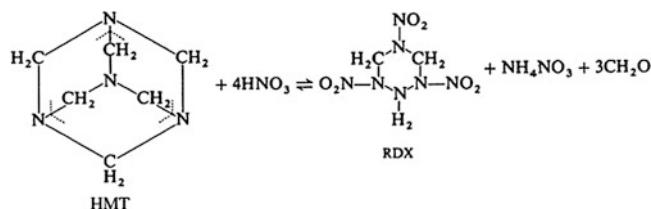
TNT is no longer manufactured in the United States for either commercial or military use. It is produced commercially in other countries and is imported into the United States for use in cast boosters to initiate industrial blasting agents. TNT use in military applications is still significant, but starting to decline as other higher technology munition and bomb fills come into use. Current TNT military needs are supplied from off-shore sources as well as through recycling from demilitarized weapons. A lot of the demilitarized TNT is also used commercially in the U.S. in cast boosters. In a relatively straightforward process, TNT is made by the direct tri-nitration 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 counter-currently. 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 SO₃ 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 (NO₂⁺). 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

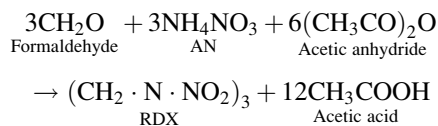
ideal for melt casting, and TNT usually is employed as a mixture with other higher-melting explosives such as PETN, RDX, HMX, and Tetryl. This feature and the excellent chemical stability of TNT have made it, historically, the most popular and widely used military explosive in the world.

RDX and HMX

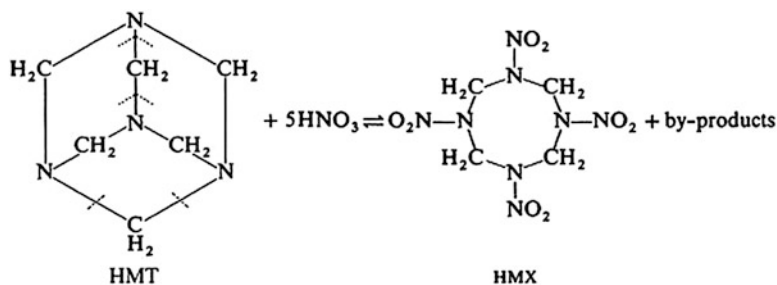
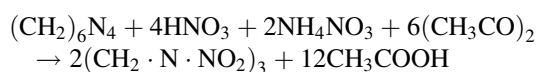
Both RDX and HMX are cyclic nitramines made by nitrolysis of hexamethylene tetramine (HMT). Their good thermal stabilities, high melting points (7200°C), and high energy properties make these crystalline compounds popular as projectile and bomb fills and for use in cast boosters and flexible, sheet explosives. 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



Reaction 2



Combined Reaction

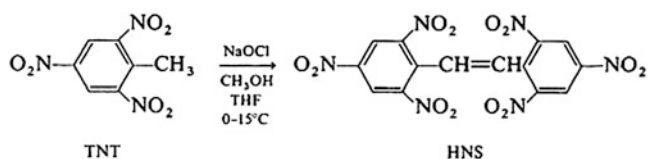


equivalent) with removal of the “inside” nitrogen and methylene ($-\text{CH}_2-$) groups. AN (NH_4NO_3) and formaldehyde (CH_2O) are produced as by-products, but can be used to form more RDX with the addition of acetic anhydride, as shown in Reaction 2. In actual practice these two reactions are run simultaneously, as shown in the combined reaction to produce approximately 2 mol 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 HMT 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.

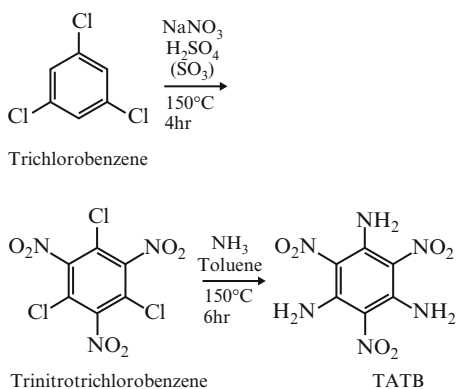
HNS (2,2,4,4,6,6-Hexanitrostilbene)

This explosive was prepared unequivocally for the first time in the early 1960s [32, 33]. It is of interest primarily 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 [34, 35].



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 ongoing interest because of its extreme insensitivity [36–38]. Because accidental initiation is highly unlikely, TATB has been used in nuclear warheads and has been explored for use in plastic bonded systems for a number of military and space applications [21]. 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 tri-nitration of trichlorobenzene followed by amination to displace the chlorine groups as shown below.

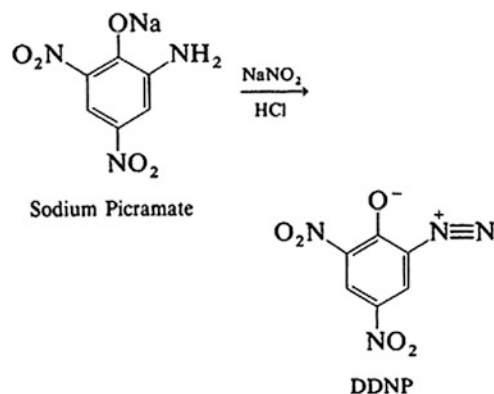


Both steps require high temperature and considerable reaction time but give 80–90% yields. The major problem areas are chloride impurities in the final product and the excessively fine particle size of the final product. Because TATB is highly insoluble in most solvents, it is difficult to purify the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

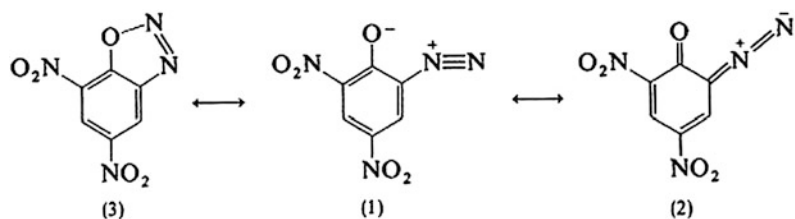
very readily available. More recently, a similar synthetic procedure starting with 3,5-dichloranisole was reported [39].

DDNP

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. 2-Diazo-4,6-dinitrophenol (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.

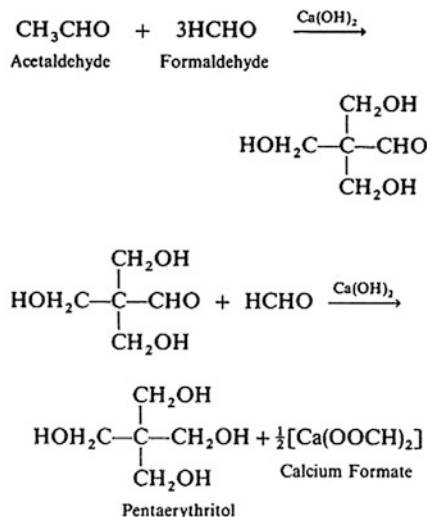


The structure shown in this reaction is convenient for visualization purposes, but DDNP actually exists in several tautomeric forms as shown below with form (2) apparently predominating. The sodium picramate starting material is itself explosive, but is commercially available as a chemical intermediate. 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

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.



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 [40]. 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 [41]. 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 a 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 Glycerol 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 140 years later. It also is used as a component in multi-based 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, combined with absorbent solids or compounded with nitrocellulose.

Packaged Explosives

Packaged explosives dominated the explosives market from the time dynamite was invented in 1867 until the middle of the twentieth century. At that time, other composite type packaged technologies began appearing, particularly in the 1960s and 1970s, concurrent with increasing market penetration of bulk explosives. During those years of rapid technology development, two packaged product types emerged, first water-gel explosives, followed in the 1970s and early 1980s by packaged emulsion explosives. All of these

packaged product technologies remain active in parts of the world as of the date of this edition, but in the U.S., emulsions are pre-eminent followed by dynamites. Both are discussed below.

Dynamite

Dynamite is not a single molecular compound, but a mixture of explosive and non-explosive 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—mixtures of finely divided fuels (including absorbent combustibles) 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 non-sparking and very-little-metal equipment, good housekeeping practices, limited personnel exposure, and barricaded separations between processing stations are necessary for manufacturing. Today, the “NG” used in dynamite is actually a mixture of EGDN (ethylene glycol dinitrate) and NG formed by nitrating mixtures of the two alcohols (ethylene glycol and glycerin), 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.

The use of NG-based dynamite continues to decline throughout the world. For example, by 1995 there was only one dynamite manufacturing plant left in North America, and in 2010 the dynamite production at this plant had dropped to about one-third 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. However (despite its higher cost), for some difficult blasting applications it remains the product of choice due to its high density and high energy and sensitivity.

Packaged Emulsions

The first major non-dynamite package product technology was water gels. These were composite mixtures of hot, concentrated, dissolved oxidizer solution slurried with other ingredients including soluble and insoluble liquid fuels, particulate fuels, solid oxidizer salts, and thickeners consisting of natural and synthetic water soluble polymers. The thickened solution could be gelled by addition of cross-linking agents, typically inorganic salts of certain metals. The gelled structure gave significant, but not excellent water resistance.

Packaged water-in-oil emulsions are made from essentially the same oxidizer solutions as used for water-gel products, but are fueled with an organic external liquid hydrocarbon phase that provides much better water resistance. These products are basically formed with the same manufacturing equipment as the bulk emulsions (see next section). The fuel 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 energy, physical stability, and improved after-blast fumes. After manufacture, the hot, 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 and is cooled which further thickens the product. Some packaged emulsions are also available in paper cartridges, designed to simulate dynamite packaging. 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. Figure 37.4 shows some commercial packaged emulsion cartridges in both plastic and paper wrappings.

Table 37.4 General types of dynamite

| | |
|--|---|
| Straight dynamite | Granular texture with NG the major source of energy |
| Ammonia dynamite (“extra” dynamite) | AN replacing part of the NG and sodium nitrate of the straight dynamite |
| Straight gelatin dynamite | Small amount of nitrocellulose added to produce soft to tough rubbery gel |
| Ammonia gelatin dynamite (“extra” gelatin) | AN replacing part of the NG and sodium nitrate of the straight gelatin |
| Semigelatin dynamite | Combination of types 2 and 4 within-between properties |
| Permissible dynamite | Ammonia dynamite or gelatin with added flame retardant |



Fig. 37.4 Commercial packaged emulsion cartridges (Courtesy Dyno Nobel)

Bulk Explosives

Ammonium Nitrate and ANFO

Ammonium nitrate (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. Ammonia is 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 ammonia is made. Figure 37.5 shows the volatility of natural gas over the last decade. This volatility translates into volatility in the cost of explosives, although significant natural gas development in the U.S. over the past few years seems to be suppressing some of the price fluctuation.

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, a composite explosive described in an earlier section. These low density AN prills are made by a specialized process, in which internal

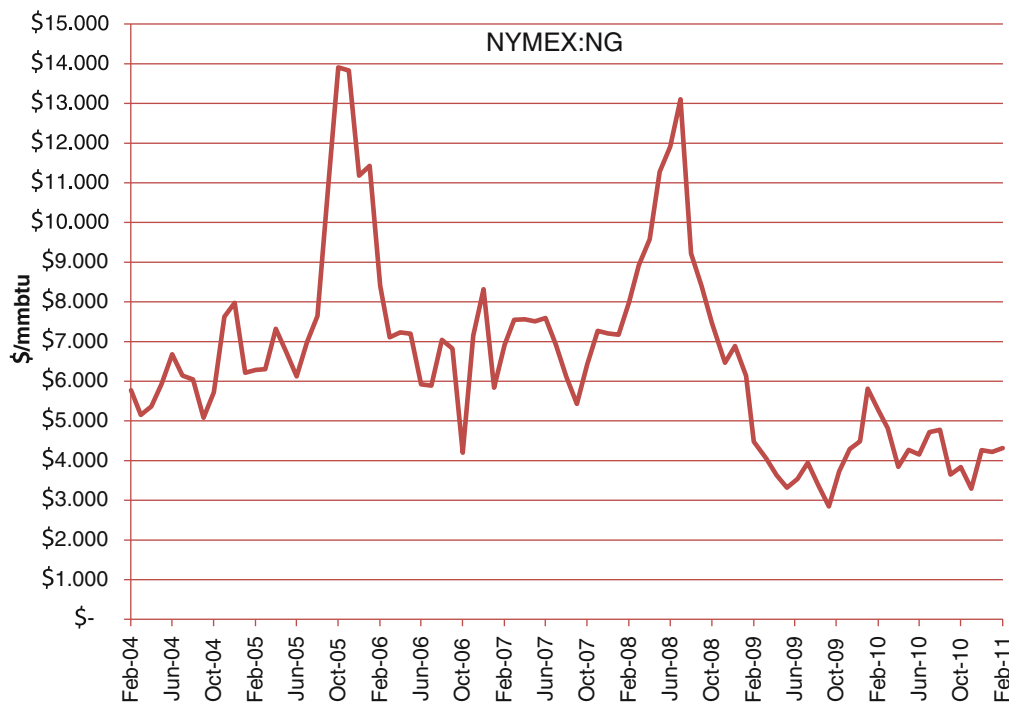


Fig. 37.5 Volatility of natural gas prices from 2004 to 2010. New York Mercantile Exchange, Natural Gas, Compiled Monthly

voids are created, making the prills porous and able to absorb the required 5.5–6% FO. ANFO remains the largest volume commercial explosive 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 about 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 to 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 about 0.80 to 0.87 g/cc. So, clearly about half of the ANFO is air or void space. Most commercial explosives require a certain amount of entrained void space in order to detonate optimally. These void spaces play a major role in the detonation reaction by creating reaction sites, “hot spots,” under adiabatic compression and interaction with the shock wave in the detonation front [42]. 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 a composite 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 in that particular diameter or other configuration. 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 commercial composite explosives such as ANFO will drop dramatically as the diameter of the charge nears the failure diameter. At a given density, the diameter below which a charge fails to propagate a detonation is called the critical diameter. As a charge diameter is increased from this point, the detonation velocity increases asymptotically to a maximum value for that particular explosive formulation. The detonation velocity of ANFO will also increase noticeably when the charge confinement is changed, such as from a PVC tube to a Schedule 40 steel pipe. A summary of test data on ANFO velocity vs. confinement and diameter is shown in Fig. 37.6. The temperature of composite explosives also affects sensitivity and critical properties.

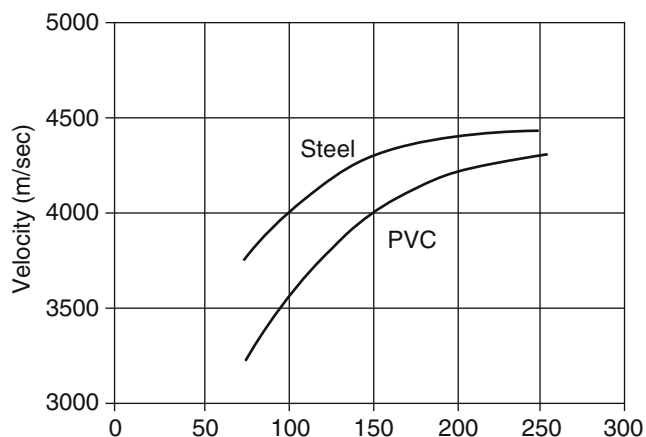
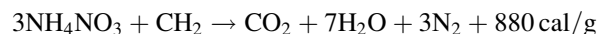


Fig. 37.6 Detonation velocity of ANFO vs. diameter and confinement

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



Using CH_2 to represent FO is generally accepted, but it really is an over-simplification, 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 2,700 °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 [43]. 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 [44]. 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 most valid comparisons are done in the field with product testing and detailed evaluation of results.

Bulk Emulsions

During the past 50 years, the commercial use of bulk delivered explosives, including ANFO and other composite explosives, has continued to increase while the use of packaged explosives continued to fall on a percentage basis. Due to low cost and superior sensitivity compared to earlier water-resistant technologies such as water gels, bulk

emulsions have been leading this trend over the last 25–30 years. Bulk products initially became very popular in large volume open-pit mining operations and this accelerated with the advent of bulk emulsion products and blends with ANFO. More recently, bulk emulsions have increasingly replaced packaged products in underground mining and particularly in quarry 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% by weight of the emulsion. It contains AN, water, and sometimes a second oxidizer salt such as 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 meta-stable, water-in-oil emulsion are basically held together with the emulsifier molecules, which migrate to the surface of the dispersed droplets and form a link between the hydrophobic external (continuous) oil phase and the hydrophilic phase within the 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 2,000.

Figure 37.7 shows a photomicrograph of an emulsion explosive at 400 power with the typical distribution of the fuel-coated oxidizer solution droplets (nominally 1–5 μm in diameter). Figure 37.8 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 thicker than mayonnaise, depending upon the application requirements. Emulsion viscosity increases with product cooling, but most emulsions continue to remain stable at temperatures well below 0°C, dramatically 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 become less stable due to chemical degradation (oxidation) of the emulsifier or other spontaneous physical and chemical processes. Movement of the emulsion is also stressful to these systems, which in reality are thermodynamically unstable, tending towards crystallization and

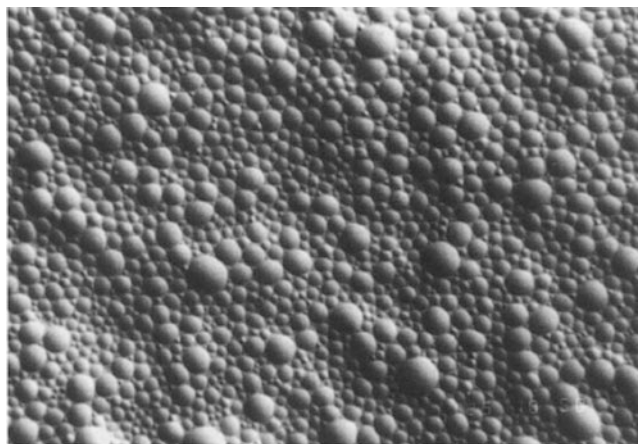


Fig. 37.7 Photomicrograph of a bulk emulsion

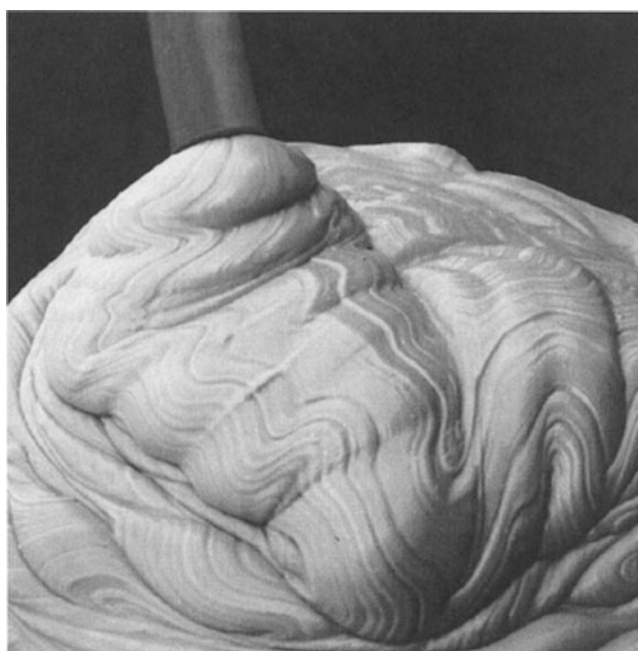


Fig. 37.8 Bulk emulsion exiting a loading hose

coalescence. Crystals can begin to form that break through the emulsifier layer and the emulsion begins to “break down” and further crystallize, thereby diminishing some of the desirable physical and detonation properties. For this reason emulsion compositions must be optimized for a particular application in terms of product stability and usable storage life.

The intimate mixing of oxidizer and fuel in emulsions gives these explosives much higher detonation velocities when compared to ANFO. For example, in 150 mm diameter PVC, ANFO at a density of ~ 0.82 g/cc has a velocity of about 4,000 m/s, and a sensitized emulsion would have a velocity closer to 6,000 m/s at a density of 1.20–1.25 g/cc.

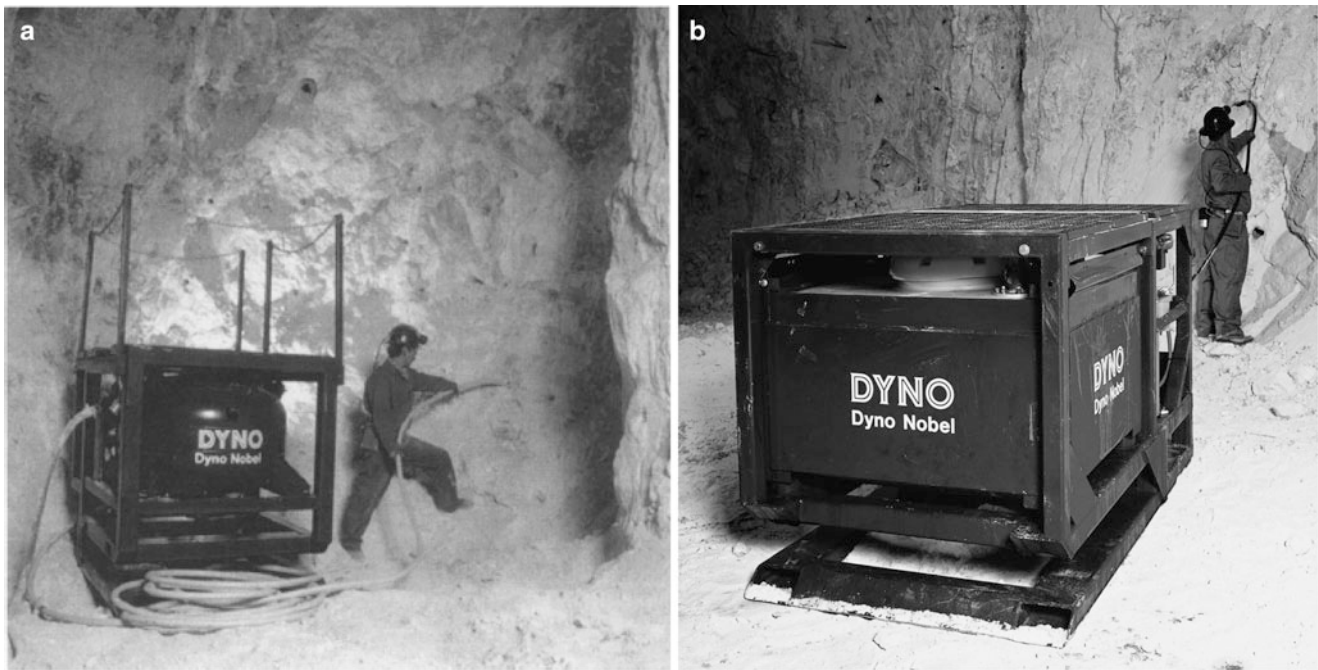


Fig. 37.9 (a) Underground pressure vessel loader. (b) Compressed-air, powered pumper for underground bulk emulsion (Courtesy Dyno Nobel)

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 non-detonable per se and are typically sensitized with some type of density control medium to become usable blasting agents. These voids interact with the shock wave, creating "hot spots," which are required to sustain the detonation front. The two most commonly used density control methods are hollow solid microspheres and 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. Emulsion blended with ANFO, with its internal and interstitial air voids, is also widely used as a less efficient but effective sensitizer in larger diameter boreholes.

Underground Bulk Emulsions

In the past decade the use of sensitized bulk emulsions has continued to increase in underground mining. In addition to

the necessary small diameter sensitivity of emulsion based explosives in these applications, much of this trend has been due to the development of innovative loading equipment and techniques. One example of this is shown in Fig. 37.9a, 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. A more recently designed air-powered pumper unit for underground delivery of bulk emulsion is shown in Fig. 37.9b. This unit typically uses compressed air, available in most underground mines, to power a pump that delivers the bulk explosive. 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 nearly 30 years ago and remain essentially the same today. They are manufactured in central plants, either sensitized with microballoons to form as a 1.5 explosive or as a gassable matrix that can be transported and stored as a non-explosive, thence sensitized with gas bubbles at the point of use. They 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,



Fig. 37.10 Bulk emulsion loading truck in a Florida quarry (Courtesy Dyno Nobel)

results in the near elimination of after-blast toxic fumes, such as CO, NO, and NO₂. 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 NO₂ was reduced from about 7 to less than 1 L/kg of explosive [45].

Surface Bulk Emulsions

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 5,000 to 30,000 lb of product. Figure 37.10 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 non-explosive 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 37.11 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.

Other surface, bulk delivery trucks use emulsions that are manufactured in central plants, then shipped to a surface depot, off-loaded into a bin or overhead silo, and loaded as needed into delivery trucks by pumping or gravity flow. The products can be shipped pre-sensitized with microballoons or as a non-sensitized, gassable matrix. The application of the product can be as a pumped straight emulsion or as a pumped or augured emulsion/ANFO blend.

Many of the large volume metal and coal mining operations around the world have both bulk emulsion and AN prills stored either on site or nearby so that any combination of these two products can be used. Figure 37.12 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 ten 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 coat the AN prills and fill the interstitial voids between the solid particles. This increases the density, detonation velocity, and water resistance compared to ANFO. The density increases nearly linearly with percent emulsion from about 0.85 g/cc with ANFO to about



Fig. 37.11 Florida quarry blast in progress (Courtesy Dyno Nobel)

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.

It is commonly accepted in the explosive and mining industry that at least 45–50% emulsion is required to protect the Heavy ANFO blend from borehole water intrusion. Pumped explosive blends with 60–80% emulsion can be used for even better water resistance 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. 37.10 can be used for these products. Most Heavy ANFO products are more simply mixed through an auger and discharged into the top of boreholes by trucks similar to the one shown in Fig. 37.12. For Heavy ANFO products, especially those with less than ~45% emulsion, the holes should be either dry or dewatered using pumps.

The basic chemical composition of a typical all-AN oxidizer emulsion explosive would be: AN plus about 16% water plus about 5% fuels. The fuels may contain fuel oil, mineral oil, 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 earlier.

By adding 16% 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 paid for using water due to converting it to steam in the detonation reaction plus the energy loss in diluting the ANFO with a non-energy producing additive (water). 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 higher bulk energy to match rock types and blasting applications.

Fig. 37.12 Typical bulk explosives staging area in a large opt-pit mine



Initiation Systems

History of 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. These early caps had to be initiated with a strong shock, limiting their safety and convenience. In 1867, Nobel developed a cap that could be initiated with a fuse, a more convenient system that allowed an element of timing (length of the fuse) to the initiation of a blast, and hence, some increase in safety and predictability. This, combined with his invention of dynamite in 1866 [46], basically ushered in the modern era of blasting. The fuse cap and dynamite dominated the emerging blasting industry for several decades. In the century that followed, the initiation systems became more and more sophisticated and safe. The electric blasting cap which could be initiated by electrical current was developed around the turn of the century,

adding further safety to blasting. Detonating cord, a flexible cord made of cloth or plastic with a core load of high explosives—usually PETN, was developed in Europe around the same time. Strings or circuits of detonating cord could be utilized to initiate several explosive charges with only one blasting cap. Electric caps were introduced in 1946 equipped with built-in, variable-delay elements (pyrotechnics that burn reproducibly) [46]. This allowed long rows of boreholes to be initiated in a sequential manner, optimizing blasting effectiveness as well as better controlling ground vibration and air blast damage to the surroundings. With caps having delays ranging from a few milliseconds to many hundreds and eventually thousands of milliseconds, the number of sequentially fired boreholes in a row depended only on the desired timing and the amperage capability of the electric blasting machine or other firing circuit. Sequential blasting machines were developed that could be used to control firing times between a number of rows of blastholes, greatly expanding the timing possibilities and size of blast patterns.



Fig. 37.13 Variety of commercial cast boosters (Courtesy Dyno Nobel)

Boosters

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. However, the use of non-cap-sensitive explosives (blasting agents) began emerging into the explosives market in the 1930s and 1940s. These products really took off with the advent of ANFO in the mid 1950s and water gels, invented by Melvin A. Cook in 1957 [47]. Emulsion based blasting agent products, which began significant commercialization in the mid 1970s, became the dominant non-ANFO product by the late 1980s and remains so to the present day. All of these blasting agents were adaptable to larger diameter packaged products and particularly to bulk loading.

These blasting agent 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. Later, TNT-based cast boosters came into the market. Cast TNT by itself is not reliably detonable with a blasting cap or detonating cord, and so 40–60% 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. Additives used for military purposes have included such as aluminum, ammonium nitrate, RDX, and also PETN, but Pentolite been dominant in commercial cast boosters. Cast boosters are available in a variety of sizes from about 10 to 800 g, as shown in Fig. 37.13, and continue to be predominant today in nearly all large mining operations and other blasting applications. Cap-sensitive composite explosives such as emulsion cartridges, dynamite, etc. are also used in less demanding situations. Coupled with the flexibility of blasting caps with variable delays to initiate the booster charge which

then initiates the main charge, large patterns containing many thousands of pounds of explosive can be blasted.

Non-electric Initiation

In 1967, Per-Anders Persson of Nitro Nobel AB in Sweden invented a non-electric initiation system, designated Nonel[®], that eventually revolutionized the explosives industry [46]. The Nonel system consists of an extruded hollow plastic tube (shock 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 simple shotgun shell primer. The explosive/aluminum mixture explodes down the inside of the tube at about 2,000 m/s and will run at this velocity until all the interconnected tubing reacts, including initiating all the blasting caps. 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 37.14 is a photograph of both an electric blasting cap with the two electrical wires and a typical Nonel unit with the plastic tubing.

During the 1980s and 1990s, Nonel products continued to replace both electric blasting caps and detonating cord down lines around the world. It has long been known that detonating cord down lines disrupt and partially react with blasting agents causing some degree of energy and sensitivity loss. Also, the use of surface detonating cords to initiate blasts can lead to noise complaints. Using a range of long-lead delay caps down the borehole, a surface trunk-line of shock tubing, surface connectors to tie the tubing together, and surface delay elements that are available with this technology, huge and complex blasting patterns can be laid out and blasted with a multitude

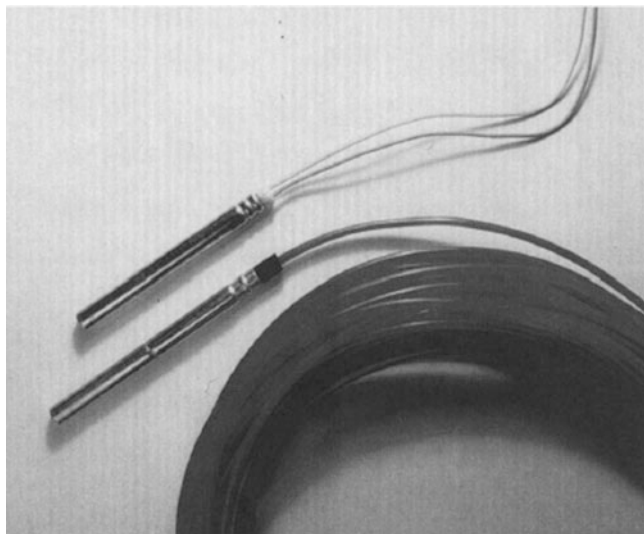


Fig. 37.14 An electric blasting cap showing electrical wires, typical Nonel unit with plastic tubing

of possibilities as to timing and sequence. As delay elements were perfected for the Nonel blasting caps, their application and use grew even further, especially in underground mining where a large percentage of blasting caps is used.

Electronic Detonators

The development of detonators with delay periods that were based on pyrotechnic elements (timing controlled by the burn rate and length of the element) had a dramatic effect on the explosives industry, enabling much of the size and complexity of modern blasting, as well as reducing off-site blast effects caused by ground vibration and air blast. When a blasting pattern is properly timed, the detonation of individual holes is such that damage from air blast and ground vibration is greatly reduced. This is a result of destructive wave interference, i.e., the ground vibration waves from detonation of each hole combine with each other and the air blast waves from the detonation of each hole combine with each other in such a way that the resulting wave patterns propagating from the blast have lower amplitudes and higher frequencies. This is key to controlling off-site structural damage. Over many years of development, the accuracy and repeatability of pyrotechnic delays was improved dramatically. However, delay times can still vary from detonator to detonator and from the target delay time by a few milliseconds to tens of milliseconds depending on the delay period of the detonator. There are also occasional fliers that occur well outside the normal scatter for a given delay detonator that can upset the blasting pattern. It was surmised that these variations could result in less than

optimum blasts, considering not just air blast and ground vibration but also ground movement, fragmentation, ore dilution, fly-rock, etc.

In the late 1980s and early 1990s, several companies began developing and testing detonators wherein the delay timing was controlled with an integrated electronic circuit. These were initially very expensive and, by today's standards, were crude devices. However, they did demonstrate the promise of very accurate caps. As electronics technology improved into the 1990s, testing and field evaluation of such caps increased. However, cost and complexity in assembling the caps, the development of user friendly controllers to program and initiate them, and the unfamiliar equipment and technology on the blasting patterns slowed widespread implementation. It wasn't until mounting commercial experience began to demonstrate improved blasting results that the tide began to turn. This in turn resulted in accelerated improvements in manufacturing technology to make the caps less expensive, more reliable, improve ease of use, and increase expertise available to blasters in the field. By the 2000s, the technical case for electronic detonators had been well established. Despite the significant cost differences that remain between electric or non-electric detonators and electronic detonators, amounting to factors of perhaps five to ten times more costly per unit, there are dramatic increases in the use of electronic detonators in the blasting industry today. As of the date of this edition, they are still a minor part of the total global detonator market, but the market share is increasing. Several manufacturing companies with independent detonator technologies are involved and use is occurring in all segments of mining, construction, and other commercial blasting applications.

The construction of an electronic detonator has some features in common across all manufacturers. The timing and programmability features depend on an integrated circuit. One or more capacitors are included to store the electrical energy necessary to run the circuitry and to initiate the detonator via bridge or igniter elements. The detonator can be built to have a preset delay time or can be programmable as to delay period at the point of use. Electrical and electronic communication with the detonators is established via two or four lead wire connections, depending on the system chosen and the blast design, flexibility, control, and programmability features desired or needed by the blasters. The lead-wires are connected to the blasting machine which enables all of the features in the particular technology chosen, including programming (if needed), arming, and eventually initiating each line of detonators. The timing accuracy is on the order of only 1 to a few milliseconds depending on delay times, and variability is typically reduced by an order of magnitude compared to pyrotechnic detonators [48, 49]. Figure 37.15 shows the components of a four wire system

Fig. 37.15 Components of an electronic cap initiating system. L-R, logger, cap, base station (blasting machine), connectors (Courtesy Dyno Nobel)



and includes the cap, connectors, tagger (identifies and tags each detonator as it is placed in the borehole), and blasting machine (herein called the base station).

References

1. Mineral Information Institute. Soc Metallurg Explor Foundation. <http://www.mii.org/MiiBabyMain>
2. United States Geological Survey. Minerals Yearbook, Explosive Statistics and Information. Compiled Information from years 2000–2009
3. Apodaca LE (2009) United States Geological Survey. Minerals Yearbook, Explosive Statistics and Information (advance release)
4. Ornellas J (1968) Phys Chem 72:2390
5. Kaye SM (1978) Encyclopedia of explosives and related items, PATR 2700, vol 8. U.S. Army Armament Research and Development Command, Dover, pp 99–100
6. Engineering design handbook: explosives series. Army Material Command Pamphlet 706–177, AD 764, 340, p 12, distributed by NTIS, Jan 1971
7. Fedoroff BT, Sheffield OE (1962) Encyclopedia of explosives and related items, PATR 2700, vol 2. Picatinny Arsenal, Dover, p B165
8. Butler AR (1990) ChemTech:202
9. Van Gelder AP, Schlatter H (1972) History of the explosives industry in America. Arno Press, New York (reprint of 1927 edition)
10. Marshall A (1917) Explosives, vol I, History and manufacture. P. Blakiston's Son, Philadelphia
11. Gregory CE (1973) Explosives for North American engineers. Trans Tech Publications, Cleveland
12. "Black Powder" (1983) Explos and Pyrotech 16(7)
13. Atlas Powder (1987) Explosives and rock blasting. Atlas Powder, Dallas
14. Johansson CH, Persson PA (1970) Detonics of high explosives. Academic, Reinhold Book Corporation, New York
15. Du Pont (1980) Blasters handbook, 16th edn. pp 14, 109
16. Kintz GM et al (1948) Report of investigations 4245. U.S. Department of Interior, Bureau of Mines, Feb 1948
17. Chem Mark Rep:6 (1983)
18. Cook MA (1974) The science of industrial explosives. IRECO Chemicals, Salt Lake City, p 2
19. Egly RS, Neckar AE (1964) US Patent 3,161,551, 15 Dec 1964
20. Bluhm HE (1969) US Patent 3,447,978, 3 June 1969
21. Bower JK et al (1980) I&EC Prod Res Dev:326
22. Mohan VK, Field JE (1984) Combust Flame 56:269
23. Spear RJ, Wilson WS (1984) J Energy Mater 2:61
24. Coburn MD et al (1986) Ind Eng Chem Prod Res Dev 25:68
25. Dobratz BM (1983) LA-9732-H, VC-45. Los Alamos National Laboratory, Los Alamos, May 1983
26. Cranney DH, Hales RH (1990) Proceedings of the fourteenth symposium on explosives and pyrotechnics, Franklin Research Center, Feb 1990
27. Code of Federal Regulations, Title 49 Transportation, Part 173.114a, p 272, 1 Oct 1979 Revision
28. Fed Regist 55(9):1306 (1990)
29. Tarver CM et al (1977) Structure/property correlations in primary explosives (Final report, 76-2). Stanford Research Institute, Menlo Park, 4 Feb 1977
30. Brunswig H (1909) Explosivstoffe. Barth, Braunschweig, p 17
31. Plets V (1953) Zh Obshch Khim 5:173
32. Shipp KG (1964) J Org Chem 29:2620
33. US Patent 3,505,413, 7 Apr 1970
34. Kayser EG (1983) J Energy Mater 1:325
35. Gallo AE, Tench N (1984) J Hazard Mater 9:5
36. Delistraty I, Brandt H (1982) Propell Explos Pyrotech 7:113
37. Rizzo HE et al (1981) Propell Explos 6:27
38. Kolb IR, Rizzo HE (1979) Propell Explos 4:10
39. Ott DG, Benziger TM (1987) J Energy Mater 5:343
40. Urbanski T (1965) Chemistry and technology of explosives, vol II. Pergamon, New York, p 181
41. Military explosives, Department of the Army technical manual TM 9-1300-214, chapter 7, p 32, Washington, DC, 1967

42. Cook MA (1958) The science of high explosives. American Chemical Society monograph series no. 139, Reinhold Book Corporation, pp 178–183
43. Ibid., Appendix II
44. Cole RH (1948) Underwater explosions. Princeton University Press, Princeton
45. Hanto K (1998) Internal report on fumes from emulsion and ANFO. Dyno Nobel, Europe
46. History of explosives and blasting. Intern Soc Explos Eng. <http://www.explosives.org/HistoryofExplosives>
47. Cook MA (1974) The science of industrial explosives. IRECO Chemicals, Salt Lake City, pp 5–7
48. Watson J (2002) Electronic Blast Initiation, A Practical Users Guide, J Explos Eng 19(3):6
49. Lusk BT, Hoffman J, Wedding WC (2011) Electronic Detonator and Modern Non-Electric Shocktube Detonator Accuracy, Proceedings thirty-seventh annual conference on explosives and blasting technique, International Society of Explosives Engineers, p 563, 2011