INDUSTRIAL EXPLOSIVES – A BRIEF HISTORY OF THEIR DEVELOPMENT AND USE

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Summary

In this article we provide a brief overview of chemical explosives history, from primitive Chinese bamboo rockets to the 17th century introduction of black powder in mining to the powerful and economical blasting agents which now support the mining and construction industries. Explosive behavior is traced to the very same combustion reactions that drive more familiar power sources, but running millions of times faster. The physical basis for the extraordinary reaction rate of explosives is outlined.

The four major classes of chemical explosives (low, or deflagrating explosives, primary and secondary high explosives, and blasting agents) are illustrated by examples. The main features of explosive initiation systems are described, including the careful sequencing required in modern industrial blasting. The recent development of economical and super - safe blasting agents is traced to accidental ammonium nitrate explosions, such as the one that devastated Texas City in 1947. Finally, the principal uses of industrial explosives in mining, quarrying and construction are described.

Introduction

The high civilizations of the ancient world carried out prodigious mining, quarrying, and building projects by the use of forced human labor. The ancient Egyptians used war captives to hack out untold miles of mine workings, irrigation canals, and other constructions. In the 6th century B.C. inhabitants of the Agean Island of Samos tunneled their way through 1500 meters of rock for a water supply. In the Far East whole temples were carved out of the living rock. Hannibal crossed the Alps by hacking out passageways with chisel and wedge. Monumental projects on a similar scale were executed in the New World as well.

It is hard to overstate the overwhelming drudgery of attacking a stone face with hammer and chisel. In hard rock a man day of effort will produce, at best, a tenth of a cubic meter or so of rubble, and only a few men can find room at the working face of a tunnel. The situation is even more desperate in mining, where the ore deposit must be followed regardless of its direction or thickness.

Armies of men have spent their whole working lives swinging a pick while on hands and knees or while lying on their sides, frequently in cold water.

Explosives provided a way to alleviate this drudgery. Igniting black gunpowder, the first explosive, in a borehole produced a pressure pulse on the order of a thousand atmospheres or more, bringing down rock or ore far more effectively and economically than any previous means. Without this explosive and its descendants we could not have obtained the metals and fuels to support the industrial revolution, nor could we have developed modern highway, rail, and water transport systems.

In this article we trace the development and uses of industrial explosives and offer a perspective on the way they do their work.

From black gunpowder to ammonium nitrate

The Adam of explosives, as most people know, is black powder, an intimate blend of potassium nitrate (saltpeter), charcoal and sulfur. All three ingredients were reasonably available, even in the ancient world. It is likely that potassium nitrate attracted the attention of our forbears by the fiery display that resulted when it was sprinkled on glowing charcoal embers. When someone ignited a blend of all three of these ingredients the mixture burned at a startling rate, far faster than any other composition available at the time. Given the fairly common occurrence of the ingredients, this discovery was probably made at many times and places.

The Chinese appear to have been the first to make explicit use of this discovery when they packed nitrate–charcoal–sulfur mixtures into bamboo tubes to make rockets. Such rockets were first used for signaling and display. Later they were fired against fortifications and troops. For many centuries thereafter developments were driven by military considerations. The first guns and cannon, invented in the early 14th century, were nothing more than wooden tubes from which a powder charge expelled a stone. Metal cannon of the 15th century could propel about 100 kg of stones for a mile or more, but another century passed before guns became effective enough to replace traditional weapons.

Early cannon were about equally dangerous at either end, partly because of mechanical failings, but substantially because of problems with the powder. The optimum proportions of the three ingredients had been worked out by the 16th century, but performance in a gun chamber is dependent on physical characteristics as well. Because gunpowder burns from the surface of the particles, fineness of grind and tightness of packing in the chamber can make the difference between an ineffectual "fizzle", an effective shot, or a burst gun. Early cannoneers were civilian specialists, able to mix their own powder in the field, then ram it into their gun with just the right touch. Feared by friend and foe alike such "artists" were employed by the French as late as 1800. Techniques for "graining" black powder and modern propellant powders eventually alle-

viated these problems. Fine-grained powder is suitable for small arms, while slower burning coarse-grained powder is suitable for large guns. The ultimate is the single huge "grain" constituting the propellant charge in a space rocket booster. Such charges must be formulated to resist crack or void formation because any extra surface area can lead to catastrophic rise in the burning rate.

Black powder was first used in mining in the early years of the 17th century. The innovators were returned Hungarian soldiers who had used black powder to breach fortifications. It took a century or so to develop effective techniques for explosive-assisted mining. This development was also delayed by limitations in the supply of potassium nitrate. The only substantial deposits, in India and Andalusia (Spain), were hardly adequate to support the interminable European wars of the times.

It was eventually found that the light colored crusts of "nitre" found on the walls of farmyard cellars and stables consisted largely of potassium nitrate that could be recovered, refined, and used in black powder. Europeans were thus provided with a local source of nitrate. Stringent methods were used to enforce collection of the nitre. Farmers were required to set up "nitre beds" in which their animal wastes were held until nitrates formed. Until the mid 19th century Swedish country people were required to pay a part of their taxes in nitre.

In 1840 enormous deposits of sodium nitrate (Chile saltpeter) were discovered in the Chilean desert, presumably representing the evaporated run-off from decaying organic matter in better-watered areas. Chile saltpeter quickly found its way into fertilizers and into gunpowder after conversion to potassium nitrate. In 1857 Lamott DuPont developed a commercially successful black powder based on sodium nitrate. Although widely used in civilian applications, sodium nitrate powder was not favored for military use.

Starting in 1912 the Haber process made it possible to synthesize nitrates from the nitrogen of the atmosphere. This development assured abundant nitrate supplies in all industrialized countries.

While all this was going on, synthetic chemistry came of age. In the early years of the 19th century chemists were busily reacting organic (carbon) compounds with all manner of reagents. One of the favorite reagents was nitric acid, the aqua fortis of the ancients, no doubt because something was almost certain to happen when strong nitric acid met an organic substance. For example, in 1799 the chemist E.O. Howard reacted mercury with strong nitric acid and then poured the reaction product into ethyl alcohol. The resulting vigorous reaction produced copious red fumes and then a gray, fearsomely explosive solid. By a series of reactions he could not possibly have explained he had produced mercury fulminate, one of the first synthetic explosives. Black powder had lost its place as the world's one and only explosive.

In 1846 Ascanio Sobrero, an Italian chemist, reacted strong nitric acid with glycerol, a by-product of soap manufacture. The oily product was glyceryl trinitrate, conventionally called nitroglycerin. Sobrero observed the tremendous

explosive power and high sensitivity of his new compound but practical use was limited by the extreme hazards associated with its synthesis and its use.

Practical use of nitroglycerin (NG) was pioneered by Emmanuel Nobel and his son Alfred in the years following 1859. The Nobel family had spent much of the previous 20 years in St. Petersburg (Leningrad, nowadays) where Emmanuel owned a munitions factory. When this enterprise was closed at the end of the Crimean War the Nobel family returned to Sweden. In search of a new opportunity, father and son carried out extensive studies of NG during the years from 1859 to 1861. Sobrero joined this effort and worked with the Nobels for many years. In 1862 the first facility for NG manufacture was set up near Stockholm. Alfred Nobel was granted several early patents on schemes for packaging and initiating NG, for example by soaking NG into black powder contained in a zinc tube. Both containment of the oily liquid and reliable initiation of the charge proved difficult. Although NG explodes with frightening ease it develops optimum shattering power only when properly initiated.

In 1863 Alfred Nobel invented the blasting cap, a device that revolutionized explosives technology. It consisted of a small copper capsule in whose closed end a charge of mercury fulminate was placed. Any desired length of safety fuse could be inserted into the open end of the capsule and crimped in place. Such blasting cap assemblies could be immersed in liquid NG or pressed into solid explosives. Following ignition at the open end, a flame propagated through the length of the fuse and detonated the fulminate, providing effective initiation for the main charge. The blasting cap is generally viewed as Nobel's most significant invention.

In the meantime NG was compiling an appalling safety record. Nobel's first plant blew up in 1864, killing his younger brother. Several other plants in Europe also blew up; NG manufacture was then proscribed in several European countries. Safety in use was also very poor. Liquid NG frequently exploded during transportation. It also leaked from boreholes and caused accidents later. It froze in cold weather (at 11°C) and then became insensitive, but exploded during careless thawing. Its continued use in view of these hazards is eloquent testimony to its performance superiority black powder.

In 1866 the American chemist George Mowbray undertook to supply NG for use in excavation of the Hoosac Tunnel. This tunnel still provides an important rail link between New England and the interior of the continent. It was the first large scale construction project in which "blasting oil" replaced black powder. Mowbray's plant made about a million pounds of NG during 1866 and 1867 without an accident. Most of the product was used in the tunnel construction, but substantial quantities were shipped frozen around eastern USA and Canada. Mowbray's success has been attributed to careful control of glycerol purity, extremely thorough washing of the product and a safe system for thawing frozen NG.

Continuing his work with NG, Alfred Nobel had built several additional

manufacturing plants by 1866. In 1876 he observed that diatomaceous earth (kieselghur) was able to absorb up to three times its own weight of NG to form a relatively dry, leak resistant paste. This paste proved to be a powerful explosive, readily set off by means of his blasting cap. He named the new composition "Dynamite" from the Greek "dynamis" i.e., strength. Proving far safer and more convenient than liquid NG it quickly replaced the latter in all blasting uses. Dozens of modified formulations followed as safety, effectiveness, and economy were improved. Dynamites became, and for some 70 years remained, the world's workhorse explosives.

Paralleling Sobrero's early studies of glycerol nitration, several early chemists experimented with the nitration of cellulosic materials. Starting in 1854 the German chemist C. Schonbein carried out some of the most extensive studies. Schonbein was attempting to make a gun propellant superior to black powder. His first compositions were much too fast-burning for this purpose, but nitrocellulose eventually became the basis for all propellant powders, thus vastly increasing the capability and reliability of firearms. Hundreds of synthetic explosives have since been synthesized and evaluated; a dozen or so have found practical use.

Many of the significant advances in explosive technology have been in the means for setting them off. The first fundamental advance was made in 1831 by William Bickford, a Cornishman, who devised a burning fuse made by incorporating a black powder core in a wrapping of jute yarn. Bickford was attempting to improve the lot of "Cousin Jack", the legendary Cornish tin miner, who regularly blew himself to bits while setting off explosive charges in the mines. The Bickford "safety fuse" replaced such makeshifts as a series of goose quills or wheat straws stuffed with powder and then inserted end to end. Modern factory-made safety fuse is so reliable and consistent that the time delay before initiation can be selected to the second by choosing the proper fuse length.

Although black powder is adequately initiated by a flame or other heat source, nitroglycerin and many other explosives require explosive initiation to reach their full potential. As previously noted, Alfred Nobel invented the blasting cap for this purpose in 1865. The modern fuse-initiated blasting cap differs only in details from Nobel's original. Electrically fired caps are now preferred for most purposes, especially if many charges are to be set off at one time or in precise sequence. In such caps a tiny electrically heated resistance wire is used to set the initiation process in motion. A time delay function may be included. The cap may be only the first element in an explosive "train" that includes one or more booster charges ahead of the main charge.

The explosive analog of Bickford's burning fuse, known as detonating cord, was invented in France in 1908. The original product was made by drawing down a lead tube containing a cast-in-place trinitrotoluene (TNT) core. The Ensign–Bickford Corporation, a USA Company, further developed the product

into its present form, a braided textile structure with a high explosive core. When set off with a blasting cap this cord can be used to initiate blasting charges in multiple and widely spaced boreholes. Delay connectors, "T" connectors, and other gear are used to achieve the precise timing and sequencing which characterize modern blasting practice.

The next 40 years were marked by increasing fundamental understanding of explosive phenomena and by steady improvement in explosive materials and techniques. Then in 1947 the ship "Grand Camp" loaded with fertilizer grade ammonium nitrate (FGAN) blew up at its dock in Texas City, Texas. A fire burning in its hold had suddenly "run up" to detonation. The ship itself disappeared. The explosion and resulting conflagration caused the loss of more than 500 lives, and property damage on the order of 100 million (1947) US dollars. FGAN-laden ships in Brest, France and in the Red Sea exploded soon after with comparable violence. Such was the tragic beginning that led to a far-reaching revolution in explosives technology.

Ammonium nitrate had been widely used as a supplemental oxidant in dynamites since the 1870's. It had also been demonstrated that blends of AN and carbonaceous materials were powerful explosives in their own right. Because of extreme insensitivity the explosive potential was largely ignored. At the time of the Texas City disaster it was the practice to load ships with bagged FGAN that was still hot from the dryers. Although hot AN in small quantities can cool without incident, it was found that large quantities, as in a ship's hold, can undergo self-accelerating decomposition that culminates in detonation. It was further found that combustible additives and packaging can contribute to the hazard. Further studies led to the institution of safe practices in handling AN and, unexpectedly, to the development of whole new families of industrial explosives. Ironically, these economical and powerful explosives, which have now replaced dynamites in most applications, are distinguished by their exceptional safety. So it has happened that ammonium nitrate, one of the sim-

TABLE 1

USA Explosives consumption in kilotons

Year	Black powder	Nitroglycerin dynamites	Ammonium–nitrate based explosives
1800	0.2	—	—
1850	9.1	—	—
1900	100.0	100.0	—
1925	115.0	200.0	—
1950	10.0	310.0	10.0
1975	0.1	120.0	1300.0
1985	0.1	80.0	1700.0

plest, least costly, and most readily available of all synthetic chemicals has become the active ingredient in the bulk of the world's industrial explosives.

Table 1 illustrates the use history of the three workhorse industrial explosives; black powder, dynamite, and ammonium nitrate, in the USA. World trends are similar.

The basics of explosive behavior

Explosives are valued for their ability to do work. Whether intended to hurl a projectile from a gun, break loose a quarry wall, or extend a mine shaft, an explosive is properly rated by the amount of energy released per unit weight, and the rate at which this energy is released. Explosives are especially suited to tasks that require extremely high energy release rates.

Energy release in explosions derives from the rapid conversion of stored chemical energy into heat, usually with formation of gaseous products as well. The resulting pressure pulse can be harnessed to do work in various ways. The potential for doing work is represented by the amount of chemical energy released during the explosion. The amount of energy released is exactly the difference between the energy content of the explosive composition and that of its decomposition products.

The chemist's energy scale is based on the (arbitrary) assignment of zero energy to each of the chemical elements at a temperature of 273.15 K and a pressure of one atmosphere. Any other assignment, consistently applied, could be used, since energy changes are the only concern. After generations of painstaking experimental and theoretical work, the energy change in virtually any chemical reaction, including any explosive reaction, can be looked up in a table or calculated to a satisfactory degree of accuracy. The usual measure of energy change is the joule, J, a unit named for the famous British physicist, James Prescott Joule (1818–1899). In order to put this unit in perspective, note that a hard-thrown baseball travelling at 145 kilometers per hour (90 mph) carries about 115 J of kinetic energy. Typical chemical explosives release about 5000 J (5 kJ) of heat energy per gram; 0.02 g of such an explosive would release heat energy equivalent to the kinetic energy carried by the baseball. A single gram of chemical explosive can release heat energy equivalent to that needed in raising a small automobile (1000 kg) about 50 centimeters.

Chemical compounds, including explosive compounds, may posses either more or less energy than the elements from which they were assembled. Fig. 1 is an energy map showing the location of a few common fuels, explosives, and reaction products. We have carried out this mapping in terms of standard heats of reaction per gram of material. The energy map shows the zero baseline arbitrarily assigned to all the chemical elements. Kerosene, a typical liquid fuel, is shown at its location 1.7 kJ/g below the zero energy line. This indicates that the assembly of one gram of kerosene from its elements (about 0.15 g of hy-
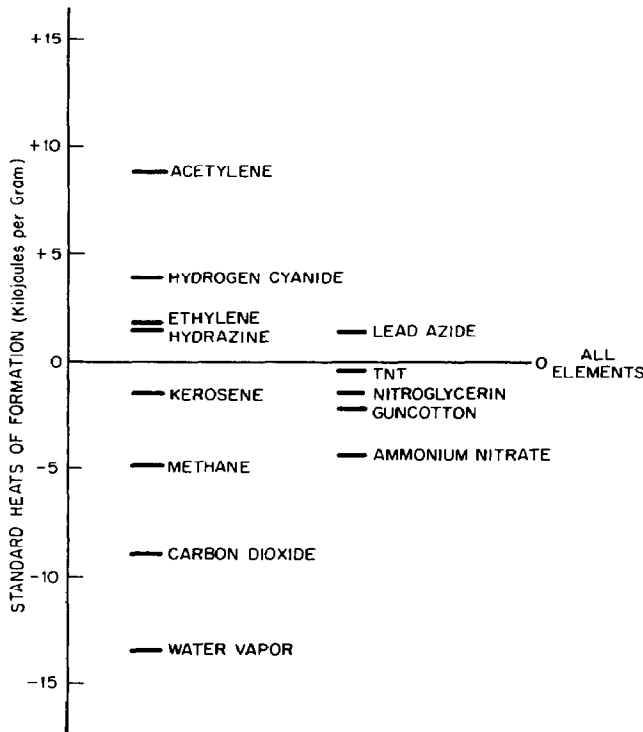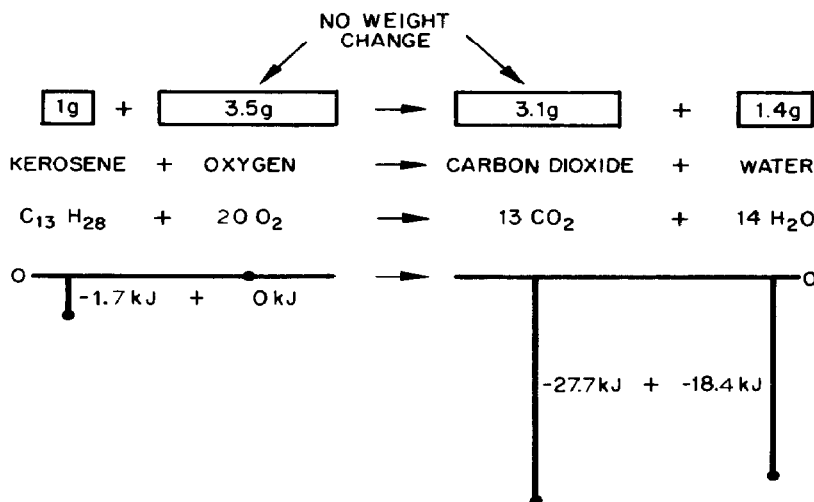
Fig. 1. Standard heats of formation, selected substances.

drogen and 0.85 g of carbon) would release 1.7 kJ of heat. The standard heat of formation, ΔH_f^0, of kerosene is said to be -1.7 kJ/g, the minus sign indicating that kerosene is lower on the energy scale than its constituent elements. Formation of kerosene from its elements is said to be a spontaneous process, in the specialist sense that it could occur without external energy input. Conversely, the decomposition of kerosene is not spontaneous; at least $+1.7$ kJ of heat energy must be expended to decompose each gram back into its elements.

Kerosene is useful as a fuel because it can react spontaneously (that is, with release of energy) with the oxygen of the air. The products of this reaction are carbon dioxide and water, as depicted in Fig. 2. The large heat release, -44.4 kJ/g, is a consequence of the large heat of formation of these reaction products, respectively, -8.9 kJ/g $CO_{2(g)}$ and -13.4 kJ/g $H_2O_{(g)}$.

Kerosene combustion, and fuel combustion in general, depend upon transport of the fuel and air (oxygen) into a combustion zone where convection and diffusion bring the fuel and oxygen within "reach" of each other. These processes are obviously apparatus sensitive; one can build a burner of any desired

NO WEIGHT CHANGE

| 1g | + | 3.5g | → | 3.1g | + | 1.4g |

KEROSENE + OXYGEN → CARBON DIOXIDE + WATER

$C_{13}H_{28}$ + $20\,O_2$ → $13\,CO_2$ + $14\,H_2O$

0 ┬ -1.7 kJ + 0 kJ → 0

-27.7 kJ + -18.4 kJ

STANDARD HEATS OF FORMATION

REACTANTS: -1.7 kJ + 0 kJ = -1.7 kJ

PRODUCTS: -27.7 kJ + (-18.4 kJ) = -46.1 kJ

NET: -46.1 kJ - (-1.7 kJ) = -44.4 kJ

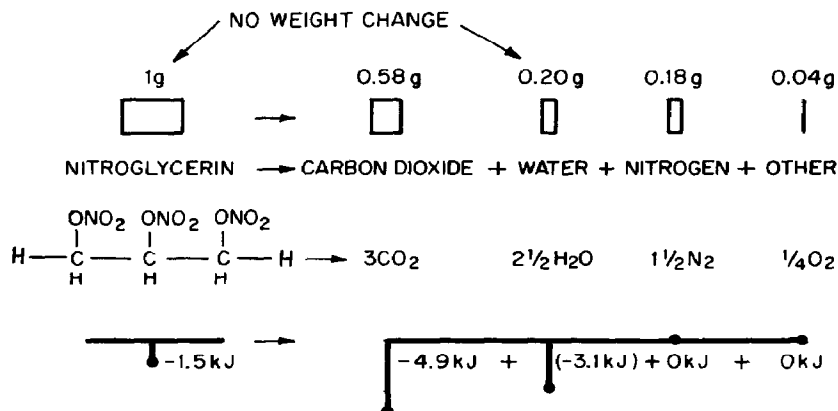BURNING 1g OF KEROSENE LIBERATES 44.4 kJ

(Minus sign is the convention for heat release)

Fig. 2. Weight and heat relationship in kerosene combustion.

heat release rate. The rate of energy release per unit volume is, however, little affected by the size of the burner.

Most chemical compounds, including most explosive compounds, are less energetic (more stable) than their elements. Kerosene is such a compound. A relatively few compounds are more energetic than their elements; they occupy positions above the zero energy line. Such unstable compounds can be made only by some chemical trickery that results in the addition of energy to the composition. A few such compounds are shown in Fig. 1. All compounds of this class have a built-in driving force toward decomposition to their elements. As such, they are all prospective members of the class of explosives.

Several familiar explosives are also shown on the energy map of Fig. 1 in their positions below the zero energy line. These and most explosive compounds are not unstable with respect to their elements. All have in common, however, the ability to release large amounts of energy upon decomposition to simpler, more stable substances. The case of nitroglycerin is illustrated in Fig. 3. Energy release during explosion of this material is due to the large heats of

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Fig. 3. Weight and heat relationship in nitroglycerin explosion.

TABLE 2

Some comparisons between kerosene combustion and nitroglycerin detonation

Physical/chemical parameter	Burning kerosene	Detonating nitroglycerin
Heat release, kJ/g	44.4	6.5
Power output, W	10^6	$10^{9 b}$
Maximum pressure, atm	7.0	10^5

[1]Jet engine.
[b]Nitroglycerin column 1 cm² in area.

formation of carbon dioxide and water, the very same products formed during the combustion of kerosene.

Table 2 contains relevant comparisons between the combustion of kerosene and the explosion of nitroglycerin. Total heat release per gram of material is far higher for the former. This is essentially a bookkeeping difference, in that the oxygen required for combustion has not been counted. Combustion oxygen

is usually supplied "free" from the air. Note, though, the vastly higher heat release rate and maximum pressure reached in the nitroglycerin reaction. How can these extraordinary differences be understood? The answer lies in the physical proximity of the prospective reacting groups. Nitroglycerin explodes when the oxidizing $O-NO_2$ groups in the molecule react with the reducing

C–H and $C{<}^H_H$ groups. Because the reacting groups are already so close there

is no mass transport limitation to the reaction rate. The reaction is an "inside job", with a characteristic reaction time on the order of 1 μs. Explosive decomposition can propagate through a column of NG at about 8000 m/s, releasing energy at a rate unattainable by combustion or other chemical means.

Explosives owe all of their special attributes to their ability to deposit energy at extraordinary rates. For example, an exploding one ton bomb can devastate a whole city block, yet an equivalent amount of energy can be deposited over the same area by sunlight in the course of a few minutes.

Metastability

The term "metastability" is used to describe the situation of compositions, such as nitroglycerin, that can remain unreacted for a time in spite of a very large driving force toward further reaction. The analogy of the boulder on a hillside ledge is useful. Both the nitroglycerin and the boulder can remain poised in their high energy state for long periods; both may release their stored energy if sufficiently disturbed.

Amazingly enough, most chemical explosives are analogous to nitroglycerin in owing their energy release to the formation of carbon dioxide or water or some combination of the two. In a word, most chemical explosives are artfully contrived compositions of carbon, hydrogen, and oxygen in the proportions required to form carbon dioxide and/or water. The required oxygen is usually linked to the oxidizable portion of the molecule through nitrogen atoms. Nitrogen plays a remarkable role in these compositions, holding the fuel and oxidizing components together strongly enough to provide metastability, but liberating them for mutual reaction upon a signal from a suitable initiator.

Effect of oxygen balance

If the oxidizing and fuel components of an explosive are present in the exact proportions required to form carbon dioxide and water the explosive is said to be oxygen balanced. Energy release per unit weight is clearly greatest at oxygen balance (stoichiometrically balanced). Composite explosives are most often formulated in the proportions required for oxygen balance. Explosive compounds, as distinct chemical species, cannot in general be manipulated into exact oxygen balance.

A few explosive compounds, notably nitroglycerin and ammonium nitrate,

TABLE 3

Idealized explosion products for selected explosives

Explosive	Reaction products[a] (approximate percentage by weight)					
	CO_2	H_2O	$CO_2 + H_2O$	N_2	O_2	Other
Black powder	49	0	49	11	0	41
LOX explosive [b]						
(at O balance)	100	0	100	0	0	0
Nitroglycerin	58	20	78	18	3.5	0
Nitrocellulose propellant	52	9	61	14	0	16
Ammonium nitrate	0	45	45	35	20	0
Carbon-fueled ammonium						
nitrate	26	42	68	33	0	0

[a]Note that actual explosion products are more complex.
[b]Activated carbon soaked in liquid oxygen.

contain more than enough oxygen for self-combustion, but the vast majority is oxygen poor. Industrial explosives based on NG or AN always contain auxiliary fuel to consume the extra oxygen. Oxygen-poor explosive compounds may be blended with auxiliary oxidants, such as nitrates, to produce balanced explosives.

In addition to providing best energy yield, oxygen balanced explosives also yield the most benign explosion products, from an environmental viewpoint, i.e., generally carbon dioxide, water vapor, and in the case of nitrogenous explosives, nitrogen gas. Oxygen-rich nitrogenous explosives yield toxic and corrosive nitrogen oxides; oxygen-lean explosives yield soot and toxic or irritating partial oxidation products, the so called products of incomplete combustion (PICs). Table 3 summarizes the composition of the explosion products for a few typical explosives.

Sensitivity

What remains to be discussed is the means available to relieve the metastability of explosive compositions, that is, to set them off. Some explosives are readily set off by spark or flame, while others are sensitive to mechanical impact or heat. Still others require explosive initiation to reach their full potential. Sensitivity to initiation does not correlate in any simple manner with bulk physical or chemical properties. Instead, empirical tests are used to assign explosive compositions to one or another sensitivity category. Current research efforts are only beginning to shed light on the relationship between sensitivity and molecular structure [1].

Low explosives

Black powder furnishes a convenient example of an explosive readily set off by spark or flame. To be effective the initiating spark or other means must have a minimum size and temperature, such that heat taken from the hot source by conduction and convection is more than matched by heat released by reaction of the explosive. If this heat balance condition is satisfied the reaction will propagate throughout any available quantity of the explosive at a rate governed by the temperature attained in the reaction zone. This temperature is very sensitive to the degree of confinement, since energy that would otherwise be used in doing work on the surroundings is available instead as heat in the reaction zone. Thus, black powder in a firecracker wrapper, a gun chamber, or a blast borehole attains a higher temperature and a much higher propagation rate than it does in the open. The ultimate rate of black powder propagation is limited by heat diffusion considerations to several hundreds of meters per second, which is very slow by explosive standards. The process is called deflagration; black powder is known as a deflagrating or low explosive.

High explosives

In contrast to black powder, most explosives are set off by the impact of a supersensitive (priming) explosive. The studies of Bowden and Yoffe [2] together with those of many other researchers have shown that initiation of explosives is usually thermal, even when the initiating impulse is mechanical or explosive impact. Several processes are capable of converting mechanical energy into hot spots, notably the adiabatic (no heat loss) compression of the gas in small voids in the explosive. The mechanism is the same as that responsible for ignition of the fuel in a diesel engine. If the heat balance condition is satisfied in the region around one or more voids in a quantity of explosive under impact, a self-sustaining reaction will result. This reaction will accelerate rapidly as it does following a black powder ignition. In the case of those compositions termed high explosives this culminates in the formation of a shock wave. Supported by the released explosive energy, the wave propagates through the mass of the explosive at a rate higher than the local speed of sound. This process is termed detonation. The ability to support a detonation wave is exactly the hallmark of a high explosive [2].

High explosives detonate at stable, reproducible, and characteristic rates, typically on the order of 5000 m/s or more, provided that the column of explosive is long enough and of adequate diameter. The most sensitive compositions, such as those used in primers, maintain their characteristic detonation rates in columns of about one millimeter in diameter. Very insensitive highly explosive compositions such as some ammonium nitrate blasting agents will detonate only in columns of many centimeters in diameter.

As noted, high explosives are usually initiated by the explosion of a highly sensitive priming explosive, even though reaction started by a flame or other

heat source may "run up" to detonation. In fact, "run up" from flame initiation is too erratic and too slow for practical use, especially in view of the precise sequencing needed in most explosives applications.

Confinement

On first thought it might seem that confinement of an explosive would inhibit explosive reaction, especially deflagration, on the basis of Le Chatelier's principle. It is true, of course, that increasing the pressure tends to inhibit or reverse gas generating reactions in systems close to equilibrium. Explosive reactions are so far from equilibrium that even the enormous pressures generated under confinement have but limited effect on the course of the reaction. Furthermore, the temperature reached in deflagration is much higher if the gaseous products are not free to expand; as a result the reaction rate is much higher under confinement.

Note that confinement can be overdone. For example, an isolated borehole in massive rock may withstand a powerful explosion without rupture. The explosive may have developed its maximum rate and released all its contained energy, but no useful work will have been performed. Similarly, an explosive charge detonated in the open air may do no useful work. On the other hand, a properly sized and emplaced charge in good contact with the walls of the borehole may achieve high thermal efficiency. In the best case some 70% or more of the thermal energy released may be converted to useful work in fracturing and moving the rock.

Some typical chemical explosives

Since the advent of synthetic chemistry in the mid 19th century, hundreds of explosive compositions have joined black powder, the world's only explosive for some 600 years. It is convenient to assign these many explosives to one of two main classes: those that deflagrate but do not detonate (low explosives), and those that detonate (high explosives). High explosives are further classified according to ease of initiation. Those that detonate readily upon heating or impact are called primary explosives. Those requiring explosive initiation are called secondary explosives. Blasting agents are a relatively new class, insensitive to an ordinary blasting cap but detonable by a powerful booster charge.

Low explosives

Black powder is a non-detonating (low) explosive. It is made by blending potassium nitrate, an oxidizing substance, with carbon and sulfur. Sulfur is believed to have a special role in promoting ignition and propagation. The ingredients are ground separately, then milled together for hours. The individual particles of the resulting blend, however, still contain billions of molecules. The oxidizing and reducing constituents are, consequently, much further apart

than they are in an explosive compound such as nitroglycerin. As a result, black powder explosions propagate at only about 6% the rate achieved by high explosives. The pressure pulse delivered by black powder is well adapted to heaving chunk coal out of a seam, or hurling a projectile from a gun. More specialized explosives, however, have taken over almost all former applications of black powder. Principal classes of explosives now in use are discussed briefly below.

Powerful, reliable, and smokeless nitrocellulose gunpowders have replaced black powder in almost all propellant uses. This class of synthetic explosives, formulated so as to deflagrate rather than to detonate, provides a pressure pulse suitable for propulsion rather than shattering.

High explosives

Primary high explosives are the active ingredients in caps and detonators used to set off secondary explosives. Much too dangerous to use or handle in bulk, they are, nevertheless, an essential part of most explosive systems. Many primary explosives were discovered by chance. Mention has been made of mercury fulminate, the first primary explosive, now obsolete. Diazodinitrophenol, a currently used primary explosive, was first investigated by P. Griess, a German dyestuff pioneer; he noted its explosive properties with dismay!

Hundreds of secondary explosives have been made and used, but the nitroglycerin dynamites furnish the archetypical examples. Reasonably safe in storage and use, the many varieties of dynamite satisfied most of the world's industrial explosive needs from Nobel's time until the 1950's. Although now displaced from most large-scale uses, dynamites continue to fulfill many vital specialty needs.

Blasting agents are extremely insensitive but powerful explosives based on ammonium nitrate. They require massive high explosive booster charges, but are exceptionally safe and economical in use. The many varieties of AN explosives are taking over most large scale explosives applications.

Industrial uses of explosives

The industrial applications of explosives can be grouped into four categories: mining, quarrying, transportation-related uses, and a grab bag of miscellaneous uses.

Mining

Mining in rudimentary form has been practiced since long before the dawn of history – first with tools of bone, stone, and wood, later with tools of metal. In the "cold" method, mine faces, vertical or horizontal, were penetrated with a pattern of drill holes into which wedges were driven to split off the rock or ore. In the "hot" method, huge wood pyres were burned against a vertical work-

ing face to induce thermal stresses resulting in cracks and fissures. Either method required prodigal use of labor and was horribly cruel to the miners. It has been said with good reason that only the advent of explosives made mining a fit occupation for free men.

Black powder became a mainstay of underground mining following its introduction in the 17th century. Boreholes were made in the working face just as in the traditional "cold" method, but they were packed with the black powder and then fired. As compared with wedging, the results were spectacular. As usual, there was a price to be paid. Hundreds of powder makers and miners were maimed or killed in accidental explosions over the course of the next century until reasonably safe techniques were developed. Black powder charges must be confined (stemmed) to produce blast effects. Wooden plugs used for this purpose became deadly missiles when the charges were fired. Substitution of clay plugs finally alleviated this hazard. Bickford's reliable factory-made burning fuse vastly reduced accidents related to firing the charges. Hundreds of additional innovations contributed to mining safety and productivity.

When dynamites were introduced in the 1870's they proved to be far more effective than black powder and soon displaced the latter. Varieties of different strength were developed to match the properties of various rock structures. Here too, proper confinement (stemming) proved necessary to achieve efficient and safe use of the explosive energy. The smoke and fumes of black powder were eliminated in favor of the relatively innocuous explosion products of oxygen-balanced dynamites. Specialized explosives were developed for use in mines. For example, "permissibles" featuring relatively low explosion temperatures were developed to minimize the risk of igniting flammable gases in coal mines.

In recent years explosives more economical than dynamites have been introduced, as have sophisticated, precisely timed sequential blasting patterns. Underground mining is now a highly technical operation in which working conditions have been brought to approximate parity with many surface occupations.

The development of gargantuan machinery and extremely economical explosives has made it practical to carry out many mining operations from the surface. For example, most large iron and copper deposits are worked by stripping away the earth or rock overburden, then digging out the valuable mineral.

Copper ores are frequently compact and mechanically strong; they must be broken up by blasting before they can be removed. The taconite iron ore deposits now being worked in the Lake Superior region are also extremely tough. Only the development of inexpensive but powerful AN explosives has made possible their exploitation.

Strip mining currently accounts for about 90% of all US coal production. The path of the coal seam is marked out on the surface, then drilled with a pattern of blast holes extending to the depth of the coal. These holes may be

as much as 50 cm in diameter and 50 m deep. The holes are charged with ammonium nitrate explosive, frequently AN mixed with fuel oil, then fired in a carefully planned pattern. The broken-up overburden is then removed by large shovels or drag line machines with buckets capable holding as much as 140 m^3. The coal is removed from the open trench and hauled away. This sort of mining is feasible only in view of the extremely economical ANFO explosives which can be mixed on site for about 40 US dollar cents/ kg. Strip mining of coal in the USA consumed about a million metric tons of AN explosives in 1988 and accounted for some 60% of all explosives used during that year. Restoration of the countryside ravaged by this sort of mining is another issue.

Quarrying

Building stone (dimension stone) is usually cut from the quarry face by means of a wire saw. Explosives are used only for clearing overburden or to remove obstacles.

Quarrying for crushed rock or to win rocky mineral deposits, is similar to open pit mining. The formation is drilled from above with carefully planned rows of blast holes. These are charged with explosive and fired in sequence, row after row, so as to clear the working face before the next row is fired. The aim is to bring down the whole working face, leaving the broken rock in the desired location and in a size manageable for removal. The intricate firing systems used include precision timers and detonation trunk lines to connect the multiple charges.

Transportation-related uses

Rapid transportation is a hallmark of modern civilization. In spite of increases in air transport, most cargo is still carried on the earth's surface. High speeds can be sustained only on routes with gentle grades and wide curves. Highway construction now requires nothing less than re-shaping the landscape. For example, in one 30 mile stretch of Interstate Route 87 in the state of Vermont there are some 30 major rock cuts, the largest of which required the removal of about half a million m^3 of solid granite. Crushed rock fills have been used on a similarly lavish scale. Working of granite on this scale is unthinkable without explosives.

In blasting for highway cuts geologists and explosive experts develop a strategy based on such factors as the physical properties of the rock and its natural fault and fracture patterns. Borehole patterns and depths as well as firing patterns are carefully planned to match the properties of the selected explosive. It is imperative that the whole wall be brought down, since under-shooting may leave jagged remnants that are difficult to reach for re-blasting. Rock fragments must not be propelled beyond the boundaries of the evacuated zone. Finally, the broken rock must be laid down in a position and in a size range that the loading and hauling equipment can handle.

If an obstacle is too massive to be removed it may be penetrated with a tunnel. Hard rock tunnels are advanced in much the same manner as horizontal mine workings and gain the same advantages from the use of explosives.

The first black powder tunneling seems to have been carried out in 1680 to pass the famous Canal Du Midi through a hill near Beziers, France. Blasting for canal tunnels became commonplace in Europe and in the US during the early 18th century. Railroad building, however, provided the incentive for the great age of tunneling in the late 18th century. Dynamite appeared in time to play a key role in the construction of the famous Alpine tunnels as well as many equally important but less famous tunnels elsewhere. With mechanical rock drills, powerful explosives, and power driven "muck" removal, tunnel advance rates increased as much as ten fold in the years from 1860 to 1890. By the turn of the century methods had achieved essentially their present level.

As hills and rocks interfere with land transport, underwater obstacles can interfere with water transport. For example, the Hudson River together with Long Island Sound provides New York City with one of the world's finest natural harbors. Nevertheless, these waters once contained several dangerous obstacles to navigation. In 1851 an obstacle known as "Pot Rock" was removed by the explosion of about 100 tons of black powder, one of the largest intentional blasts ever with this explosive. In 1885 a rocky structure in the Hell Gate channel between Long Island Sound and New York harbor proper was blasted away with a charge containing some 150 tons of a potassium chlorate–nitrobenzene composite explosive. In 1958 a submerged rocky peak in the harbor of Vancouver, Canada, was removed by the explosion of a 1000 ton charge. The obstructing rock was "mined" by drilling a tunnel from the shore, then excavating a series of horizontal passages to hold the explosive.

Removal of underwater obstacles is a near-ideal application of explosives, far more effective than any other means.

Miscellaneous uses

Urban residents seldom lay eyes on explosives, but they are nevertheless indispensable in such tasks as preparing building foundations on rocky sites. Construction of streets and laying of utility lines in rocky ground are equally dependent on explosives. Individual explosions in such activities are usually quite small but the results achieved are spectacular in comparison with alternative means to the same ends.

Dynamite was a standard feature of farm life a century ago. Blasting was the method of choice for excavating drainage ditches, for removing stumps, and for breaking up boulders. Before dynamite, black powder was manufactured in hundreds of local powder mills and commonly stocked by rural hardware stores. Explosives were considered indispensable for opening up a new land. Today the need has lessened, in part because the most onerous obstacles have been

removed and in part because powerful bulldozers now can do what only blasting once could.

Explosives are also used in demolishing overaged or damaged structures. Using charges of high explosives in the form of metal-lined hollow cones it is possible to shear off almost any structural element in a blast of hot plasma. This "shaped charge" technique makes it easy to demolish a bridge, or collapse a tall building upon itself. Where it is appropriate to use, explosive demolition is frequently the most expeditious method, considerably less hazardous to the workmen than conventional wrecking techniques.

The current status of explosives science

The products of an explosive decomposition are among the most exotic on earth. For a few microseconds the temperature may be several thousands of degrees, the pressure several hundreds of thousands atmospheres. In spite of the obvious experimental and theoretical difficulties, several generations of researchers in chemistry, thermodynamics, and hydrodynamics have produced reasonably complete knowledge of the explosion process and its products. This knowledge has led to striking advances in explosives safety, efficacy and economy. In addition, study of materials under the extreme conditions following explosion has led to fundamental advances in our understanding of the physical world.

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Further reading

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