EXPLOSIVES
AP-42 Section 5.6
Reference Number
1

third edition

CHEMICAL PROCESS INDUSTRIES

R. NORRIS SHREVE
CONSULTING CHEMICAL ENGINEER
PROFESSOR EMERITUS OF CHEMICAL ENGINEERING
PURDUE UNIVERSITY

McGRAW-HILL BOOK COMPANY
NEW YORK ST. LOUIS SAN FRANCISCO
TORONTO LONDON SYDNEY

22 EXPLOSIVES, TOXIC CHEMICAL AGENTS, AND PROPELLANTS

INDUSTRIAL AND MILITARY EXPLOSIVES

Many professional chemists and chemical engineers tend to view the subject of explosives from a purely military standpoint. Although explosives have contributed much to the destruction of man, they have also enabled him to perform many great engineering feats which would have been physically or economically impossible without their use. Large engineering projects such as Hoover Dam and the St. Bernard Tunnel would have taken hundreds of years if performed by hand labor alone. Explosives are among the most powerful servants of man. Mining of all kinds depends on blasting, as does such a prosaic but necessary act as the clearing of stumps and large boulders from land. Truck brakes are relined and airplanes are constructed with rivets which have an explosive in the shank, fired by heat, with the consequent saving of much time and effort. Recent use of controlled underwater explosives to shape metals offers a steadily growing outlet and presents a new, versatile, and economical method for fabrication techniques.

HISTORY AND ECONOMICS An explosive mixture of sulfur, charcoal, and saltpeter, or *black powder*, was known to the Chinese centuries ago; its use in propelling missiles was demonstrated shortly after 1300. The discoveries of nitroglycerin and nitrocellulose shortly before 1850 and the invention of dynamites and the mercury fulminate blasting cap soon after were epochal events of the *high-explosives* era. *Atomic explosives*, discussed in the preceding chapter, first detonated in 1945, mark the third broad stage in the history of explosives. Superior products, such as smokeless powder, first made in 1867, have been developed through the years; the demand for more powerful explosives for the present space program serves as a continuing challenge to chemical engineers. In peacetime large quantities of commercial explosives are consumed, as listed in Table 22.1. In times of war tremendous quantities are required; for example, roughly 60 billion lbs were manufactured between January, 1940, and V-J Day in the United States. In the decade 1950–1960, sales increased from 720 to 1,080 million lb/year. There are at least 150 chemicals or chemical formulations useful as explosives. However, a wide variety of other chemicals which have had military or commercial use have been abandoned or replaced by more effective explosives. Among those having only a limited use as such today are trinitrobenzene and starch nitrate.

CLASSIFICATION An explosive is a material which, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and much gas. The hot gases cause extremely high pressure if the explosive is set off in a confined space. Explosives differ widely in their sensitivity and power. Only those of a comparatively insensitive nature, capable of being controlled and having a high energy content, are of importance commercially or in a military sense. There are three fundamental types of explosives, mechanical, atomic, and chemical; the primary concern of

TABLE 22.1 ***Industrial Explosives Sold for Consumption in the United States, by Use, 1963–1964 (In pounds)***

	Coal mining		*Metal mining*		*Quarrying and nonmetal mining*		*Railway and other construction work*		*Seismograph*		*All other purposes*	
Kind of explosive, apparent consumption of:	*1963*	*1964*	*1963*	*1964*	*1963*	*1964*	*1963*	*1964*	*1963*	*1964*	*1963*	*1964*
Black blasting powder:												
Granular	259,700	108,375	....	6,300	168,650	144,850	30,225	40,125	2,000	5,400	41,250	146,125
Pellet	496,850	341,300	900	....	84,800	47,800	49,500	72,550	100	50	3,900	33,100
Total	756,550	449,675	900	6,300	253,450	192,650	79,725	112,675	2,100	5,450	45,150	179,225
High explosives:												
Permissible	75,149,925	75,949,780	73,750	116,850	560,465	740,765	226,625	291,350	7,200	27,900	301,500	279,725
Fixed, other than permissible	23,397,356	23,556,914	84,657,286	119,782,339	133,216,056	133,022,388	133,334,307	133,161,885	44,663,622	67,997,244	3,510,724	3,930,588
Ammonium nitrate blasting agents:												
Processed	404,906,660	183,126,142	168,068,342	83,013,541	186,603,026	150,070,909	172,195,875	117,678,955	16,376,256	17,704,203	5,703,428	3,787,805
Unprocessed		264,018,557		115,380,578		77,218,737		80,875,068		5,503,319		5,185,479
Total	503,453,941	546,651,393	252,799,378	318,293,308	320,379,547	361,052,799	305,756,807	332,007,258	61,047,078	91,232,666	9,515,652	13,183,597
Liquid oxygen explosives	1,833,720	2,183,851										
Grand total	506,044,211	549,284,919	252,800,278	318,299,608	320,632,997	361,245,449	305,836,532	332,119,933	61,049,178	91,238,116	9,560,802	13,362,822

Source: Mineral Industry Survey, 1964, Bureau of Mines.

this chapter is with chemical explosives. For purposes of classification it is convenient to place chemical explosives in two divisions in accordance with their behavior:

1. Detonating, or high, explosives. (*a*) Primary, or initiating, explosives (detonators): lead azide, mercury fulminate, lead styphnate (lead trinitroresorcinate), diazonitrophenol, nitromannite. (*b*) Secondary: TNT-AN, tetryl,[1] PETN, RDX, TNT, ammonium picrate, picric acid, DNT (dinitrotoluene), and EDNA.

2. *Deflagrating, or low, explosives.* Smokeless powder (colloided cellulose nitrate), black powder, NG, DNT (dinitrotoluene), nitrocotton.

Cook[2] lists the major chemicals according to military or commercial use. Variations in their blasting characteristics are attained by (1) physical conditions such as density and granulation and (2) combinations of ingredients—paraffin, aluminum, and waxes, for example. A table of nonexplosive ingredients appears in the same reference.

Initiating, or primary, high explosives are quite sensitive materials which can be made to explode by the application of fire or by means of a slight blow. They are very dangerous to handle, and are used in comparatively small quantities to start the explosion of larger quantities of less sensitive explosives. Initiating explosives are generally used in primers, detonators, and percussion caps. They are usually inorganic salts, whereas the secondary high explosives and many conventional propellants are largely organic materials.

Secondary high explosives are materials which are quite insensitive to both mechanical shock and flame but which explode with great violence when set off by an explosive shock, such as that which would be obtained by detonating a small amount of an initiating explosive in contact with the high explosive. Decomposition proceeds by means of a detonation, which is a rapid chemical destruction progressing directly through the mass of the explosive. This detonation is thought to be a chain reaction, and proceeds at rates that are frequently as high as 20,000 ft/sec for high-velocity dynamites. It is this *high rate of energy release*, rather than the total energy given off, that makes a product an explosive. Nitroglycerin has only one-eighth the potential energy of gasoline. On the other hand, most high explosives, when unconfined or unshocked, will merely burn if ignited.

Low explosives, or *propellants*, differ in their mode of decomposition from high explosives; they only burn. Burning is a phenomenon that proceeds not through the body of the material, but in layers parallel to the surface. It is quite slow in its action, comparatively speaking, rarely exceeding 0.25 m/sec. The action of low explosives is therefore less shattering. Low explosives evolve large volumes of gas on combustion in a definite and controllable manner.

The industrial classification used in Table 22.1 is that of the U.S. Bureau of Mines, where *black blasting powder* refers to all black powder having sodium or potassium nitrate as a constituent. Here *permissible explosives* include ammonium nitrate explosives, hydrated explosives, organic nitrate explosives, and certain nitroglycerin explosives that contain an excess of free water or carbon. The permissible explosives must pass certain tests[3] to ensure a minimum of flame and temperature to reduce fires in coal mines where

---

[1] Because of higher brisance, tetryl is also used as a booster between the primary and secondary high explosives.

[2] Cook, Science of High Explosives, ACS Monograph 139, p. 4, Reinhold, 1958; in Riegel, Industrial Chemistry, Reinhold, 1962, pp. 676–683, will be found an extensive list, together with characteristics and uses.

[3] Active List of Permissible Explosives and Blasting Devices, *U.S. Bur. Mines, Explosives Div., Rept. Invest.* 5910.

TABLE 22.2 *Summary of Characteristics of Explosives*

Name	Formula	Products per formula weight	Qv, cal/kg	Te, C	f, kg/sq cm	V, m/sec	Trauz expansion,
Gunpowder	$2KNO_3 + 3C + S$	$N_2 + 3CO_2 + K_2S$	501	2090	2,970	.....	30
Nitrocellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5CO + 3.5CO_2 + 14.5H_2O + 5.5N_2$	1,250	2800	10,000	6,100	420
Nitroglycerin	$C_3H_5(NO_3)_3$	$3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$	1,526	3360	9,835	8,500	590
Ammonium nitrate	NH_4NO_3	$2H_2O + N_2 + 0.5O_2$	384	1100	5,100	4,100	300
TNT	$C_7H_5(NO_2)_3$	$6CO + C + 2.5H_2 + 1.5N_2$	656	2200	8,386	6,800	260
Picric acid	$C_6H_2(OH)(NO_2)_3$	$6CO + H_2O$ $0.5H_2 + 1.5N_2$	847	2717	9,960	7,000	300
Ammonium picrate	$C_6H_2(NO_2)_3ONH_4$	$6CO + H_2O + 2H_2 + 2N_2$	622	1979	8,537	6,500	230
Tetryl	$C_7H_5N_5O_8$	$7CO + H_2O + 1.5H_2 + 2.5N_2$	908	2781	10,830	7,229	320
Mercury fulminate	$Hg(ONC)_2$	$Hg + 2CO + N_2$	420	4105	5,212	3,920	21.5
Lead azide	PbN_6	$Pb + 3N_2$	684	3180	8,070	5,000	250

Qv = heat of explosion at constant volume (small in comparison with fuels, but explosives exert their energy rapidly
Te = explosion temperature.
f = specific pressure, i.e., exerted by 1 kg in volume of 1 liter at *Te* heat.
V = velocity of detonation wave (currently measured by high-speed photography).

Source: After Meyer, Science of Explosives, Crowell, 1943; for more recent investigations of characteristics of explosives Cook, Science of High Explosives, ACS Monograph 139, p. 284, table 12.1; a more extensive list will be found Industrial Chemistry (Kent ed.), pp. 676–683, Reinhold, 1962, together with characteristics and uses.

99% of the permissibles are employed. Ammonium nitrate constitutes over 65% of the weight of the permissibles. The *high explosives* used in industries are the usual dynamites. In general, commercial explosives are not applicable to military use since they are sensitive to impact and shock, especially the dynamites, thus presenting serious risks. Furthermore, they do not possess the necessary brisance, mentioned below.

PROPERTIES OF EXPLOSIVES In order to compare explosives for suitable use, the most important standard tests are those employed to determine sensitivity, stability, brisance, and strength. Additional tests for volatility, solubility, density, hygroscopicity, and also for compatibility with other ingredients and resistance to hydrolysis are made if explosive meets the first ones listed before use for commercial or military purposes be evaluated. Cost of manufacture and toxicity of materials must also be taken into consideration.

The *brisance* (shattering action) of an explosive may be measured by exploding a small quantity of it in a *sand bomb*, a heavy-walled vessel designed to resist the explosion without being ruptured. Another test of a somewhat similar nature is the *Trauzl block*. This test measures the strength of the explosive by measuring the ballooning of a soft lead cylinder in which the explosive is inserted and exploded. The standard Trauzl block is 200 mm in diameter and 200 mm high, with a central hole 25 mm in diameter and 125 mm deep. Ten grams of the explosive is used in making the test, and the results are reported as terms of the cubic centimeters of increase in volume caused by detonation of the explosive. Brisance is probably a combination of the strength and the velocity. Cook states that there is no reason to believe that brisance is power: it seems to be directly related to detonation pressure.[1]

The *sensitivity*[2] of an explosive to *impact* is determined by finding the height from which a standard weight must be allowed to fall in order to detonate the explosive. This test is of greatest importance in the case of initiating explosives.

It is important that explosives for use in mines, particularly coal mines, be of such a type that they evolve no poisonous gases on explosion and produce a minimum of flame. This latter requirement is necessary in order that the explosive be incapable of igniting mixtures of air and coal dust, or air and methane (fire damp), which inevitably occur in coal mines. Explosives for mine use are tested, and their properties specified by the U.S. Bureau of Mines; they are commonly known as *permissibles*. Permissibles differ from other explosives, particularly black powder, most markedly in the fact that they produce a flame of small size and extremely short duration. Permissibles contain coolants to regulate the temperatures of their flames, and hence further reduce the possibility of their ignition of combustible mixtures. Permissibles are tested by explosion in a long gallery filled with coal dust, air, and methane, which should not ignite this mixture.

MILITARY EXPLOSIVES

Possibly the most powerful nonatomic military explosives are the cast aluminized mixtures such as Torpex and HBX (RDX, TNT, aluminum, and wax). As their requirements are extremely strict, only a few of them have survived the competitive testing, and even fewer will be described here. In this connection it is fundamental to understand the construction of a high-explosive artillery shell as depicted in Fig. 22.1. Such a shell consists of a thin brass or steel cartridge case holding the primer, igniter, and propellant charge. This case is designed to fit smoothly into the gun and, on explosion, to expand (obdurate), sealing the breech of the gun so that the escape of gases from the burning of the propellant charge is prevented, thus allowing the full effect of the propellant to be exerted on the projectile, or destructive half of the shell. The *primer* contains a small amount of a primary explosive or sensitive mixture [e.g., lead azide or a mixture such as $KClO_3$ + $Pb(CNS)_2$ + Sb_2S_3 +

---

[1] Cook, *op. cit.*, p. 271.

[2] [illegible], Sensitivity of Explosives. *Chem. Rev.*, **62**, 41 (1962). With 140 refs.

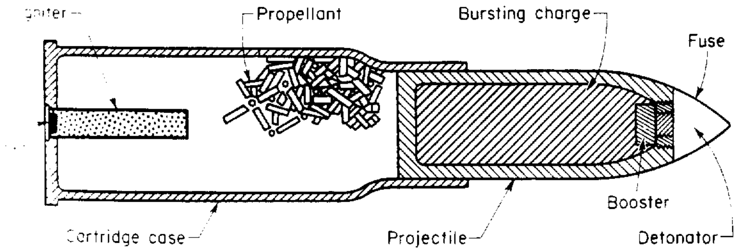


Fig. 22.1 Complete round of high-explosive ammunition.

TNT + ground glass]. This mixture explodes under the impact of the firing pin and produces a flame which ignites the black-powder[1] charge in the *igniter*, in turn igniting the *propellant* charge of smokeless powder. The burning of the smokeless powder causes the rapid emission of heated gas, which ejects the *projectile* from the gun. At the target, upon impact or upon functioning of the time-fuse mechanism, a small quantity of a primary explosive (*detonator*) is set off; this causes the explosion of the *booster*—an explosive of intermediate sensitivity (between that of a primary explosive and the bursting charge) which picks up the explosive wave from the primary explosive, amplifies it, and ensures the complete detonation of the bursting charge. The *bursting charge*, or high explosive, is usually TNT alone or in admixture with, for example, PETN, RDX, or tetryl.

NITROCELLULOSE[2] The explosive properties of nitrated cotton were recognized at an early date. The discovery of methods of colloiding the material into a dense uniform mass of resinous appearance reduced the surface and the rapidity of explosion. With the discovery of suitable stabilization methods to prolong its storage life, nitrocellulose soon put black powder out of use as a military propellant.

The cellulose molecule is a highly complicated one, with a molecular weight that is frequently as high as 300,000. Any given sample of cellulose will contain a wide distribution of molecular weights, all having the empirical formula $(C_6H_7O_2(OH)_3)n$. There are thus three hydroxyl groups per fundamental (glucose) unit that may be esterified with nitric acid, indicating a theoretical nitrogen content of 14%, which is higher than any commercially used product. The reaction may be formulated

$$C_6H_7O_2(OH)_3 + 3HONO_2 + H_2SO_4 \longrightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O + H_2SO_4$$

Celluloses that have not been nitrated completely to the trinitrate are used for the various industrial cellulose nitrates, as shown in Fig. 22.3. In addition to the nitrate esters, some sulfate esters are formed by the sulfuric acid, which is added to tie up the water resulting from the nitration reaction and to permit the reaction to progress to the right. These sulfate esters are unstable, and their decomposition would give rise to a dangerous acid condi-

---

[1] Black powder is easy and smokeless powder difficult to ignite; therefore black powder is frequently used to ignite smokeless powder.

[2] Although the word "nitrocellulose" is commonly used for nitrated cellulose fiber, it should be noted that the material is not a nitro compound but a true nitrate ester. The name *cellulose nitrate* is therefore chemically more proper, but nitrocellulose is much more widely employed in technical spheres.

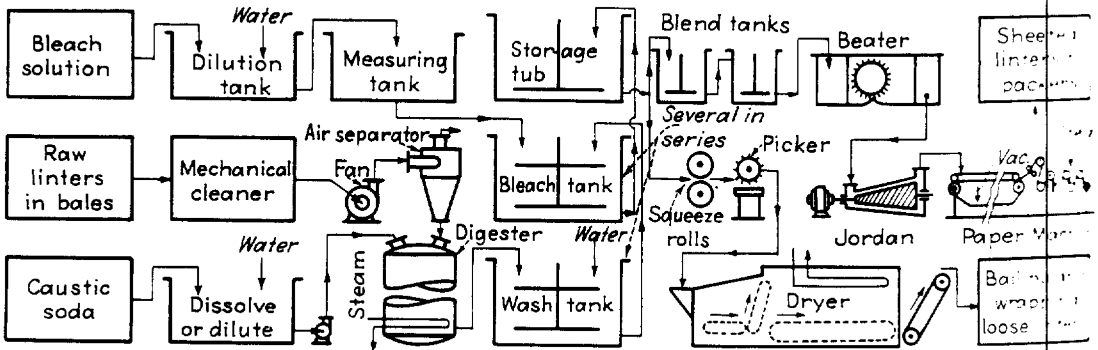


Fig. 22.2 Flowchart for chemical cotton.

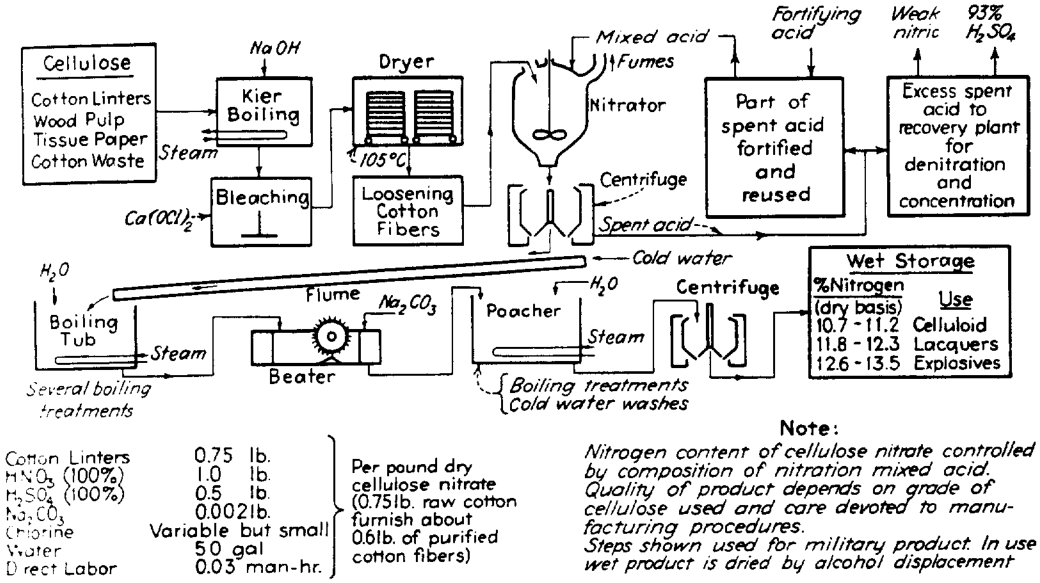
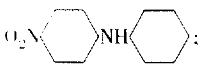
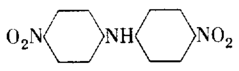


Fig. 22.3 Flowchart for nitrocellulose (cellulose nitrate).

tion in the stored powder if not removed; they are decomposed in the poaching process. A cold, dilute NH_4OH solution was recently proposed to attain the same net effect of the poaching step.

The finished nitrocellulose should not be allowed to become acid in use or storage since this catalyzes its further decomposition. A stabilizer is therefore added which reacts with any trace of nitrous, nitric, or sulfuric acid that may be released because of the decomposition of the nitrocellulose and thus stop further decomposition. For smokeless powder diphenylamine is used (diphenylurea in Great Britain), and for Celluloid, urea. The diphenylamine forms a series of innocuous compounds with the evolved gases, of which the following are examples:


;


The commercial manufacture of cellulose nitrate is illustrated in Fig. 22.3, with the following sequences:

Cotton linters, or specially prepared wood pulp, are purified by boiling in Kiers (vats) with [illegible] caustic solution (Ch). (See Fig. 22.2.)

Bleaching is effected with CaCl.OCl or NaOCl or $Ca(OCl)_2$ (Ch).

The cotton is dried, fluffed, and weighed (Op).

Mixed acid is made up from fortifying acid and spent acid, brought to proper temperature and [illegible] into the nitrator (Op).

Nitration (esterification) is usually conducted under carefully controlled conditions in a "mechanical-dipper" nitrator (Ch).

One nitrator charge is formed by 32 lb of purified and dried cotton linters. The cotton is agitated with approximately 1,500 lb of mixed acid at 30 C for about 25 min. The composition of the acid used averages: HNO_3, 21%; H_2SO_4, 63%; N_2O_4, 0.5%; H_2O, 15.5%.

The entire nitrator charge is dropped into a centrifugal, where the spent acid is centrifuged from the nitrated cellulose (Op).

The spent acid is partly fortified for reuse and partly sold or otherwise disposed of, as by denitration and concentration of the sulfuric acid (Op and Ch).

The nitrated cotton is drowned with water, washed by boiling, and again washed in a beater (Op).

In order to produce a *smokeless powder* more stable on storage, the following purification is employed in these two steps and the poaching, to destroy unstable sulfate esters and to remove free acid completely:

(1) 40 hr of boiling with at least four changes of water, and (2) pulping of fiber by means of beater or a Jordan engine followed by:

Poaching of the washed nitrated cotton by boiling first with a dilute Na_2CO_3 solution (5 lb soda ash per ton of the cellulose nitrate) and then with many washes of boiling pure water (Op).

The poached nitrocellulose is freed of most of its water by centrifugation. This usually results in a water content of approximately 28% (Op).

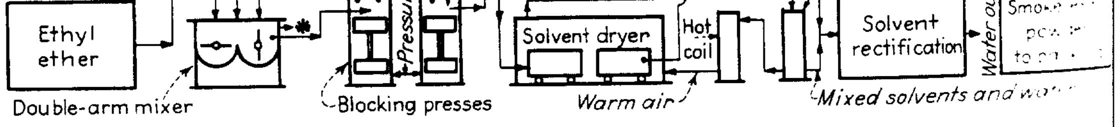
At this point the nitrocellulose is usually stored until desired, and the complete laboratory examination can be made (Op).

The water content of the nitrated cotton is reduced to a low figure by alcohol percolation under pressure dehydration (Op).

The nitrated cellulose is disintegrated, then "colloidized" by mixing with alcohol, ether, diphenylamine, and other modifying agents (Op).

Grains are formed by extrusion through dies, and these are dried and blended to form smokeless powder (Op); see Fig. 22.4.

The nitrocellulose produced in this manner contains about 12.6% nitrogen, and is known as *pyrocotton*. By using a stronger acid, the nitrogen content may be made as high



For a flow sheet for nitrocellulose manufacture see Fig.3

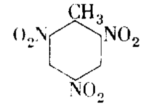
✱ **Note:** Asterisks denote equipment connected to solvent recovery system

Fig. 22.4 Flowchart for smokeless powder.

as 13.6% nitrogen. Cotton nitrated to contain 13.2% nitrogen or greater is known as *guncotton.* Modern military smokeless powder contains about 13.15% nitrogen, and is made from a blend of pyro- and guncotton.

Smokeless powder is colloided nitrocellulose containing about 1% of diphenylamine to improve its storage life and a small amount of a plasticizer (e.g., dibutyl phthalate). The manufacturing sequences are given by Fig. 22.4. The British form their colloided double-base powder (Cordite) by treating a high, or 13% nitrogen, nitrocellulose with a mixture of acetone and nitroglycerin and some petroleum jelly. The nitroglycerin increases the heat of burning of the powder and keeps the grains from becoming brittle.

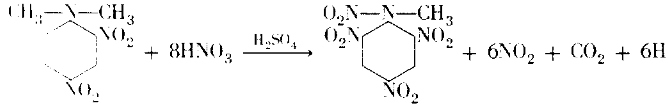
TRINITROTOLUENE In spite of other new explosives developed during World War II,



symmetrical trinitrotoluene (TNT) is still the most important military high explosive used in this country. Because of the low melting point of commercial TNT (80.3 C), it is loaded into shells in the molten state by mechanical devices. It is superior to picric acid from the standpoint of safety by reason of its lower melting point and the fact that it has no tendency to form sensitive salts with metals. TNT is made by three-stage[1] nitration of toluene with mixed acids in cast-iron or steel nitrators. The crude TNT, or "tri-oil," may be purified by a water and soda ash wash, followed by a sellite (acidulated 16% Na_2SO_3) wash. The first two serve to neutralize the excess acid, and the sellite reacts preferentially with the unsymmetrical TNT to produce water-soluble sodium dinitrosulfonates. Overall yields are excellent.

TETRYL (2,4,6-trinitrophenyl)-methylnitramine ($C_6H_2(NO_2)_3NCH_3NO_2$) is chiefly used as a base charge in blasting caps, as the booster explosive in high-explosive shells, and as an ingredient of a binary explosive. It is generally prepared by the action of mixed sulfuric and nitric acid on dimethylaniline in a multiple-stage nitration.

$$C_6H_5N(CH_3)_2 + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_3N(CH_3)_2.NO_2.NO_2 + 2H_2O$$



It may also be made by alkylating 2,4-dinitrochlorobenzene with methylamine, then nitrating.[2] Tetryl is an extremely powerful high explosive with great shattering power.

PICRIC ACID (2,4,6-trinitrophenol) is not made directly by the nitration of phenol because too many oxidation by-products are formed. It is manufactured instead by the mixed-acid nitration[3] of mixed phenolsulfonates.

EXPLOSIVE D, OR AMMONIUM PICRATE, is made by the neutralization of a hot aqueous solution of picric acid with ammonia water. It is used as an ingredient of picratol;

[1] See ECT, vol. 8, 581 (1965) for more exact conditions of time and composition of the three nitrating acids.

[2] Military Explosives, Depts. of the Army and Air Force, Technical Manual TM9–1910, p. 157, April, 1955.

[3] Formerly, strong nitric acid alone was used. Mixed acids cut down the health hazard caused by fuming, reduce the amount of acid required, and increase the yield of desired products. The use of mixed acid is now almost universal. For further details of manufacture, see Military Explosives, *op. cit.*, p. 161.

it is particularly suitable for use in *armor-piercing shells* because of its insensitivity to shock.

PETN, pentaerythritol tetranitrate ($C(CH_2ONO_2)_4$), is one of the most brisant and sensitive of the military high explosives. For use as a booster explosive, a bursting charge, or a plastic demolition explosive, it is desensitized by admixture with TNT (called Pentolite) or by addition of wax. PETN may be made by the nitration of pentaerythritol with strong nitric acid, 96% HNO_3, at about 50 C. The reaction of decomposition is probably

$$C(CH_2ONO_2)_4 \longrightarrow 3CO_2 + 2CO + 4H_2O + 2N_2$$

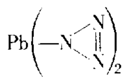
RDX, cyclonite, or *sym*-trimethylene trinitramine ($(CH_2)_3N_3(NO_2)_3$), is one of the most powerful explosives known at the present time. RDX is used in a mixture with TNT and aluminum, known as *Torpex*, for mines, depth charges, and torpedo warheads. It is also employed as an ingredient for explosive for shells and bombs, and it is desensitized by wax or oily materials. Pentolites, made by casting slurries of PETN with TNT, have specialized uses; for example, cast 50-50 pentolite is used as a booster for slurry blasting agents and prilled ammonium nitrate–fuel-oil mixtures and as the main charge in Procore boosters. The British developed the first practical process, which involved the destructive nitration of hexamethylenetetramine with concentrated nitric acid:

$$C_6H_{12}N_4 + 3HNO_3 \longrightarrow C_3H_6O_6N_6 + 3HCHO + NH_3$$

A combination process was developed by Bachman,[1] at the University of Michigan, who utilized the by-products to get a second mole of RDX. This method was developed on a *continuous scale* by Tennessee Eastman, who were able to manufacture it the most economically (yields of 70%):

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \longrightarrow 2C_3H_6O_6N_6 + 12CH_3COOH$$

LEAD AZIDE



has partially replaced mercury fulminate as an initiating, or primary, explosive for blasting caps. The fulminate had less than desirable stability, had to be manufactured in small batches, and involved the scarce raw material mercury. On the other hand, lead azide has remarkable stability, involves no strategic materials, and can be manufactured in large batches by treating sodium azide with lead acetate or nitrate. Sodium azide may be made from sodium amide and nitrous oxide:

$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O \qquad NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

$$2NaN_3 + Pb(C_2H_3O_2)_2 \longrightarrow Pb(N_3)_2 + 2Na(C_2H_3O_2)$$

EDNA, haleite, ethylenedinitramine ($(CH_2NHNO_2)_2$), developed first as a military explosive, has been found useful as a bursting-charge explosive and as an ingredient of the binary explosive ednatol. Its most economical manufacture involves the preparation of ethyleneurea (2-imidazolidine), nitrating with either concentrated acid or a mixture of nitric and sulfuric acid to the dinitro compound which is hydrolyzed to form haleite.[2] The

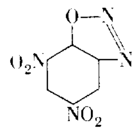
---

[1] Bachman, *J. Am. Chem. Soc.*, **71**, 1842 (1949).

[2] Military Explosives, *op. cit.*, p. 173.

latter separates as shining crystals, is caught on a filter, washed, and dried. It is more powerful than TNT, almost as sensitive to initiation as tetryl, and not stable as RDX.

DINOL Diazodinitrophenol, or 4,6-dinitrobenzene-1,2-diazooxide, was the first diazo



compound ever discovered (Griess, 1858). Its valuable properties as a primary explosive were not generally recognized until recent years. It is made by diazotizing picramic acid. An internal coupling yields the product desired.

INDUSTRIAL EXPLOSIVES

For blasting purposes large quantities of black powder, an intimate mixture of KNO_3, charcoal, and sulfur, usually in the approximate proportions 75-15-10, are still used. Thorough mixing is essential for good black powder; consequently, it is customary to work the mixed raw materials under a wheel mill, as depicted in Fig. 22.5. Black powder is relatively undesirable for use in mines because of the persistent flame produced on explosion and the ability of this flame to ignite gas and coal-dust mixtures. The considerable quantities of carbon monoxide evolved on its explosion are also a disadvantage. It remains in use principally because of its cheapness and because it is not shattering in its action. Upon explosion it liberates from each gram 718 cal and about 270 cc of permanent gases, but about 50% of the products are solids. Among these products are CO_2, CO, N_2, H_2S, H_2, K_2CO_3, K_2SO_4, K_2S, and unreacted constituents.

AMMONIUM NITRATE–FUEL-OIL BLASTING COMPOUNDS have almost completely replaced the majority of other industrial explosives in the surface mining, quarrying, and in construction industries. This blasting process reduces cost as much as 60% when compared with commercial dynamite. In 1962 alone, more than 600 million lb of AN was consumed in blasting.

NITROGLYCERIN AND DYNAMITE Nitroglycerin (NG) was the first high explosive to be employed on a large scale. The nitration is effected by slowly adding glycerin of high purity (+99.9%) to mixed acid having the approximate composition H_2SO_4, 59.5%; HNO_3, 40%; and H_2O, 0.5%. The nitration is accomplished in from 60 to 90 min in

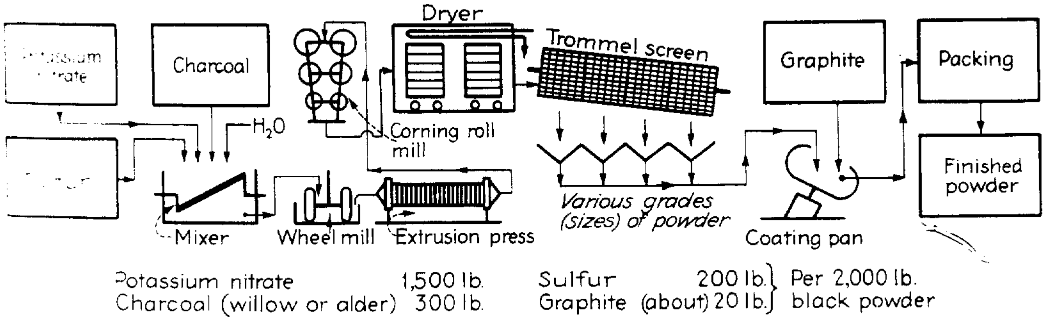
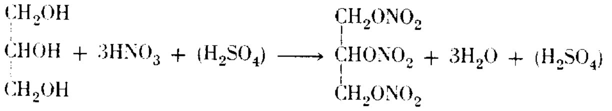


Fig. 22.5 Flowchart for manufacture of black powder.

agitated nitrators equipped with steel cooling coils carrying brine[1] at 5 C to maintain temperature below 10 C. After nitration, the mixture of nitroglycerin and spent acid allowed to flow through a trough (a trough is easier to clean completely than a pipe) in separating and settling tanks at some distance from the nitrator. The nitroglycerin is carefully separated from the acid and sent to the wash tank, where it is washed twice with warm water and with a 2% sodium carbonate solution to ensure complete removal of any remaining acid. Additional washes with warm water are continued until no trace of alkalinity remains. See Fig. 22.6, where the quantities of raw material are also listed. The product is really glyceryl trinitrate, and the reaction falls under the (nitrate) esterification classification.

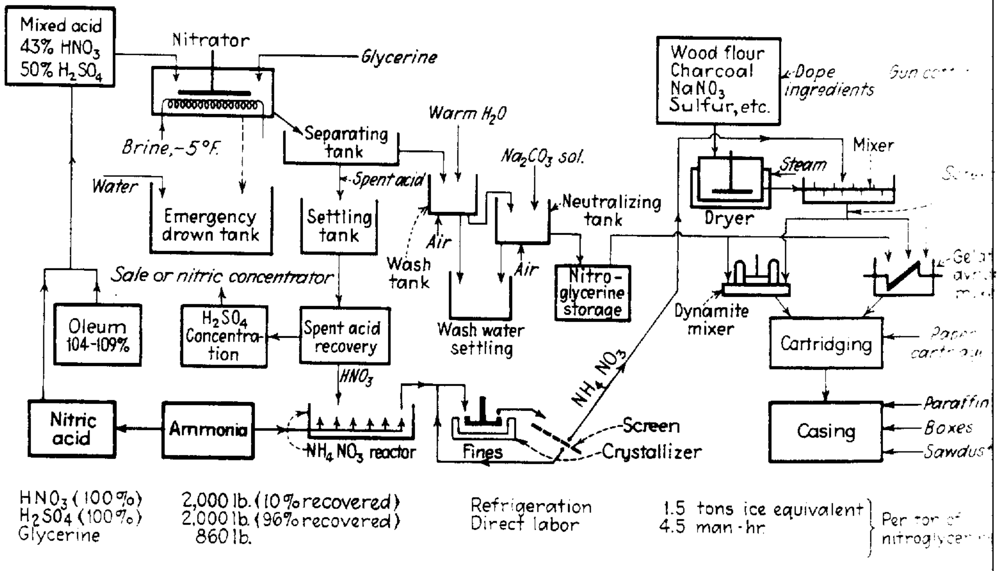


$$\begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3HNO_3 + (H_2SO_4) \longrightarrow \begin{array}{l} CH_2ONO_2 \\ CHONO_2 \\ CH_2ONO_2 \end{array} + 3H_2O + (H_2SO_4)$$

Nitroglycerin is a liquid similar in appearance to the original glycerin. It is quite sensitive to blows and freezes at 56 F; when solid it is less sensitive. Since it has a strong tendency in this state to explode incompletely, frozen nitroglycerin must always be thawed before using. To make nitroglycerin easier and safer to handle, it is usually manufactured into dynamite. The original dynamite was made by absorbing nitroglycerin in kieselguhr. Modern dynamites generally use wood flour, ammonium nitrate, or sodium nitrate as the agent employed to absorb the nitroglycerin, to which an oxidizer is added. Such a mixture is easy to handle, and can be made to contain as much as 75% nitroglycerin and yet

---

[1] Brine can be a little cooler than 5 C, but pure nitroglycerin freezes at 12.8 C. Freezing would be hazardous, since it might interfere with the temperature control.



HNO_3 (100%)	2,000 lb. (10% recovered)	Refrigeration	1.5 tons ice equivalent
H_2SO_4 (100%)	2,000 lb. (96% recovered)	Direct labor	4.5 man-hr
Glycerine	860 lb.		

Per ton of nitroglycerin

Fig. 22.6 Flowchart for nitroglycerin and dynamites. Usually an evaporator is needed between the ammonium nitrate reactor and the crystallizer.

retain its solid form. Because of the demand for a nonfreezing dynamite for work in cold weather, several dynamites containing other material designed to lower the freezing point of the nitroglycerin have been put on the market, for example, ethylene glycol dinitrate.[1] Such nonfreezing dynamites have potentials almost as great as "straight" dynamite. Nitrocellulose can be gelatinized by nitroglycerin, and the resulting firm jelly is an exceptionally powerful high explosive commonly known as *gelatin dynamite.* Almost without exception the nitro compounds and nitric acid esters used as explosives are toxic. The degree of *toxicity* varies widely with the material in question, but most are capable of causing acute distress if taken orally. Some materials used in the past have been extremely toxic; hexanitrodiphenyl amine, for example, is an active vesicant. Extremely toxic properties would weigh heavily against any new explosive that might be introduced.

TOXIC CHEMICAL WEAPONS[2]

Toxic chemical weapons, in modern parlance, include those substances which, by their chemical action, produce powerful physiological effects, screening smokes, or defoliant incendiary action. Although it is currently assumed that the employment of such chemicals began with World War I, incendiary and asphyxiating substances have been used over the centuries in warfare, but they reached a really effective stage on Apr. 22, 1915, with the release by the Germans of 600,000 lb of chlorine along a 2-mile front against an unprotected enemy. Although vast preparations for offensive and defensive use of toxic gases were made during World War II by all countries, gas warfare was rejected by all for various reasons.[3] Mutual distrust and fear, however, made preparedness a matter of vital importance. In World War II screening smokes and incendiaries proved to be extremely effective as well as in the Korean conflict.

TOXIC MATERIALS The use of the so-called *poison gases* in warfare[4] is a widely misunderstood and much maligned subject, the major cause of the misunderstanding being unreasoning fear and a lack of knowledge of the physical difficulties incident to establishing effective concentrations of casualty-producing[5] agents over wide areas. It should never be forgotten that, to apply any toxic-warfare chemical agent effectively, there is always

---

[1] DEGN, diethylene glycol dinitrate, was developed by the Germans as a replacement for nitroglycerin in double-base powders. After field testing in the Spanish Civil War, the Germans concentrated on this explosive, since it appeared to be superior to nitroglycerin. Diethylene glycol is nitrated to the dinitrate in practically the same manner as glycerin nitration (Fig. 22.6).

[2] Much of the older literature used the term "chemical warfare." CBR is an acronym meaning chemical, biological, and radiological operations. The two latter categories are outside the scope of this book. *Biological* weapons encompass the use of bacterial toxins, bacteria, rickettsia, and viruses for the production of casualties. The term *radiological* refers to the various isotopes of a number of elements produced in the fission process which might be used to contaminate an area but are considered impracticable. In selected areas, human, animal, and plant life might be destroyed with CBR by an enemy unless complete means for detection, protection, and decontamination are available. Cf. H.R. Rept. 815, Research in CBR Warfare, Committee on Science and Astronautics, 86th Cong., 1st Sess., 1959; Armed Forces Doctrine for Chemical and Biological Weapons Employment and Defense, FM 3-10, NPW 36 (c), AFM 355-2, LFM 03, Depts. of the Army, Navy, and Air Force, April, 1964.

[3] Rothschild, Tomorrow's Weapons: Chemical and Biological, McGraw-Hill, 1964; Rassweiler, What's So Terrible about Germ Warfare?, *Sat. Eve. Post*, Jan. 30, 1965, pp. 12–16; Lykken, L., Scientists, Social Problems, Science, **151** (3715), 1172 (1966).

[4] ECT, 2d ed., vol. 4, pp. 869–907 (1964). Excellent article with many references.

[5] It should be clearly understood that, in the military sense, a *casualty* is one who cannot perform his assigned military task. Casualties include both the wounded and the killed.