CHAPTER 8
UNITED STATES BOOSTER AND SECONDARY EXPLOSIVES

8-1. Introduction. This chapter contains discussions of military high explosive compounds. The explosives are arranged by chemical class. The chemical, physical, and thermochemical characteristics, sensitivity, performance, and stability are discussed for each explosive. The chemical structure of each compound is given, and for composition explosives, the ingredients are given. The method of manufacture is also given.

8-2. Aliphatic Nitrate Esters. Compounds in this class are prepared by *O-type* nitration in which a nitro group is attached to an oxygen atom of the compound being nitrated.

a. *1,2,4-Butanetriol Trinitrate (BTN).* This explosive is also known as α, β, γ− trihydroxybutane trinitrate and is sometimes referred to as BTTN. The compound (figure 8-1) is a light yellow liquid with a density of 1.520 at 20°C, a molecular weight of 241, a melting point of −27°C, an oxygen balance to CO_2 of −17 percent, and a refractive index of 1.4738 at 20°C. The liquid has a viscosity of 62 centipoises at 20°C. 1,2,4-Butanetriol trinitrate is slightly soluble in water, miscible with alcohol, ether, acetone, and a solution of 2 parts ether and 1 part alcohol. BTN has a heat of formation of 368 calories per gram, a heat of combustion of 2,167 calories per gram, and a heat of detonation of 1,458 calories per gram. This compound is a good gelatinizer for nitrocellulose and can be used as a substitute for nitroglycerin in double-base propellants. Heat, vacuum stability, and volatility tests indicate more stability than nitroglycerin. Impact sensitivity is about the same as for nitroglycerin. Brisance, as measured by the sand test, is about the same: 49 grams crushed versus 51.5 grams for nitroglycerin or 47 grams for TNT. The five second explosion temperature is 230°C versus 220°C for nitroglycerin. BTN can be manufactured by the nitration of 1,2,4-butanetriol with a mixture of nitric and sulfuric acids.

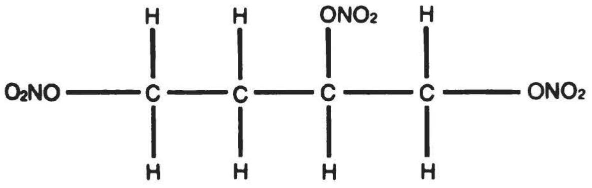


Figure 8-1. Structural formula for BTN.

b. *Diethyleneglycol Dinitrate (DEGN).*

(1) This explosive is also known as dinitrodiglycol or 2,2'-oxybisethanol dinitrate and is sometimes referred to as DEGDN. The compound (figure 8-2) is a clear, colorless, odorless liquid with a nitrogen content of 14.29 percent, a theoretical maximum density of 1.39 grams per cubic centimeter, an oxygen balance to CO_2 of −41 percent, and a molecular weight of 196. DEGN boils between160° and 161°C and can, upon cooling, form a stable solid with a melting point of 2°C or remain liquid to a freezing point of −11.2° to −11.4°C. Other characteristics of the liquid are: refractive index at 20°C with sodium light, 1.450; viscosity at 20°C, 8.1 centipoises; vapor pressure at 20°C, 0.0036 torr; vapor pressure at 25°C, 0.00593 torr; vapor pressure at 60°C, 0.130 torr; specific gravity, 1.385. At 60°C DEGN has a volatility of 0.19 milligrams per square centimeter per hour. At constant pressure, the heat of combustion is 2,792 calories per gram. The heat of formation is −99.4 kilogram calories per mole. The heat of detonation is 1,161 calories per gram. DEGN is readily soluble in ether, acetone, chloroform, benzene, nitrobenzene, toluene, nitroglycerin, and glacial acetic acid but is insoluble in ethanol, carbon tetrachloride, and carbon disulfide. Solubility in water at 25°C and 60°C is 0.40 and 0.46 gram per 100 grams, respectively. DEGN's chemical reactivity is similar to nitroglycerin's, but is less subject to hydrolysis and is not readily saponified by alcoholic sodium hydroxide. DEGN can be used as an explosive and can be used in propellants as a colloiding agent for nitrocellulose. Propellants based on DEGN and nitrocellulose develop relatively low temperatures and cause relatively little erosion of guns, but are unduly volatile.

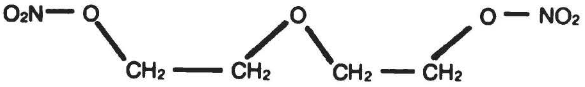


Figure 8-2. Structural formula for DEGN.

(2) DEGN can be manufactured with a yield of approximately 85 percent of the theoretical by adding diethylene glycol to mixed acid containing approximately 50.3 percent nitric acid, 44.7 percent sulfuric acid, and 5.0 percent water. The temperature of the mixture is kept at 10° to 15°C. The spent acid is very unstable and fumes off if heated or allowed to stand for a few hours. The separated DEGN is purified by washing with successive portions of water, dilute sodium carbonate solution, and water until neutral. The purity of the product is dependent mainly on the purity of the diethylene glycol used in the manufacturing process.

(3) DEGN is so insensitive that mixing with another nitrated compound is required to produce a useful explosive. DEGN alone, however, does explode in the pendulum friction test. The explosion temperature test value for DEGN is 237°C.

(4) As indicated by the vacuum stability tests, DEGN is much more stable than nitroglycerin at 100°C and will, when free from acidity, withstand long term storage at ordinary temperatures.

(5) The brisance of DEGN, as judged by the modified sand test, is equal to that of TNT and 81 percent that of nitroglycerin. At a density of 1.38 grams per cubic centimeter, DEGN's rate of detonation is 6,760 meters per second, slightly less than TNT's. The Trauzl lead block test indicates DEGN to be 144 to 150 percent as powerful as TNT and 77 percent as powerful as nitroglycerin. The ballistic pendulum test indicates DEGN to be 127 percent as powerful as TNT and 90 percent as powerful as nitroglycerin.

c. *Nitrocellulose (NC).*

(1) Nitrocellulose or cellulose nitrate is a mixture of nitrates obtained by nitrating cellulose. Cellulose (figure 8-3) is a long chain polymer of anhydroglucose units ($C_6H_{10}O_5$). The number of anhydroglucose units or degree of polymerization (DP) is variable. Cellulose used for preparation of military grades of nitrocellulose have a DP of approximately 1,000 to 1,500. Cellulose threads possess micellar structure and consist of numerous rod-like crystallites oriented with their long axis parallel to the thread axis, thus forming a fiber. Almost pure cellulose is found in the pith of certain plants, in absorbent cotton, and in some filter papers. Pure cellulose is most readily obtained from cotton by treating with a dilute acid or base solution then thoroughly washing with water. At the present time most of the cellulose for nitrocellulose preparation is obtained from coniferous wood, which is 50 to 60 percent cellulose. Another source is straw, which is 30 to 40 percent cellulose.The nitration of cellulose involves replacement of the hydrogen in the three hydroxyl (OH) groups in the anhydroglucose units with NO_2 groups. A representative formula for the nitrated cellulose may be written as $C_6H_7(OH)_x(ONO_2)_y$ where $x + y = 3$. The mononitrate, $x = 2$ and $y = 1$, has a nitrogen content of 6.76 percent; the dinitrate, $x = 1$ and $y = 2$, has a nitrogen content of 11.11 percent; the trinitrate, $x = 0$ and $y = 3$, has a nitrogen content of 14.14 percent. As a practical matter, however, any desired degree of nitration up to 14.14 percent may be obtained by adjusting the composition of the mixed acid used for nitration, the acid to cellulose ratio, the time of nitration, or the temperature of nitration. In nitrocellulose with less than 14.14 percent nitrogen, the NO_2 groups are distributed randomly along the entire length of the cellulose polymer, so x and y should be regarded as average values over the entire length of the chain. The nitrogen content determines the chemical and physical properties of any particular nitrocellulose. The five grades of nitrocellulose listed below are recognized and used.

(a) Pyroxylin or collodion, which contains from about 8 to 12.3 percent nitrogen, is light yellow, matted filaments. The theoretical maximum density is 1.653 grams per cubic centimeter, the melting point with decomposition is greater than 135°C, and the heat of formation is −216 kilocalories per mole for pyroxylin with a nitrogen content of 12 percent. When dissolved in 3 parts ether and 1 part alcohol, the solution is pale yellow and viscous. Pyroxylin is also soluble in acetone or glacial acetic acid, and is precipitated from solution by water. When thin layers of solutions are permitted to evaporate, the pyroxylin forms a tough, colorless film. Pyroxylin is very flammable and is decomposed by light. The pyroxylin used for the manufacture of celluloid contains 11.0 to 11.2 percent nitrogen, while that used in the manufacture of blasting explosives has a nitrogen content of 11.5 to 12.0 percent. The pyroxylin used for military purposes contains 12.20 ± 0.10 percent of nitrogen. Pyroxylin with 11.13 percent nitrogen is hydrolyzed to the extent of 1.71 percent of the available nitrogen after 240 hours of boiling in water. The heat of detonation of pyroxylin with a nitrogen content of 12 percent is 1.16 kilocalories per gram for liquid water and 1.02 kilocalories per gram for gaseous water.

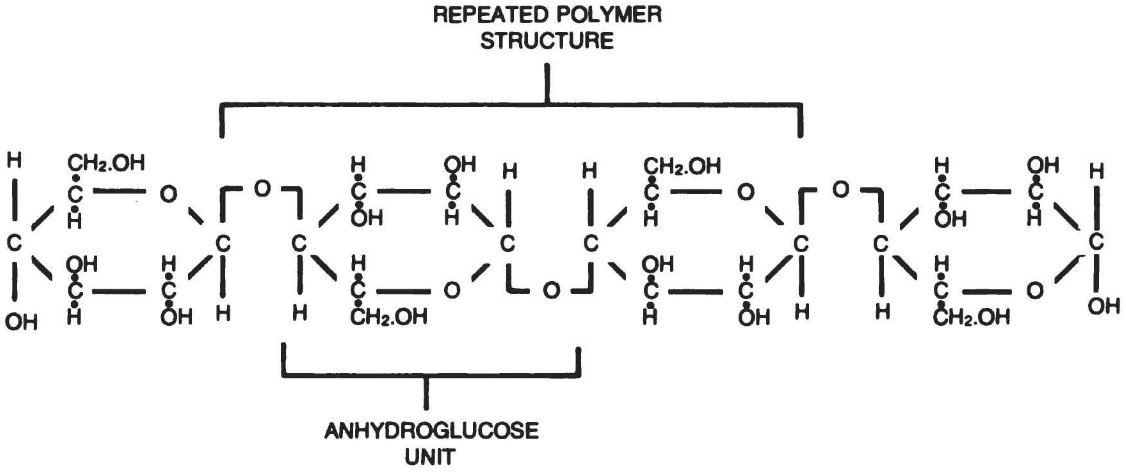


Figure 8-3. Cellulose.

(b) Pyrocellulose is a type of nitrocellulose which has a nitrogen content of 12.60±0.10 percent. Pyrocellulose is insoluble in water and ether but 99 percent dissolves in a solution of 2 parts ether and 1 part alcohol, 21 percent dissolves in ethyl nitroacetate, and 11 percent dissolves in alcohol. Pyrocellulose is soluble in acetone, ethyl acetate, methyl acetate, propylene oxide, nitromethane, and nitroethane but solubility is not limited to these. Pyrocellulose is used as a propellant and in propellant mixtures. Pyrocellulose with 12.6 percent nitrogen is hydrolyzed to the extent of 1.22 percent of the available nitrogen after 240 hours of boiling in water. The specific heat of pyrocellulose with a nitrogen content of 12.6 percent is 0.3478 calories per gram per degree centigrade at 25°C.

(c) Guncotton is the grade of nitrocellulose that contains the highest percentage of nitrogen obtainable by nitrating cellulose with mixed nitric and sulfuric acids. The percentage of nitrogen is 13.35 to 13.45 percent. The theoretical maximum density is 1.656 grams per cubic centimeter, the melting point with decomposition is greater than 135°C, and the heat of formation is −200 kilocalories per mole for guncotton with a nitrogen content of 13.35 percent. Guncotton is insoluble in water and ether, very slightly soluble in alcohol, about 4 to 10 percent soluble in a solution of 2 parts ether and 1 part alcohol, and soluble in acetone, ethyl acetate, and other organic solvents. Guncotton is used as a propellant and as a primer in electric detonators. Guncotton with 13.44 percent nitrogen is hydrolyzed to the extent of 1.03 percent of the available nitrogen after 240 hours of boiling in water. The heat of detonation of guncotton with a nitrogen content of 13.35 percent is 1.16 kilocalories per gram for liquid water and 1.02 kilocalories per gram for gaseous water. The specific heat of guncotton with a nitrogen content of 13.4 percent is 0.3408 calories per gram per degree centigrade at 25°C.

(d) High nitrogen nitrocellulose is the grade of nitrocellulose that contains from 13.75 to 14.14 percent nitrogen. The theoretical maximum density is 1.659 grams per cubic centimeter and the heat of formation is −191 kilocalories per mole for nitrocellulose with a nitrogen content of 14.14 percent. The compound is insoluble in water, ether, n-propyl alcohol, and isopropyl alcohol, but about 0.6 percent soluble in ethanol, 1 percent soluble in methyl alcohol, 1.4 percent soluble in a solution of 2 parts ether and 1 part alcohol, 20 percent soluble in methyl acetate, 42 percent soluble in nitromethane, 86 percent soluble in 1-nitropropane, and 100 percent soluble in acetone, ether acetate, propylene oxide, and amyl acetate. High nitrogen nitrocellulose can be used in the preparation of propellants with higher ballistic potential than guncotton, but it is not used in U.S. standard propellants because it is too costly to manufacture. The heat of detonation for nitrocellulose with a nitrogen content of 14.14 percent is 1.95 kilocalories per mole for liquid water and 1.81 kilocalories per mole for gaseous water. The specific heat for nitrocellulose with a nitrogen content of 14.14 percent is 0.3362 calories per gram per degree centigrade.

(e) Blended nitrocellulose is a mixture of 60 to 65 percent guncotton and 35 to 40 percent pyrocellulose. The guncotton should have a nitrogen content of 13.4 percent and the pyrocellulose nitrogen content should be 12.6 percent. Straight guncotton has a higher ballistic potential than blended nitrocellulose but is only slightly soluble in an ether-alcohol solution, the mixture most commonly used in the United States to colloid nitrocellulose. Blended nitrocellulose of the proportions given above is soluble to the extent of about 37±2 percent in a mixture of 2 parts ether and 1 part alcohol. This property makes blended nitrocellulose suitable as a single-base propellant. Two grades of nitrocellulose are commonly used: one with a nitrogen content of 13.15±0.05 percent and one with a nitrogen content of 13.25±0.05 percent.

(2) X-ray diffraction studies have yielded the following information regarding the nitration of cellulose. In the first stage of nitration, nitric acid penetrates the entire cellulose structure. The amorphous part of the cellulose is more reactive than the crystalline part, so the second stage involves nitration of the amorphous part. At the same time the micellar arrangement is being broken down. The third stage of nitration involves the swelling and breakdown of the micellar arrangement. Swelling takes place as shown in figure 8-4. The nitrating agent, as is the case with any esterifying reagent, attacks one end of the micelle and causes a gradual sliding apart of the chain as nitration proceeds. When 12.2 percent nitrogen content is reached, an orderly arrangement of the chains becomes possible and there is a sudden appearance of the trinitrate crystalline structure. The nitration of cellulose is a reversible reaction, proceeding as:

$$(C_6H_7O_2)(OH)_3 + xHNO_3 (C_6H_7O_2) \rightleftharpoons (OH)_{3-y}\,(ONO_2)_y + xH_2O$$

where y varies between 0 and 3 over the length of the polymer. Therefore, an equilibrium exists for each concentration of nitrating acid, which corresponds to a definite degree of nitration, provided all other conditions, such as temperature and pressure, remain the same. This means that if the concentration of nitrating bath containing nitrocellulose nitrated to a certain nitrogen content, is slightly weakened by the addition of water, the reaction will go from right to left and nitrocellulose will be partly hydrolyzed to the nitrogen content corresponding to the concentration of the new nitrating bath. This reaction is known as denitration. The rate of denitration is insignificant if the acid is rapidly diluted to a very low concentration and cooled at the same time as, for example, when nitrocellulose wet with acid is drowned in a large amount of ice water. If, on the other hand, drowning is done into a small amount of water and the temperature is allowed to rise, a certain amount of denitration takes place. During the wringing operation, which removes the spent mixed acid, if the nitrocellulose is left in contact with a humid atmosphere longer than usual, considerable denitration takes place, especially in the outer layers of the wrung nitrocellulose.

(3) A point should be made here regarding the mechanism of solubility of nitrocellulose. As a general rule, solvents for polymers like nitrocellulose act at first as swelling agents and only afterwards as dispersing reactants. The fibrous structure of nitrocellulose is not lost when swelling compounds such as cyclohexanone, fenchone, and meta-xylene are used. When nitrocellulose is treated with a solvent a gel is obtained and the phenomena known as gelatinization occurs. A volatile solvent can be evaporated in order to obtain a plastic-like colloided material. A smokeless nitrocellulose propellant processed with the aid of an ether-alcohol mixture is an example. If the solvent is nonvolatile or only slightly volatile, the nitrocellulose forms a gel, but usually heat is required for completion of the operation. A double-base, solventless, smokeless propellant is an example. If heating is undesirable because of danger, gelatinization can be achieved by blending nitrocellulose at room temperature with a gelatinizer dissolved or suspended in a liquid, such as alcohol, which is not necessarily a solvent for nitrocellulose. If a solid solvent such as camphor is used in the preparation of celluloid, the water-wet nitrocellulose is mixed with powdered camphor, some alcohol is added, and the mass is kneaded at room temperature for several hours. The process is usually called plasticization. Both gelatinization and plasticization yield similar materials which are flexible and crack resistant. The difference is a gelatinizer tends to draw the molecules together and a plasticizer spreads them out. The solubility of nitrocellulose in organic solvents and the formation of gels is attributed to formation of molecular addition compounds between nitrocellulose and the solvent.

(4) In the manufacture of nitrocellulose, the first step is the pretreatment of the cellulose. Short fibered cotton or cotton linters that have been suitably purified by washing with water are dried at 105° to 110°C until the moisture content is reduced from 6 to 7 percent to about 0.5 percent. If the starting material is wood pulp, the pulp sheets are fed into a drier maintained at 110° to 115°C. During a drying time of about 15 minutes, the moisture content is reduced from 4 to 5 percent to about 0.5

percent. The dried pulp sheets pass from the drier into a shredder where they are reduced to pieces about five millimeters in length. In storage, the cellulose should be kept in airtight containers to prevent moisture from being absorbed. The cellulose is nitrated by the mechanical dipper process which has displaced other, more hazardous processes. The composition of the mixed acid used in this process varies depending on the type of cellulose nitrated, the degree of nitration desired, and the season of the year. Higher temperatures cause denitration of the mixed acid, so the nitric acid content must be greater during the summer than during the winter. Table 8-1 lists typical compositions of mixed acid.

Table 8-1. Compositions of Mixed Acids for Nitrating Cellulose

	For pyrocellulose from -		For guncotton from -		For high nitrogen nitrocellulose	
	Cotton linters Percent	Wood pulp cellulose Percent	Cotton linters Percent	Wood pulp cellulose Percent	13.8%N Percent	13.8%N Percent
Sulfuric acid	59.2	57.0	60.5	59.5	-	-
Nitric acid	21.5	23.5	24.5	28.5	49	70-85
Nitrosylsulfuric acid	3.5	4.4	4.0	3.0	-	-
Water	15.8	15.1	11.0	9.0	-	-
Phosphoric acid	-	-	-	-	49	-
Phosphoric anhydride	-	-	-	-	2	-
Ammonium nitrate	-	-	-	-	-	15-20
or potassium nitrate	-	-	-	-	-	or 30

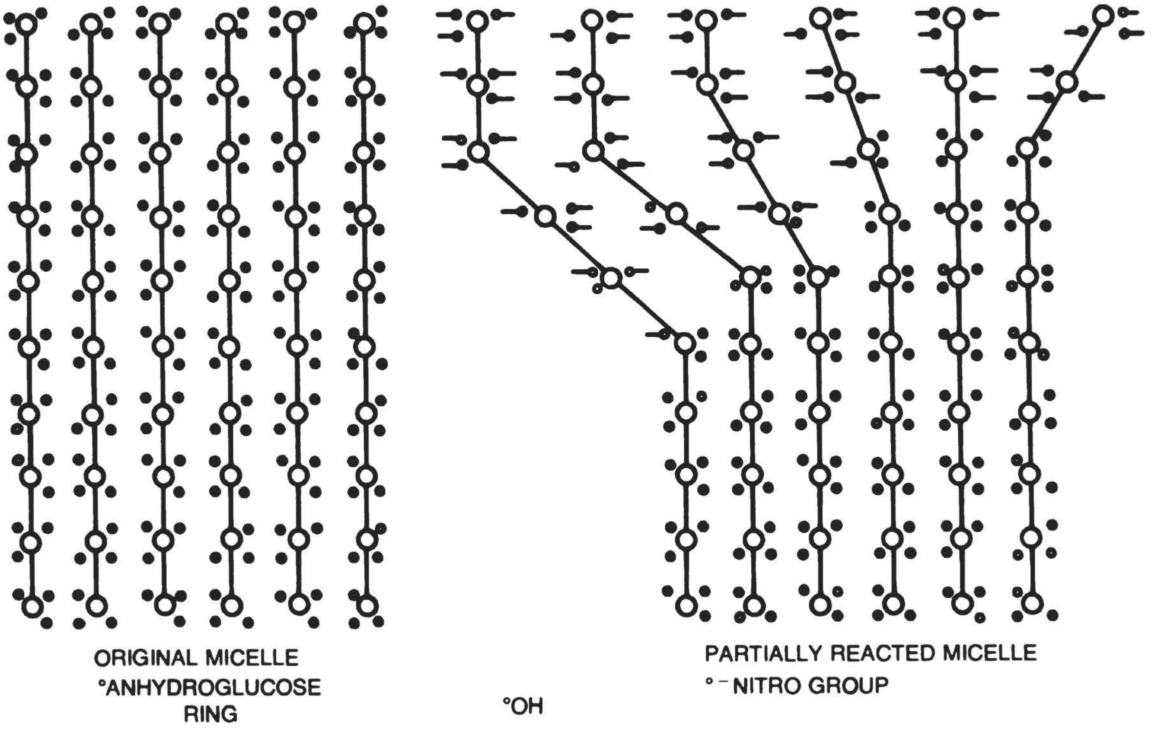


Figure 8-4. Nitration of cellulose.

About 1,500 pounds of mixed acid are placed in a stainless steel nitrator at a temperature of 30°C. The nitrator is equipped with two vertical agitators revolving in opposite directions that impart motion toward the center. Approximately 32 pounds of cellulose are added. The paddles of the agitator are designed to immediately draw the cellulose below the surface of the acid, away from the fume exhaust line. The addition of the cellulose requires about four minutes; agitation is then continued for twenty minutes. Nitration is exothermic, so provisions must be made to prevent the temperature from rising above 30°C. When nitration has been completed, the slurry is discharged through a valve in the bottom to a centrifuge, called a wringer, where most of the mixed acid is removed. The composition of the spent acid can be adjusted if the acid is to be reused in nitration. The acid-wet, crude nitrocellulose is then forked through an opening in the bottom of the wringer into a drowning basin where rapid submersion in cold water takes place. The nitrocellulose must then be stabilized and purified. High nitrogen nitrocellulose can be prepared in the following additional ways. Guncotton wetted with 25 percent water can be nitrated to 14 percent nitrogen content by a mixed acid containing either 60 percent nitric acid, 20 percent acetic acid, and 20 percent acetic anhydride or 50 percent nitric acid, 25 percent acetic acid, and 25 percent acetic anhydride.This process yields nitrocellulose with 14 percent nitrogen of low viscosity which is suitable for military use. Other nitrating agents may be used to produce different percentages of nitrogen. Another method of nitration is to heat concentrated nitric acid to form N_2O_5 vapors which are passed over cellulose in the shape of paper rolls. This process yields a 14 percent nitrogen content.

(5) Removal of the impurities in the raw nitrocellulose is critical to obtain a product with suitable stability. Acids and other impurities are absorbed on the fibers of the nitrocellulose and are hard to remove. The first step in the process, called the sour boil, is carried out in large cypress wood tubs equipped with ducts for heating and circulating water at approximately 100°C. During the first two hours, the acidity of the water is adjusted to 0.05 to 0.50 percent, calculated to H_2SO_4. Pyrocellulose and pyroxylin are subjected to 40 hours of boiling treatment with three changes of water during this period.Guncotton is subjected to 60 hours of boiling treatment followed by two five-hour boiling treatments with a change of water after each treatment. The next step in the process is pulping. Because cellulose fibers are tubular, having capillary channels running through them, part of the impurities present in guncotton are included in these channels and cannot be removed unless the fibers are cut into very short fragments. This operation is done in an apparatus called a beater, or Jordan engine similar to that employed in the paper industry. The beating operation is carried out with a large volume of water with just enough sodium carbonate solution added to preserve a slightly alkaline reaction to phenolphthalein. Beating is continued until the nitrocellulose has been reduced to the desired degree of fineness, as determined by a settling test. After the slurry from the beater has been settled and decanted, the nitrocellulose is subjected to poaching. Poaching consists of one four-hour, one two-hour, and two one-hour boiling treatments with settling, decantation, and the addition of fresh water after each treatment. In the four-hour boiling treatment, sodium carbonate equalling 0.5 percent of the weight of dry nitrocellulose is added. The poaching treatment is followed by not less than two washes with cold water, each wash consisting of agitation of the nitrocellulose with fresh water for at least half an hour. The next step in the process is called screening. Uniformity of characteristics is difficult to obtain in the various batches of nitrocellulose. To ensure uniform characteristics in the final product, portions of batches having high nitrogen content and high viscosity are mixed with portions having low nitrogen content and viscosity. The resulting mixtures possess properties intermediate between those of the individual batches. The mixed slurry is fed through a distributor which spreads the nitrocellulose uniformly on packer screens. The screen, with 0.02 inch slots, is vibrated mechanically and the properly pulped nitrocellulose passes through the screen into collecting boxes. If a blended nitrocellulose is desired, blending is the next step in the manufacturing process. Each blending unit consists of two tubs, equipped with propeller type agitators, interconnected so that the contents are kept in constant circulation. The receiving tub, or high tub, is filled with slurry from the screening operation so that the overflow discharges into the low tub. When the low tub is partially full, a circulating pump is started and part of the slurry is returned from the low tub to the high tub. This process is continued for 6 to 7 1/2 hours after which time a sample is tested for nitrogen content and solubility in a solution of 2 parts ether and 1 part alcohol. The last step in the

manufacture of nitrocellulose is wringing. Nitrocellulose from the screening or blending process is placed in a centrifugal wringer with a perforated brass basket lined with a 24 mesh copper screen. The basket revolves at 950 rpm for about seven minutes. The wrung nitrocellulose, with a moisture content of about 31 percent is stored in rustproof metal cans with tight fitting covers.

(6) Dry nitrocellulose is very sensitive to impact, friction, heat, and spark and is never handled in quantity in the United States. The results of impact sensitivity tests for all types of nitrocellulose are approximately 8 centimeters, which indicates nitrocellulose is 460 percent as sensitive as TNT or about the same as mercury fulminate and lead azide. Rifle bullet impact tests indicate nitrocellulose to be very sensitive with 100 percent of the trials yielding complete detonations. While the five second explosion temperature test value for pyrocellulose (170°C), blended nitrocellulose (200°C), and guncotton (230°C) are not particularly low, the rapid rate of decomposition of the material at temperatures greater than 100°C and the exothermicity of such decomposition make the material very sensitive to ignition by a spark. Nitrocellulose can be detonated even when wet. A mixture of 60 percent nitrocellulose and 40 percent water confined in a steel barrel sometimes is detonated by a stick of dynamite. The frequency of detonation is greater when the water is frozen. Tests have shown that nitrocellulose uniformly wetted with 35 percent ethanol will also detonate, on occasion, when initiated with dynamite.

(7) The brisance of nitrocellulose, as determined by the sand test, is directly comparable with TNT but less than tetryl. The brisance of nitrocellulose increases with increases in the nitrogen content. The rate of detonation of guncotton with a nitrogen content of 13.45 percent and density of 1.2 grams per cubic centimeter is 7,300 meters per second; greater than that of TNT. As nitrocellulose propellants can be detonated as well as burned, their brisance values are high. Trauzl lead block tests show guncotton (13.2 to 13.4 percent nitrogen) to be 136 to 147 percent as powerful as TNT and the ballistic mortar test indicates guncotton is 118 percent as powerful as TNT.

(8) The great care taken in the purification of nitrocellulose is due to the necessity for removing impurities that are much less stable than the nitrocellulose. Cellulose sulfate is unstable with respect to heat and moisture. Propellants made from nitrocellulose containing even comparatively small amounts of such esters give decreased 134.5°C heat test values and deteriorate more rapidly. The nitrates of oxidized cellulose are also objectionable and cause increased instability of nitrocellulose if not removed during the purification process. Elevated temperature tests show that even nitrocellulose of high purity is much less stable than most of the noninitiating military high explosives. The stability of pyrocellulose and blended nitrocellulose is 35 minutes, minimum, by the 65.5° KI test and 30 minutes, minimum, by the 134.5°C heat test. Figure 8-5 shows the DTA and pyrolysis curves for nitrocellulose. Vacuum stability tests indicate the stability of nitrocellulose decreases with increasing nitrogen content. For nitrocellulose with a nitrogen content of 12 percent, 5.0 cubic centimeters of gas are evolved in 48 hours at 120°C. In the LLNL reactivity test, 1.0 to 12 cubic centimeters of gas are evolved per .25 grams of sample. Nitrocellulose appears to undergo very slow decomposition even at ordinary temperatures. The rate of decomposition increases 3.71 times with each 10°C increase in temperature. The presence of moisture increases the rate of decomposition considerably and the presence of free acid or alkali has an even more pronounced effect. Rates of decomposition of pyrocellulose under various conditions are shown in table 8-2.

Table 8-2. Decomposition of Nitrocellulose

Decomposition medium	Percent available nitric acid liberated per hour at - 50°C.	97.5°C.
Heat	0.0000045	0.0028
Water	0.0000111	0.0051
0.06 Percent nitric acid solution	0.0000325	-
0.035 Percent nitric acid solution	-	0.0088
0.035 Percent sodium carbonate solution	0.0006870	0.1358
95 Percent ethanol	0.0000290	-

From these data, it is apparent that alkali is more effective than acid in causing the deterioration of nitrocellulose. Pyrocellulose is hygroscopic to the extent of 3 percent at 30°C and 90 percent relative humidity. Under the same conditions blended nitrocellulose, 13.15 percent nitrogen, is hygroscopic to the extent of 2.5 percent, guncotton, 13.45 percent nitrogen, to 2 percent, and high nitrogen nitrocellulose, 14 percent nitrogen, to 1 percent.

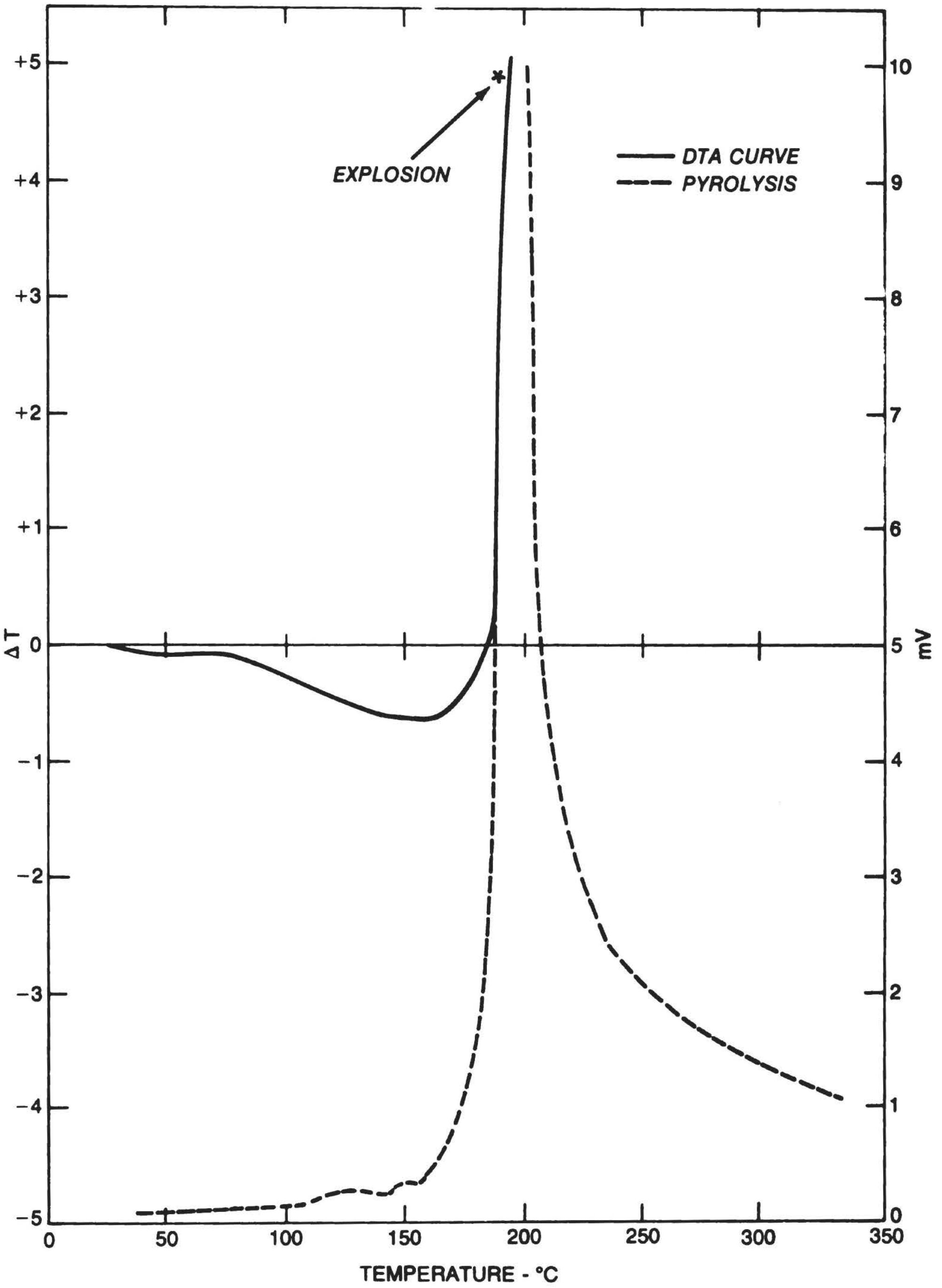


Figure 8-5. DTA curve for nitrocellulose.

(9) Military grades of nitrocellulose are:

	Class	Nitrogen, percent
Grade A	Pyrocellulose	
Type I		12.60±0.10
Type II		12.60±0.15
Grade B	Guncotton	13.35 minimum
Grade C	Blended	
Type I		13.15±0.05
Type II		13.25±0.05
Grade D	Pyroxylin	12.20±0.10
Grade E		12.00±0.10

The maximum allowable ash left after ignition of the nitrocellulose in any grade is 0.4 percent. The minimum percentage that is insoluble in ether alcohol in grades A, D, and E is 99 percent. The solubility limit for grade C in ether alcohol is left to discretion of the contractor manufacturing propellants from the nitrocellulose.

d. *Nitroglycerin (NG).*

(1) Nitroglycerin, glycerol trinitrate, or 1,2,3-propanetriol trinitrate, shown in figure 8-6, is a clear, colorless, odorless, oily liquid with a theoretical maximum density of 1.596 grams per cubic centimeter. Nitroglycerin has a sweet, burning taste and a molecular weight of 227.1.

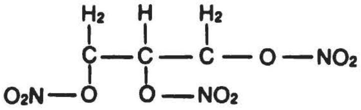


Figure 8-6. Structural formula for nitroglycerin.

(2) Pure nitroglycerin freezes to form dipyramidal rhombic crystals with a heat of crystallization of 33.2 calories per gram. This is a stabile form with a freezing point of 13.2°C and melting point of 13.5°C. Under some conditions, glassy triclinic crystals with a heat of crystallization of 5.2 calories per gram are formed. This is a labile form with a freezing point of 2.1°C and a melting point of 2.8°C. The labile form gradually changes into the stabile form after a week or two with a heat of conversion of 28 calories per gram. Nitroglycerin has an apparent boiling point of 145°C, but this is merely the temperature at which nonexplosive decomposition becomes vigorous enough to resemble boiling. True boiling takes place at reduced pressure; at 2 torr the boiling point is 125°C and at 50 torr the boiling point is 180°C. Even under high vacuum boiling, however, some decomposition takes place.

(3) Nitroglycerin has a specific gravity value of 1.596 20/15 and a refractive index value of 1.4732 at 20°C. Viscosity values are 0.36, 0.21, 0.094, and 0.068 poise at 20°, 30°, 50°, and 60°C, respectively. The vapor pressure values for nitroglycerin in torr are 0.0013 at 15°C, 0.0015 at 20°C, 0.00177 at 25°C, 0.00459 at 35°C, 0.0075 at 40°C, 0.01294 at 45°C, 0.03587 at 55°C, and 0.06 at 60°C. Decomposition begins at 50° to 60°C. Nitroglycerin is volatile to the extent of 0.11 milligram per square centimeter per hour at 60°C. The specific heat of nitroglycerin is 0.356 calories per gram per degree centigrade between 35°C and 200°C.

(4) The heat of detonation is 1,486 calories per gram for gaseous water and 1,590 for liquid water. One gram/mole of nitroglycerin produces 715 millititers/163.5 liters. The heat of formation is −90.8 kilocalories per mole.

(5) Nitroglycerin is soluble in one liter of water to the extent of only 0.173, 0.191, 0.228, and 0.246 gram at 20°, 30°, 50° and 60°C, respectively and is essentially nonhygroscopic when exposed to atmospheric humidity. Absolute ethanol dissolves 37.5 and 54 grams of nitroglycerin per 100 grams of solvent at 0° and 20°C, respectively. 96 percent alcohol dissolves 40 grams per 100 grams of solvent at 20°C. Carbon tetrachloride dissolves 20 milliliters per liter and trichloroethylene dissolves 20 parts per 100 parts of solution. Carbon disulfide at room temperature dissolves only 12.5 grams per liter of solvent. Hot ethanol and nitroglycerin are miscible in all proportions. Nitroglycerin is miscible in all proportions with ether, acetone, glacial acetic acid, ethyl acetate, benzene, toluene, phenol, nitrobenzene, chloroform, ethylene chloride, and nitric esters such as glycol dinitrate. Nitroglycerin can be used as a solvent for other explosives; 35 grams of dinitrotoluene dissolve in 100 grams of nitroglycerin at 20°C and 30 grams of trinitrotoluene dissolve per 100 grams at 20°C. Nitroglycerin is used extensively in propellant compositions as a gelatinizing agent for nitrocellulose as well as in dynamites and for the shooting of oil wells.

(6) Concentrated sulfuric acid decomposes nitroglycerin resulting in the formation of nitric acid. In the presence of metallic mercury, nitric oxide is formed quantitatively, and this reaction is the basis for determination of the purity of nitroglycerin by the nitrometer method. The reaction between nitroglycerin and aqueous sodium hydroxide is slow because of their immiscibility, but if ethanol is added the reaction is rapid. Sodium nitrate, nitrite, formate, and acetate are produced in this reaction and resinous material, oxalic acid, and ammonia are produced as byproducts. Nitroglycerin is hydrolysed to a very slight extent by water; producing less than 0.002 percent of acidity in 10 days

at 22°C or 0.005 percent of acidity in 5 days at 60°C. An aqueous solution of sodium sulfide decomposes nitroglycerin producing great heat. This reaction can be used for the destruction of waste material.

(7) Nitroglycerin is manufactured by nitrating glycerin with a mixed acid. Several processes are currently used in the United States and Europe. The processes can be generally classified according to whether they are continuous or batch production.

(a) In batch production, high grade glycerol is added to mixed acid that consists of 45 to 50 percent nitric acid and 50 to 55 percent sulfuric acid. The mixed acid is prepared well in advance to allow metallic sulfates to settle out. The metallic sulfates might otherwise interfere with separation of the nitroglycerin. Two important factors determine the proportions in the mixed acid. First, that the ratio of the sulfuric acid to water at the end of the reaction, the dehydrating value of the sulfuric acid or DVS, is maintained between 4.35 and 4.5. The water includes both the water in the original reactants and that produced during the reaction. This ensures that the nitric acid is maintained at a sufficient concentration to ensure completion of the reaction so that completely nitrated products that are subject to exothermic oxidation reactions are not formed. Second, that enough nitric acid is present to drive nitration, which is a reversible reaction, to completion. A slight excess of nitric acid will accomplish this. The reaction between the glycerol and mixed acid is carried out in a nitrator equipped with a mechanical agitator and cooling coils that carry a brine solution of calcium chloride at −20°C. A 6,800 pound charge of mixed acid is placed in the nitrator and the glycerol is added in a small stream. The mixed acid to glycerol ratio, by weight, is between 5.5 and 6.5. If too much glycerol is added, exothermic decomposition and oxidation reactions occur and temperature control becomes difficult. The temperature is maintained at 2° to 3°C by cutting off the flow of glycerol as necessary. If the temperature does rise above 3°C, the contents are drowned in a water tank beneath the nitrator. Stirring must be adequate to prevent freezing on the cooling coils. Stirring is continued for a few minutes after the 50 to 60 minutes required to add the glycerol. Then the nitroglycerin is allowed to separate completely. The lower layer of spent acid is drained off to be recycled or otherwise disposed of, and the nitroglycerin is run off into a neutralizer. An initial 40°C water wash removes most of the acid. Then a wash with a 2 to 3 percent sodium carbonate solution neutralizes the residual acid. Washing with water is continued until the water is free of alkali and the nitroglycerin is neutral to litmus. The final step in this manufacturing process is to wash with a sodium chloride solution to remove any nitroglycerin water emulsion. Moisture content gives the product a milky appearance, but on storage in a heated building, the material becomes clear and the moisture content decreases to 0.4 percent or less. The yield of nitroglycerin is 230±5 parts by weight per 100 parts of glycerin.

(b) The chemistry involved in the continuous manufacture of nitroglycerin is basically the same as that described for batch processing except the equipment is designed to allow nonstop production. The advantages of continuous processes are: faster production, better process control, lower labor costs, and, perhaps most important, safety, as a result of the smaller accumulations of nitroglycerin at any given plant location. In the United States the common practice is to nitrate mixtures of glycol and glycerol. The nitration proceeds in the same manner as with pure glycerol.

1 The Schmid-Meissner process (figure 8-7) involves continuous nitration of glycerin or other liquids, such as ethyleneglycol or diethyleneglycol, separation of the nitrated product from spent acid, and purification by neutralization and washing. The stainless steel nitrator is equipped with a motor driven, steel propeller, vertical cooling coils, and an overflow tube to separator. A two way valve, which may be connected to the mixed nitric-sulfuric acid line or may be opened to the drowning tank, is fitted centrally to the bottom of the nitrator. Brine at about −5°C is circulated at a controlled rate around the cooling tubes in the annular space outside the nitrator. As a measured amount, per unit time, of mixed acid is fed in from the bottom, a calculated amount of glycerin is fed in from the top at a level below that of the overflow pipe. The flow of materials into the nitrator is by means of automatically controlled air pressure. The propeller mixes the two liquids and glycerin is nitrated to nitroglycerin. The temperature in the nitrator is not allowed to exceed 18°C. The emulsion of nitroglycerin and spent acid flows off continuously through the overflow to the separator, which is a stainless steel, inclined, rectangular tank provided with a number of vanes, equipped with a bottom draw off valve for spent acid, a sight glass near the top, and a steel neck with overflow pipe for the nitroglycerin. Because of difference in density, the spent acid settles to the bottom of the separator and the nitrated product rises. The withdrawal of acid from the bottom is regulated to keep the separated nitrated product in the top of the separator at a predetermined level. The spent acid is discharged to the acid recovery plant and the nitroglycerin flows by gravity to the base of the first of the washing columns.

Each column consists of superimposed cylindrical glass sections (rings) separated by perforated stainless steel plates and rubber ring gaskets. The nitrated product from the separator enters the bottom of the first washing column, is mixed with cold water and emulsified by means of air injected into the liquid. This also forces the material to rise to the top of the column, where the emulsion overflows into a tank which serves as an intermediate separator. Here the nitrated product rapidly settles to the bottom, and flows to the base of the second wash column. In the second column the separated nitroglycerin is mixed with a hot dilute solution of soda and ammonia and then emulsified with air. The emulsion flows from the top of the column to another intermediate separator where the nitrated product settles to the bottom and is separated from the soda ash water, which is conducted to waste via settling tanks. Any nitroglycerin held in the tanks is drawn off periodically and rewashed. The nitrated product is subsequently passed through additional wash columns and separators until the desired stability is attained. Finally the purified product is passed through a flannel filter bag before being caught in a lead tank for storage and use.

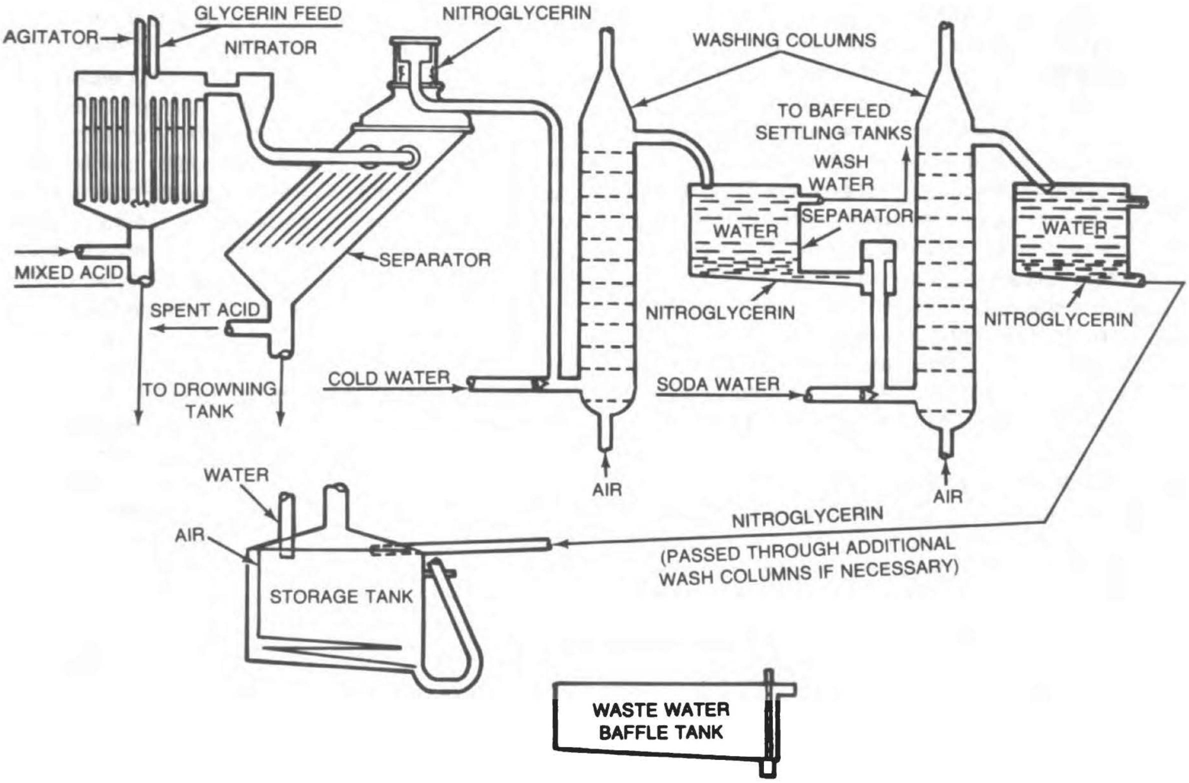


Figure 8-7. Schmid-Meissner continuous method for manufacturing nitroglycerin.

2 The Biazzi process (figure 8-8) is similar to the Schmid-Meissner, but is considered to be safer because of the smaller amount of nitroglycerin in the system at a given time. The nitrator is a small, cylindrical, stainless steel vessel provided with a bank of helical cooling coils. A high speed, shrouded, impeller-type agitator forces the nitrating acid up through the bank of coils and down through the cylindrical space in the center of the coils. The fresh, mixed acid and the material to be nitrated stored in large scale tanks or bins enter, in controlled ratio, at the top of the nitrator, striking the liquid at such a point in the vortex that the feed is immediately thrust beneath the surface and carried down through the central space formed by the coils. The mixture then spirals back, up and out, through the banks of cooling coils and a portion is carried off by the overflow pipe which leads to the separator. The flow of mixture past the coils is counter to the flow of cooling brine circulating through the coils. Because of this arrangement which permits rapid reaction through rapid heat absorption, the mixed acid can be stronger than that used in the Schmid-Meissner process. The cooling coils, agitator, and cover of the nitrator are mounted as a unit separate from the cylindrical body, which can be lowered hydraulically for inspection. The Biazzi acid separator is a stainless steel vessel of the shape shown in the figure. The emulsified mixture of nitrated product and spent acid enters tangentially through the side about midway up and imparts a slight centrifugal action to the upper layer of liquid in the separator. This action helps to break the emulsion and to prevent local overheating. The spent acid flows continuously from the bottom of the separator through a draw off valve, controlled by an adjustable collar, which can be raised or lowered by means of a micro screw attachment. After leaving the first separator, the acid is passed through an after-separator from which some of the nitrated product is recovered. The spent acid leaving the after-separator is usually diluted with water to dissolve traces of dissolved nitrated product. The separated, nitrated product is continuously drawn off from the first separator into a stainless steel wash tank equipped with a cylindrical baffle and an impeller-type agitator. Water is continuously added to the washer and the mixture overflows into a second separator. The nitrated product is drawn from the bottom of the separator and is conducted to the second washer where some soda wash solution is added with agitation. If a high purity nitrated product is required, such as for nitroglycerin used in propellants, the emulsion from the second washer, together with some soda ash solution, is conducted through a battery of three or four washers in which wash waters are running countercurrent to the movement of nitroglycerin. From there the emulsion passes through a series of separators arranged in cascade and is collected in a storage tank. In cases of overheating, the nitrator and the first separator can be emptied quickly into a drowning tank which is generally filled with water but can be filled with sulfuric acid. The Biazzi process is also used in the manufacture of DEGN and other aromatic and alphatic nitrocompounds. Only one nitrator is required for mononitration but for higher degrees of nitration more nitrators are added in series. Such nitrations usually employ the spent fortified acid from the higher nitration as the mixed acid for the next lower nitration.

3 The Swedish Nobel Aktiebolaget process for nitrating glycerin consists of an injector nitrator and a centrifugal separator for separating nitroglycerin from spent acid. The mixed acid used in this process is a mixture of about 1.7 parts spent acid and one part conventional, 50 percent nitric and 50 percent sulfuric acids, mixed acid. This mixture contains about 27 percent nitric acid and 10 percent water. Glycerin flow into the injector is controlled by the acid flow through the injector in the same manner that suction is produced by a water aspirator. Thus, if the acid flow is reduced by some equipment malfunctioning, the glycerin flow is automatically decreased. This process, unlike most of the others, operates at a high temperature, about 45° to 50°C. The glycerin or glycerin-glycol mixture is heated to 45° to 50°C before entering the injector. The mixed acid is cooled to 0°C. In the injector the heat of reaction maintains the fluid temperature at 45° to 50°C. Automatic controls give warning or shut down the operation if the temperature rises a few degrees above the normal range. The nitroglycerin acid emulsion enters a cooling system immediately after leaving the injector. The temperature of 45° to 50° is maintained for only about half a second. During the next 80 to 90 seconds the mixture is cooled to 15°C. In the following 30 seconds the nitroglycerin is separated from the spent acid. A continuous centrifugal separator separates nitroglycerin from the spent acid. The centrifuge operates at 3,200 rpm. For a unit with a capacity of 25,000 liters per hour the quantity of nitroglycerin in the separator bowl during operation is only 3.5 kilograms. The separated acid free nitroglycerin is emulsified immediately by a wash jet to form a nonexplosive mixture and is removed continuously from the separator house to the nitroglycerin wash-and-weigh house.

4 Another proposed method is very similar to the Nobel Aktiebolaget process where the reaction is carried out in a tube. The significant difference is that the mixed acid and glycerin are pumped and turbulent flow is maintained in the tube to ensure a complete, rapid reaction. The reactants are then cooled, separated, and washed.

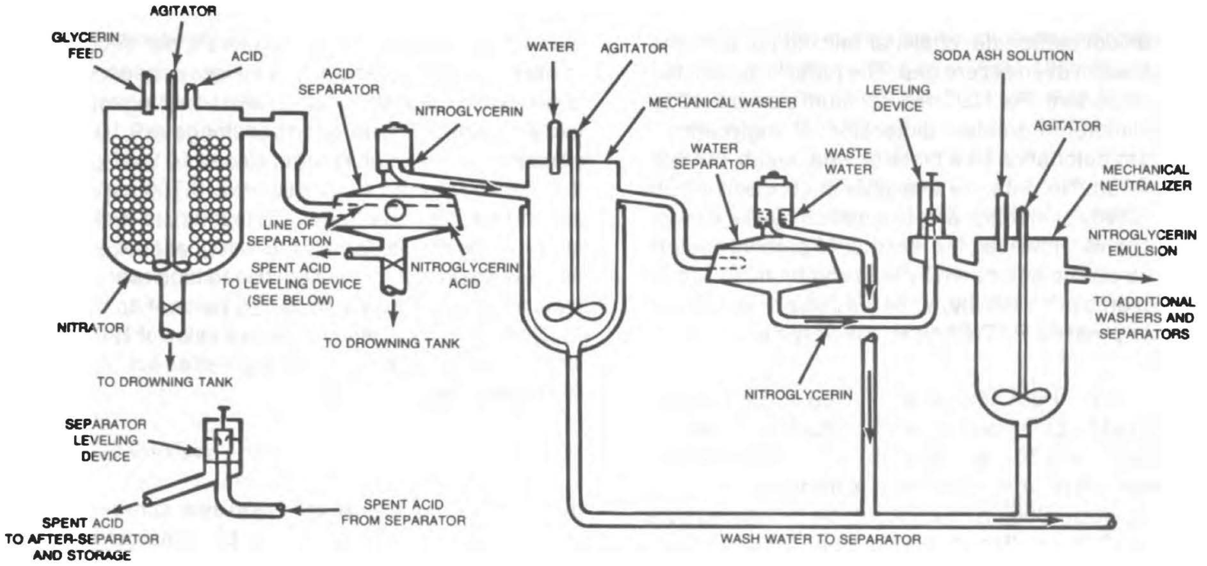


Figure 8-8. Biazzi continuous method for manufacturing nitroglycerin.

(8) There are two grades of nitroglycerin specified for military use. Type I uses grade B glycerin for manufacture. Type II uses partially polymerized glycerin. These two grades must comply with the following requirements:

	Type I	Type II
Moisture content, maximum	0.5 percent	0.5 percent
Acidity or alkalinity, maximum	0.002 percent	0.002 percent
Nitrogen content	18.40 percent, minimum	17.8 percent, minimun 17.9 percent, maximum
82.2°C, KI test, Minimum	10 minutes	10 minutes

The KI test does not measure stability but indicates the presence or absence of trace impurities not found in highly purified nitroglycerin.

(9) The great sensitivity of nitroglycerin is generally recognized. The pendulum friction test indicates nitroglycerin is very sensitive to friction. Impact test results vary with the instrument used, however, they all indicate nitroglycerin is very sensitive to impact. The Picatinny Arsenal impact test shows nitroglycerin is more sensitive than mercury fulminate. The results of impact tests have been found to depend on the area of the impacted nitroglycerin, the smoothness of the two surfaces involved, and the aeration of the nitroglycerin. The tests indicate a force of at least 1000 gram centimeters is necessary when using a five centimeter diameter weight but with a 2.5 centimeter diameter weight a greater force is required. Even the slightest dents in the anvil will greatly increase the sensitivity as measured by an impact test. Detonation is attributed to thermal ignition from compressed gas bubbles with the degree of compression being higher in the area of a dent. An increase in temperature increases sensitivity to impact markedly. Frozen nitroglycerin is much less sensitive than liquid and the liquid increases in sensitivity as the temperature rises. The most sensitive form, however, is when crystals are in contact with the liquid. Many accidents have occurred when frozen dynamite was jarred while being thawed. In general, unconfined bulk nitroglycerin is difficult to ignite by flame or heat, the ease of ignition improving as the nitroglycerin layer becomes thinner. Nitroglycerin may explode instead of igniting if large quantities are subjected to localized, sudden heating. If a very small quantity of the material is contained in a capillary glass tube and this is exposed to a flame, the nitroglycerin detonates with a loud report. When compared with similar values for other explosives, the five second explosion temperature test value of nitroglycerin, 222°C, does not indicate the observed sensitivity to initiation by heat. At 50° to 60°C nitroglycerin liquid or the liquid saturated in filter paper does not explode or ignite from a 13 kilovolt spark from an eight micro farad capacitor. In gap sensitivity tests, blends of 15 percent nitroglycerin and 85 percent inert salts were packed in two identical 30 to 32 millimeter diameter tubes and placed end to end on dry sand a definite distance apart. Detonation of one tube resulted in detonation of the other at maximum gaps for these salts of: NH_4Cl at 25 centimeters, NaCl at 11 centimeters, $NaHCO_3$ at 10 centimeters. Diammonium sulfate,

diammonium carbonate, chalk, or talc did not transmit the detonation even at zero gap. The particle size of the salts is important. For NaCl the optimum size is 0.10 to 0.12 millimeter in greatest dimension. Nitroglycerin is initiated to detonation by a black powder squib, but not uniformly so. No data are available in connection with the sensitivity of nitroglycerin to initiation by initial detonating agents. However, the fact that 40 percent straight dynamite can be detonated by lead styphnate indicates a high degree of sensitivity, since lead styphnate will not detonate pressed PETN and this is very sensitive to initiation.

(10) Pure nitroglycerin is too sensitive to be transported by common carrier. A mixture of 70 parts of nitroglycerin and 30 parts of acetone by weight is relatively insensitive and sometimes is transported by wagon or truck. Such a mixture can be detonated by a No. 8 blasting cap. Modified Bureau of Mines impact tests of various mixtures gave the sensitivity values shown by table 8-3.

Table 8-3. Impact Sensitivity of Nitroglycerin-Acetone Mixtures

Composition, percent		Impact test centimeters
Nitroglycerin	Acetone	
100	0	16
90	10	23
80	20	41
75	25	60
73	27	64
70	30	100+

The nitroglycerin in such a mixture can be separated from the acetone by precipitating the nitroglycerin by addition of an excess of water or by evaporating the acetone with a current of air. An emulsion of 87 percent nitroglycerin and 13 percent water that has been stabilized with methyl cellulose also has been found to be sufficiently insensitive to permit safe handling. This mixture is not detonated by a blasting cap.

(11) The detonation velocity of nitroglycerin varies according to the method of initiation. When properly initiated, the normal rate of detonation at a density of 1.60 grams per cubic centimeter is given as 7,700 meters per second. When improperly initiated, the rate can be as low as 1,500 to 2,000 meters per second. The rate of detonation also varies according to the state of the nitroglycerin. In a 22 millimeter inner diameter glass tube with a 7,000 meters per second picric acid fuse, detonation velocities of 9,150 meters per second, 0 meters per second, and 1,165 meters per second were obtained for the stabile, labile, and liquid forms, respectively. Use of a 20 gram tetryl booster gave 9,100 meters per second for the labile form. Use of 10 to 15 grams of the stabile form as a booster gave 8,750 meters per second for the liquid form. Tests indicate that the brisance of the stabile form is much higher than either the labile or liquid form. The Trauzl lead block compression test indicates nitroglycerin is 115 percent as brisant as TNT while the sand test indicates a value of 120 percent. The temperature of explosion is given as 4,577°C for the decomposition as shown:

$$NG \longrightarrow 3CO_2 + 2.5H_2O + 1.5_2N + 0.5O_2$$

and a resultant pressure of 10,000 atmospheres. Trauzl lead block test results of 390 cubic centimeters, 518 cubic centimeters, and 560 cubic centimeters were obtained for the stabile, liquid, and labile forms, respectively. The Trauzl lead block test value for nitroglycerin is greater than that for any other military explosive. This is in agreement with the correspondingly high heat of explosion value. The ballistic pendulum test values indicate RDX and PETN to be more powerful than nitroglycerin. This can be explained by the fact that nitroglycerin has a ratio of combined oxygen to oxygen required for complete combustion of 105.9 percent, while RDX and PETN have corresponding ratios of 66.7 and 85.7 percent, respectively. In the Trauzl test, the samples are not in contact with air, while in the ballistic pendulum test, air surrounds the sample when placed in the explosion chamber. This would tend to increase the test value for explosives that are less than oxygen-balanced but have no effect on the test value for nitroglycerin.

(12) Nitroglycerin is quite stable at temperatures less than 50°C, as shown by storage tests over a period of years. At higher temperatures, the rate of decomposition increases rapidly, and 100°C vacuum stability test data show that at that temperature nitroglycerin is the least stable of the standard military explosives of the noninitiating type. Nitroglycerin does not cause significant corrosion of metals. This is attributed to the low solubility in water, the stability, and the neutrality of nitroglycerin. Rust markedly increases the decomposition of nitroglycerin, as indicated by 100°C vacuum stability tests. The presence of more than a trace of free acid renders nitroglycerin quite unstable; decomposition with the appearance of red fumes takes place within a few days.

e. *Nitrostarch (NS).*

(1) Nitrostarch is a mixture of nitrates obtained by nitrating starch. The general formula for starch is $C_6H_{10}O_5$. The structure of starch is the same as for nitrocellulose, as shown in figure 8-3, with the exception that the polymer chains are spiral rather than straight. The starch molecule consists of approximately 1,000 anhydroglucose units. The nitration of starch involves replacement of the hydrogen in the three hydroxyl (OH) groups in the anhydroglucose units with NO_2 groups. A representative formula for the nitrated starch may be written as $C_6H_7(OH)_x(ONO_2)_y$ where $x+y=3$. The NO_2 groups are distributed randomly along the entire length of the starch molecule, so x and y should be regarded as averages over the entire length of the chain. The following empirical formula can be employed to obtain y as a function of the nitrogen content N:

$$y=162N/(1400\text{-}45N)$$

The appearance of nitrostarch is practically the same as the unnitrated starting material. Nitrostarch's solubility characteristics are determined by nitrogen content. With a nitrogen content below 8 percent, nitrostarch is scarcely soluble in a mixture of ether and alcohol. If the nitrogen content is between 8 percent and 12.8 percent, the solubility is complete but with a nitrogen content of over 12.8 percent, nitrostarch is only partially dissolved. For a nitrogen content of 6.4 percent, the solubility is 8.4 percent and for a nitrogen content of 13.1 percent the solubility is 78 percent. In acetone the solubility is complete for a nitrogen content of more than 6.4 percent. In ethyl alcohol the solubility is complete if the nitrogen content is between 10 and 11.5 percent. From a chemical viewpoint, nitrostarch may be considered to be another form of nitrocellulose with the same nitrogen content. Decomposition can be accomplished with sulfuric acid in the presence of mercury. Therefore nitrogen content can be measured by an nitrometer. When dissolved in nitric acid and allowed to stand, nitrostarch is decomposed. As with nitrocellulose, aqueous alkali solutions cause saponification. Nitrostarch has a wide variety of gelatinizing agents and is used rather than nitrocellulose in explosive compositions chiefly as a substitute for nitroglycerin. These compositions have the major advantage of being nonfreezing and not subject to the desensitization that accompanies the freezing of nitroglycerin explosives. Nitrostarch explosives have been used as successfully in the Antarctic and Arctic regions as in temperate climates. There is no standard grade of nitrostarch used for military purposes, but there is a specified commercial grade having a nitrogen content from 12.8 to 13.3 percent.

(2) The methods of production and stabilization of nitrostarch are considered trade secrets, so details are scarce. The starch used is produced from corn or cassava and can be obtained from potatoes. This is purified to some extent by washing with a dilute sodium hydroxide or ammonia solution to remove fats and pectic acid and then washing with water. The starch is then dried so that the moisture content is less than 0.5 percent. Nitrostarch can be prepared by dissolving starch in an excess of nitric acid and pouring this solution into an excess of sulfuric acid to precipitate the nitrostarch as an amorphous powder. This method is uneconomical and hard to control and consequently, not used commercially. The usual preparation methods employ mixed acids. The nitrogen content of the nitrostarch depends on the composition of the mixed acid and on the mixed acid to starch ratio. A ratio of 4 parts mixed acid to 1 part starch is used in one manufacturing process. The starch is added to the mixed acid in a nitrator, the temperature not exceeding 38° to 40°C. The composition of the mixed acid varies with the degree of nitration desired; an acid for nitration to 12.75 percent nitrogen contains 38 percent nitric acid and 62 percent sulfuric acid. After nitration is complete, the contents of the nitrator are drowned in cold water and the nitrostarch caught on a filter. Nitrostarch is purified by washing with cold water, with the addition of ammonia during the preliminary washing, until all traces of free acid are removed. After separation on a filter or in a centrifugal wringer, the nitrostarch is dried on trays in a dry house, heated to 35° to 40°C. The drying operation is the most dangerous of those involved in the manufacture of nitrostarch because the dry material is sensitive to ignition by spark and burns with great violence. Nitrostarch can also be prepared via nitration with nitric and phosphoric acids N_2O_5 dissolved in nitric acid; N_2O_5 dissolved in chloroform; or nitric acid with P_2O_5.

(3) Nitrostarch is slightly less sensitive to impact than guncotton, or about 280 percent as sensitive as TNT. The explosion temperature test value of nitrostarch, 217°C, is essentially the same as that for nitrocellulose, 230°C.

(4) The brisance and power of nitrostarch are similar to those of nitrocellulose of comparable nitrogen content. The detonation velocity depends on the nitrogen content. The range for properly detonated nitrostarch is from 1,000 meters per second at 8.9 percent to 6,190 meters per second at 13.4 percent.

(5) Heat tests at 120° and 134.5°C indicate nitrostarch is less stable than nitrocellulose; at ordinary temperatures, the two appear to be of similar stability as judged by long term storage tests.

f. *Pentaerythritol Tetranitrate (PETN).*

(1) PETN is also known as 2,2-bis [(nitrooxy) methyl] – 1,3-propanediol dinitrate; penthrite; or nitropenta and may be referred to as TEN. The compound (figure 8-9) is a white solid with a molecular weight of 316.2. PETN has two polymorphs: one with a tetragonal crystalline structure and the other with an orthorhombic crystalline structure. The phase change between the two polymorphs occurs at 130°C. The tetragonal crystals have a density of 1.778 grams per cubic centimeter and the orthorhombic crystals have a density of 1.716 grams per cubic centimeter. Normal manufacturing yields tetragonal crystals. The unit cell dimensions of the tetragonal crystals are a=9.38 Angstroms, b=9.38 Angstroms, and c=6.71 Angstroms. The dimensions for the orthorhombic crystals are a=13.29 Angstroms, b=13.49 Angstroms, c=6.83 Angstroms. There are two molecules per cell in the tetragonal form and four molecules per cell in the orthorhombic form. The interatomic distances have been determined as 1.50 Angstroms for the C-C bonds, 1.37 Angstroms for the C-O bonds, 1.36 Angstroms for O-N bonds, and 1.27 Angstroms for N-O bonds. PETN melts at 141.3°C. The boiling point is 160°C under a pressure of 2 torr; 180°C under a pressure of 50 torr. Under atmospheric pressure at temperatures above 210°C, PETN decomposes rapidly and in some cases detonates. The vapor pressure of solid PETN can be found by the empirical equation:

$$\log p = 16.73 - 7750/T$$

where p is the vapor pressure in millimeters of mercury and T is in degrees Kelvin. The vapor pressure of liquid PETN can be determined by the relationship:

$$\log p = 14.44 - 6352/T$$

The standard heat of formation of PETN is given as – 128.7 kilocalories per mole. The heat of detonation is 1.65 kilocalories per gram for liquid water and 1.51 kilocalories per gram for gaseous water. The specific heat is given by the equation $0.239 + 0.008T$ for T in the range of 32°C to 127°C. Two equations are given for the specific heat of PETN as a function of temperature:

$$C = 0.257 + (5.21 \times 10^{-4})T \text{ for } T \leq 140^\circ C$$

and

$$C = 0.239 + (8.0 \times 10^{-4})\,T \quad \text{for } 32^\circ C < T < 127^\circ C$$

where C is in units of calories per gram per degree centigrade. The heat of combustion is 618.7 kilocalories per mole and the heat of formation is – 110.34 kilocalories per mole. Table 8-4 lists the packing density as a function of loading pressure.

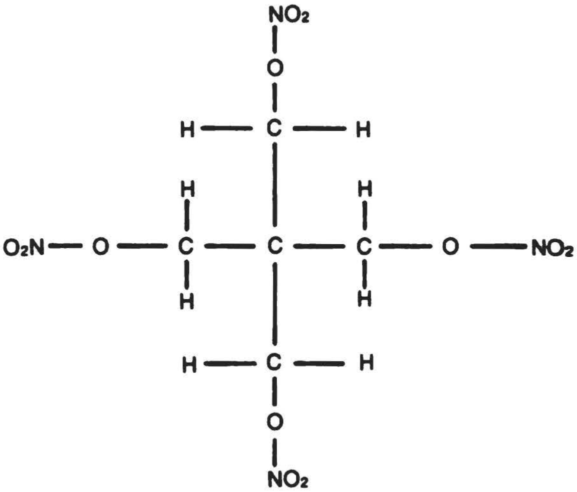


Figure 8-9. Structural formula of PETN.

Table 8-4. Packing Density

Pressure kilograms per square centimeter	Density grams per cubic centimeter
351	1.575
703	1.638
1,406	1.710
2,109	1.725
2,812	1.740

PETN crystals have a scratch hardness of slightly less than 2 on the Mohs scale. PETN is practically insoluble in water; at 25°C and 96°C the solubility is only 0.0043 and 0.018 grams per 100 grams of water, respectively. Table 8-5 lists the solubility of PETN in acetone-water mixtures.

Table 8-5. Solubility of PETN in Acetone Water Mixtures

Amount of PETN, in grams, dissolved in 100 grams of solvent	Acetone concentration				
	55%	70%	80%	90%	92%
	Temperature of solution, °C				
1	41	-	-	-	-
2	52	-	-	-	-
2.5	-	24.5	-	-	-
4	62	-	-	-	-
5	-	41.5	22	-	-
10	-	54.5	38.5	15	10
15	-	62	48	24.5	20.5
17.5	-	65	-	-	-
20	-	-	54	34.5	29
25	-	-	59	41.5	34
30	-	-	63	46.5	40.5
35	-	-		51.5	45
40	-	-	-	55	50
45	-	-	-	58.5	54
50	-	-	-	61.5	57.5
55	-	-	-	-	60.5
60	-	-	-	-	62.5

PETN forms eutectic mixtures with a number of compounds as shown in table 8-6.

Table 8-6. PETN Eutectics

Composition	Melting point (°C)
1.5 percent PETN with 98.5 percent nitroglycerin	12.3
20 percent PETN with 80 percent m-dinitrobenzene	82.4
10 percent PETN with 90 percent 2,4-dinitrotoluene	67.3
13 percent PETN with 87 percent trinitrotoluene	76.1
30 percent PETN with 70 percent tetryl	111.3
20 percent PETN with 80 percent mannitol hexanitrate	101.3

(2) PETN is decomposed much more slowly by a boiling 2.5 percent solution of sodium hydroxide than nitrocellulose. Several hours are required for complete decomposition. At 50°C a solution of sodium sulfide decomposes PETN slowly, but decomposition proceeds rapidly in a boiling solution of ferrous chloride. PETN does not reduce Fehling's solution even on boiling. Hydrolysis of PETN takes place in water about 100°C; at 125°C under pressure the reaction proceeds quite quickly. Addition of 0.1 percent nitric acid enhances the hydrolysis. The main product of hydrolysis is pentaerythritol dinitrate. At temperatures up to about 50°C, dry PETN does not react with copper, brass, aluminum, magnesium, magnesium-aluminum alloys, stainless steel, mild steel, mild steel coated with acid-proof black paint, and mild steel plated with copper, cadmium, nickel or zinc. Wet PETN does not react with stainless steel, and aluminum is affected only slightly after long periods of storage. However copper, brass, magnesium, magnesium-aluminum alloys, mild steel, mild steel coated with acid-proof black paint, and mild steel plated with cadmium, copper, nickel or zinc are affected. PETN is used in the explosive core of industrial detonating fuses, in the charge of commercial blasting caps, and as the entire explosive charge in exploding bridge wire detonators. PETN is also used in certain plastic bound explosives and in a mixture with TNT called pentolite.

(3) While PETN can be manufactured by treating pentaerythritol with nitric acid and adding concentrated sulfuric acid to complete the separation of the PETN, manufacture in the United States has been with nitric acid alone:

$$C(CH_2OH)_4 + 4HNO_3 \longrightarrow C(CH_2NO_3)_4 + 4H_{2}0$$

This is accomplished by adding approximately 75 pounds of pentaerythritol to 350 pounds of 98 percent nitric acid in a nitrator, and stirring and cooling the acid continuously. The pentaerythritol is added at a rate that, with an initial acid temperature of 18°C, the temperature increases to and is maintained at 22° to 23°C. Stirring and cooling are continued for 20 minutes after addition of the pentaerythritol is complete. The acid solution then is added, with agitation, to about 850 pounds of cold water in a drowning tank. The precipitated PETN is caught on a glass-cloth filter and washed with water. The precipitate is then mixed with 1,300 gallons of cold water containing 2 pounds of sodium carbonate and separated from the slurry by refiltering. After being washed again with water, the PETN is dissolved in 440 pounds of 98 percent acetone heated to 50°C and containing 14 ounces of ammonium bicarbonate. The solution is filtered and the PETN precipitated by the addition of cold water to the acetone solution. The precipitated solid is caught on a filter and washed with water to remove acetone. The water wet material is considered the final product. Drying is done at the point of use. The yield of PETN by this process is approximately 93 percent of the theoretical. The spent acid resulting from the drowning operation contains approximately 20 percent nitric acid. This is recovered and concentrated. The mother liquor, resulting from the precipitation of PETN, contains approximately 25 percent acetone, which also is recovered. The purity of PETN produced by this process depends upon that of the pentaerythritol nitrated. Ordinarily, the pentaerythritol used for nitration contains 2 or 3 percent of dipentaerythritol and a small amount of tripentaerythritol:

$(HOH_2C)_3C.CH_2O.CH_2.C(CH_2OH)_3$ and
$(HOH_2C)_3C.CH_2O.CH_2C(CH_2OH)_2.CH_2O.$
$CH_2C(CH_2OH)_3.$

PETN produced on a large scale contains corresponding amounts of the hexanitrate and octanitrate of these compounds, respectively.

(4) One grade of PETN is used for military purposes and this complies with the following requirements:

Color: White or light buff.
Moisture[1]: Minimum, 40 percent.
Melting point: 141°±1°C.
Nitrogen content: Minimum, 17.50 percent.
Acetone insoluble[1]: Maximum, 0.10 percent
Insoluble particles[2]: None
Acidity or alkalinity[2]: Maximum, 0.01 percent
120°C vacuum stability test: Maximum, 5 milliliters of gas from 2.3 grams in 20 hours.

Granulation:

Through sieve No.		Class A	Class B	Class C	Class D
30	Minimum	-	-	95	100
80	Minimum	100	-	-	-
100	Maximum	-	-	-	20
100	Minimum	85	96	-	5
140	Maximum	55	-	-	-
200	Maximum	30	80	30	-
200	Minimum	-	65	-	-

[1] Not applicable to class C PETN used in coprecipitated pentolite.
[2] Not applicable to class C PETN.

Class A PETN is used in detonating fuses and boosters; class B is used in priming compositions; class C is used in the manufacture of pentolite; and class D is used in blasting caps and detonators. Pure PETN has a nitrogen content of 17.72 percent and a melting point of 141.3°C. The military grade is approximately 99 percent pure. The insoluble particles requirement is important because of the sensitivity of PETN and the known effect of gritty material in increasing sensitivity. The acidity or alkalinity requirement is important since the presence of as little as 0.01 percent of either has been found to accelerate the deterioration of PETN markedly. The granulation requirements are those found optimum for specific uses of PETN.

(5) PETN is not as sensitive to impact as nitroglycerin or nitrocellulose, but is slightly more sensitive than RDX and distinctly more so than tetryl. Experiments using a five kilogram weight dropped one meter onto a 15 milligram sample of polycrystallin PETN show the physical changes that occur before initiation. The layer of PETN compresses to about 0.1 millimeter thick. After about 10 microseconds, lateral spreading stops and jetting occurs at 150 meters per second. The initially opaque layer of PETN becomes gradually translucent in an additional 10 to 15 microseconds and completely transparent in 15 to 20 microseconds. The transparency and rapid mobility of the PETN is associated with surface fusion and then melting of the entire sample. About 25 microseconds after the lateral spreading has stopped, the jetting velocity has increased to 300 meters per second and five microseconds after that several hot spots develop simultaneously. The exact mechanism of how the hot spots form is controversial and no generally satisfactory explanation has been put forward. The hot spots are points where deflagration has started. Initially, the deflagration proceeds at several tenths of a meter per second. The products of gaseous combustion raise the pressure of the reaction region and accelerate the rate of deflagration. At the same time, the products of hot combustion penetrate into unreacted regions to produce new ignition sites and a further pressure increase, accelerating deflagration even more. At about 5 to 15 millimeters from the point of initiation, the velocity of the flame front has increased to several hundred meters per second. The flame front drives a compression wave into the unreacted material. When this compression wave attains a velocity of about 700 to 800 meters per second, there is a sharp increase in the propagation velocity to about 1000 meters per second. Depending on the condition of the explosive, this low velocity detonation can propagate over considerable distances or can go over into a normal detonation whose propagation velocity is determined by the density and dimensions of the PETN layer. One condition that can cause acceleration of the detonation velocity to normal is going from a region of 90 percent crystal density to one of 80 percent crystal density. Initiation by friction and electrical spark proceeds like initiation by impact after the formation of the hot spots. The maximum nonignition spark voltage and nonignition energy for PETN with a particle size of 2.6 microns is 12000 volts and 0.036 joules, respectively, at 500 micro farads capacitance and a spark gap of 0.005 inches. The energy required to detonate PETN 50 percent of the time is 0.19 and 0.36 joules for brass electrodes with lead foil coatings of 3 and 10 mils, respectively. For a steel electrode, the energy required is 0.1 and 0.41 joules with lead foil coatings of 1 and 10 mils, respectively. The physical condition of the explosive appears to have some influence on the amount of energy required for initiation. The discharge energy required increases with PETN particle size, packing density, water content, circuit inductance, and a decrease in ambient temperature. PETN is not particularly sensitive to electrostatic spark. The electrostatic sensitivity parameters should not be confused with the initiation of PETN by an exploding bridge. The exploding bridge is a wire through which a large current is passed, causing the wire to burst. There is an optimum length for each wire material and a minimum critical volume of explosive that must be detonated to cause initiation. Other factors that enhance the ability of the bridge to detonate PETN are: high power input to increase temperature and pressure, a sustained electrical energy input just after the wire bursts to provide simultaneous electrical and chemical energy contributions during the critical growth to detonation period, and use of wire materials with low boiling points and heats of vaporization for greater heat transfer. Attempts to initiate PETN by normal light have been generally unsuccessful although a few instances of some deflagration have occurred with very intense light. Lasers can be used to initiate PETN. The energy required for initiation increases with increased packing density. PETN five millimeters thick with a density of one gram per cubic centimeter can be detonated by a neodymium glass laser with an output at 10600 Angstroms when the beam is focused to produce a power density in excess of 0.08 megawatts per square millimeter. The delay in producing a steady detonation under these conditions is 1.5 to 2.0 microseconds. The delay can be reduced to under 0.5 microseconds if the PETN is coated with a 1000 Angstrom thick layer of aluminum which has been deposited on the sample, and the laser radiation is from 0.5 to 4.2 joules for 25 nanoseconds. Initiation appears to be a thermal process. The laser energy is absorbed rapidly in a thin layer of explosive which produces a shock wave that causes the initiation of the entire sample.

(6) Gap tests indicate the shock sensitivity of PETN increases as packing density increases and as particle size increases. Gap test results are shown in table 8-8.

Table 8-8. Gap Test Results for PETN

	Density	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.775	0.3	6.03
	1.576	11.5	14.38
	1.355	27.9	13.56
LANL small scale gap test	1.757 (pressed)	0.7	5.21
LANL large scale gap test	0.81 (raw)	54.2	69.4

Increasing the pressure of an inert gas such as carbon dioxide, nitrogen, or a nobel gas in the interstices of a PETN pressing decreases shock sensitivity. Increasing the pressure of oxygen increases shock sensitivity. In cast PETN and PETN that has been pressed to 90 percent of the crystal density, substantial reactions take place well behind the shock front that enters the charge and proceeds through the explosive. Stable detonation occurs when the compression waves produced by this reaction catch up with the initial shock front. PETN is less sensitive to friction than RDX and more sensitive than nitroglycerin, as judged by the pendulum friction test. Explosion temperature test values indicate PETN to be as sensitive to heat as nitroglycerin or nitrocellulose. However, the minimum temperature required for the explosion of PETN, 215°C, is greater than that required for the explosion of nitroglycerin, 210°C, and nitrocellulose, 175°C. PETN is more sensitive to initiation than nitrocellulose, RDX, or tetryl, as judged by the sand test. This is shown, also, by the fact that PETN with 35 percent of water present can be detonated by a No. 6 electric blasting cap, whereas RDX fails to explode if more than 14 percent of water is present. PETN is one of the most sensitive of the standardized military explosives.

(7) As measured by the sand test, PETN is between 129 and 141 percent as brisant as TNT. Plate dent tests indicate PETN is 127 percent as brisant as TNT and the lead block compression test indicates a brisance of between 130 and 137 percent of TNT. Table 8-9 lists the detonation velocity of PETN at various packing densities determined experimentally with the confinement indicated.

Table 8-9. Detonation Velocity Versus Density

Density (g/cc)	Detonation velocity (m/sec)	Density (g/cc)	Detonation velocity (m/sec)
1.773	8,300*	1.27	6,660†
1.765	8,280†	1.26	6,760†
1.765	8,240*	1.09	5,830†
1.763	8,270*	0.55	3,850*
1.762	8,250*	0.436	3,400*
1.762	8,260*	0.241	2,810*
1.51	7,440†	0.201	2,730*
1.51	7,490†	0.185	2,670*

*Unconfined rate stick
†Cylinder test

The following equations, which are in agreement with the data in the table, specify the detonation velocity in kilometers per second as a function of density, p, for the range indicated.

$$D=2.14+2.84p \qquad p < 0.37$$

$$D=3.19+3.7(p-0.37) \qquad 0.37 < p < 1.65$$

$$D=7.92+3.05(p-1.65) \qquad p > 1.65$$

The diameter of a PETN charge has little effect on the velocity of detonation. The charge diameter below which no detonation can take place (the critical diameter) is only 0.9 millimeters for PETN at a density of one gram per cubic centimeter with 0.025 to 0.1 millimeter particles. The critical diameter becomes smaller as the density of the charge is increased. Since confinement effects parallel the diameter effects, the detonation velocity of PETN is not greatly affected by confinement for any particular charge size. This is also indicated by table 8-9. Detonation, or Chapman-Jouguet, pressure is shown as a function of packing density in table 8-10.

Table 8-10. PETN Detonation Pressures Versus Density

Density grams per cubic centimeter	Dimensions of PETN: Diameter × length Centimeters (inches)	Detonation pressure (kbar)
	Shock Electric Effect Measurements	
1.764	5 × 1.3 (2 × 0.5)	338
1.763	2.5 × 1.3 (1 × 0.5)	333
1.763	2.5 × 2.5 (1 × 1)	340
1.763	5 × 1.3 (2 × 0.5)	338
1.763	5 × 2.5 (2 × 1)	340
1.762	5 × 2.5 (2 × 1)	339
1.758	2.5 × 2.5 (1 × 1)	333
1.71	2.5 × 2.5 (1 × 1)	309
1.70	2.5 × 2.5 (1 × 1)	307
1.69	2.5 × 2.5 (1 × 1)	304
1.60	2.5 × 2.5 (1 × 1)	266
1.59	2.5 × 2.5 (1 × 1)	259
1.53	2.5 × 2.5 (1 × 1)	225
1.46	2.5 × 2.5 (1 × 1)	198
1.45	2.5 × 2.5 (1 × 1)	208
1.44	2.5 × 2.5 (1 × 1)	199
1.38	2.5 × 2.5 (1 × 1)	173
1.23	2.5 × 2.5 (1 × 1)	138
0.99	2.5 × 1.3 (1 × 0.5)	87
0.95	2.5 × 1.3 (1 × 0.5)	85
0.93	2.5 × 2.5 (1 × 1)	77
0.93	2.5 × 3.8 (1 × 1.5)	72
0.89	2.5 × 2.5 (1 × 1)	71
0.88	2.5 × 2.5 (1 × 1)	68
	Optical (Smear Camera) Measurements	
0.48	3.8 × 2.5 (1.5 × 1)	24
0.30	3.8 × 1.3 (1.5 × 0.5)	24
0.29	3.8 × 2.5 (1.5 × 1)	15
0.27	3.8 × 1.3 (1.5 × 0.5)	5
	Quartz Crystal Measurements	
0.25	4.5 × 2.5 (1.75 × 1)	8
0.25	4.5 × 2.5 (1.75 × 1)	7
0.25	4.5 × 3.8 (1.75 × 1.5)	6

The ballistic mortar test indicates PETN is 137 to 145 percent as powerful as TNT. The Trauzl test indicates PETN is 161 to 189 percent as powerful as TNT. PETN is ranked with RDX and nitroglycerin as the most potent of military explosives.

(8) The products obtained upon detonation of PETN depend on the density of the explosive. The four equations listed in subparagraphs (a) through (d) are valid at the density given. The subscript s refers to soot. The soot is produced in the Chapman-Jouguet region by the reactions:

$$CO + H_2 \longrightarrow C_s + H_2O$$
$$2CO \longrightarrow C_s + CO_2$$

(a) For PETN with density of 1.77 grams per cubic centimeter:

$$C_5H_8N_4O_{12} \longrightarrow 3.95CO_2 + 0.096CO + 0.95C_s + 4.00H_2O + 2N_2 + 477.4 \text{ kcal/mole}$$

(b) For PETN with density of 1.67 grams per cubic centimeter:

$$C_5H_8N_4O_{12} \longrightarrow 3.89CO_2 + 0.22CO + 0.88C_s + 4.00H_2O + 2N_2 + 474.2 \text{ kcal/mole}$$

(c) For PETN with density of 1.2 grams per cubic centimeter:

$$C_5H_8N_4O_{12} \longrightarrow 3.04CO_2 + 1.96CO + 3.96H_2O + 0.025H_2 + 2N_2 + 436.3 \text{ kcal/mole}$$

(d) For PETN with density of 1.0 grams per cubic centimeter:

$$C_5H_8N_4O_{12} \longrightarrow 3.04CO_2 + 1.96CO + 3.94H_2O + 0.050H_2 + 1.99N_2 + 0.02NO + 436.3 \text{ kcal/mole}$$

and minor amounts of NH_3, H, OH and CH_4.

(9) Vacuum stability tests at 100° and 120°C show PETN to be more stable than nitrocellulose or nitroglycerin at elevated temperatures but distinctly less stable than RDX, tetryl, or TNT. PETN is quite stable at 100°C and can withstand heating at this temperature for 100 hours without significant deterioration. In the LLNL reactivity test 0.10 to 0.14 cubic centimeters of gas are evolved per .25 grams of sample. Figure 8-10 shows the percentage of PETN decomposition as a function of time and temperature for temperatures over 140°C. The curves were obtained by heating a sample to the indicated temperature for the indicated time then analyzing the remaining PETN. The following six reactions, which take place simultaneously, show the mechanism of thermal decomposition:

1 $RCH_2ONO_2 \longrightarrow RCH_2O + NO_2$
2 $NO_2 + RCH_2O \longrightarrow RCH_2ONO_2$
3 $RCH_2O \longrightarrow$ intermediate decomposition products (IDP) such as H_2CO
4 $IDP + NO_2 \longrightarrow NO + N_2O + N_2 + CO + CO_2 + H_2O$
5 $RCH_2ONO_2 + H_2O \xrightarrow{HNO_3} RCH_2OH + HONO$
6 $H_2O + 3NO_2 \longrightarrow 2HNO_3 + NO$

PETN is shown as RCH_2ONO_2. Storage at 65°C for 20 months does not cause instability or undue acidity; and after 24 months only slightly excessive acidity developes. Figure 8-11 shows the DTA curve and figure 8-12 shows the TGA curve for PETN. When 0.01 percent of free acid or alkali is present, storage for only 15 months at 65°C results in rapid acceleration of the rate of decomposition. Since RDX, tetryl, and TNT are even more resistant to storage at 65°C, PETN is not as suitable for storage and use under tropical conditions.

g. *Triethylene Glycoldinitrate (TEGN).*

(1) This explosive is also referred to as TEGDN. The compound (figure 8-13) is a light yellow, oily liquid with a nitrogen content of 11.67 percent, a molecular weight of 240.20, and an oxygen balance to CO_2 of −66.6 percent. The melting point of the solid is −19°C. Other characteristics of the liquid are: refractive index, 1.4540; viscosity at 20°C, 13.2 centipoises; vapor pressure at 25°C, less than 0.001 torr; volatility at 60°C, 40 milligrams per square centimeter per hour; and density, 1.335 grams per cubic centimeter. At constant pressure, TEGN's heat of combustion is 3428 calories per gram, heat of explosion is 725 kilocalories per kilogram, and heat of formation is −603.7 kilocalories per kilogram. TEGN is very soluble in acetone, ether, and a solution of 2 parts ether and 1 part ethanol. TEGN is soluble in carbon disulfide and slowly soluble in water. The primary use of TEGN is as a gelatinizing agent for nitrocellulose in propellants, but TEGN can also be used as a component in a liquid explosive, a plasticizer in the fabrication of flexible explosive sheets, and as a plasticizer in pytrotechnic flares.

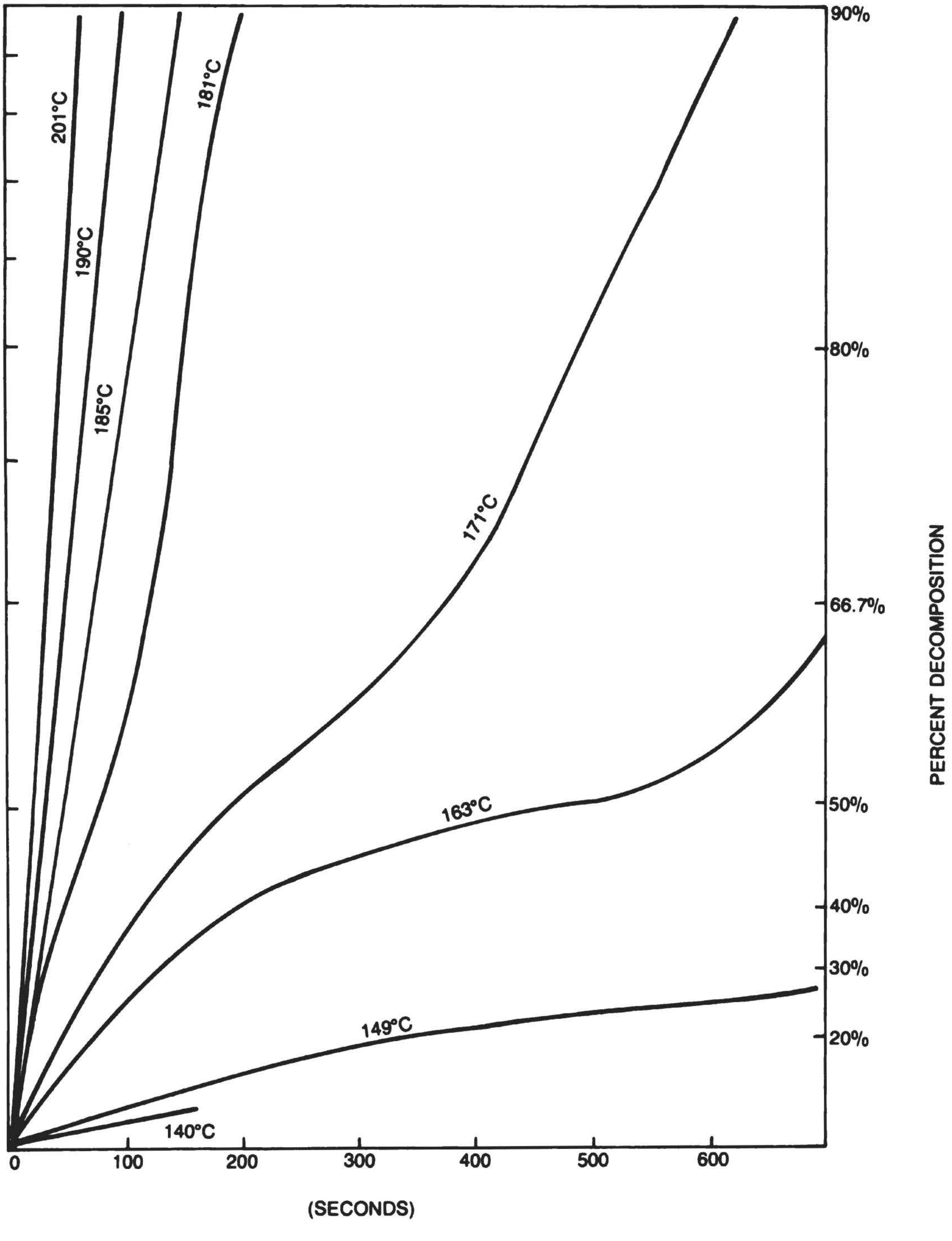


Figure 8-10. Thermal decomposition of PETN.

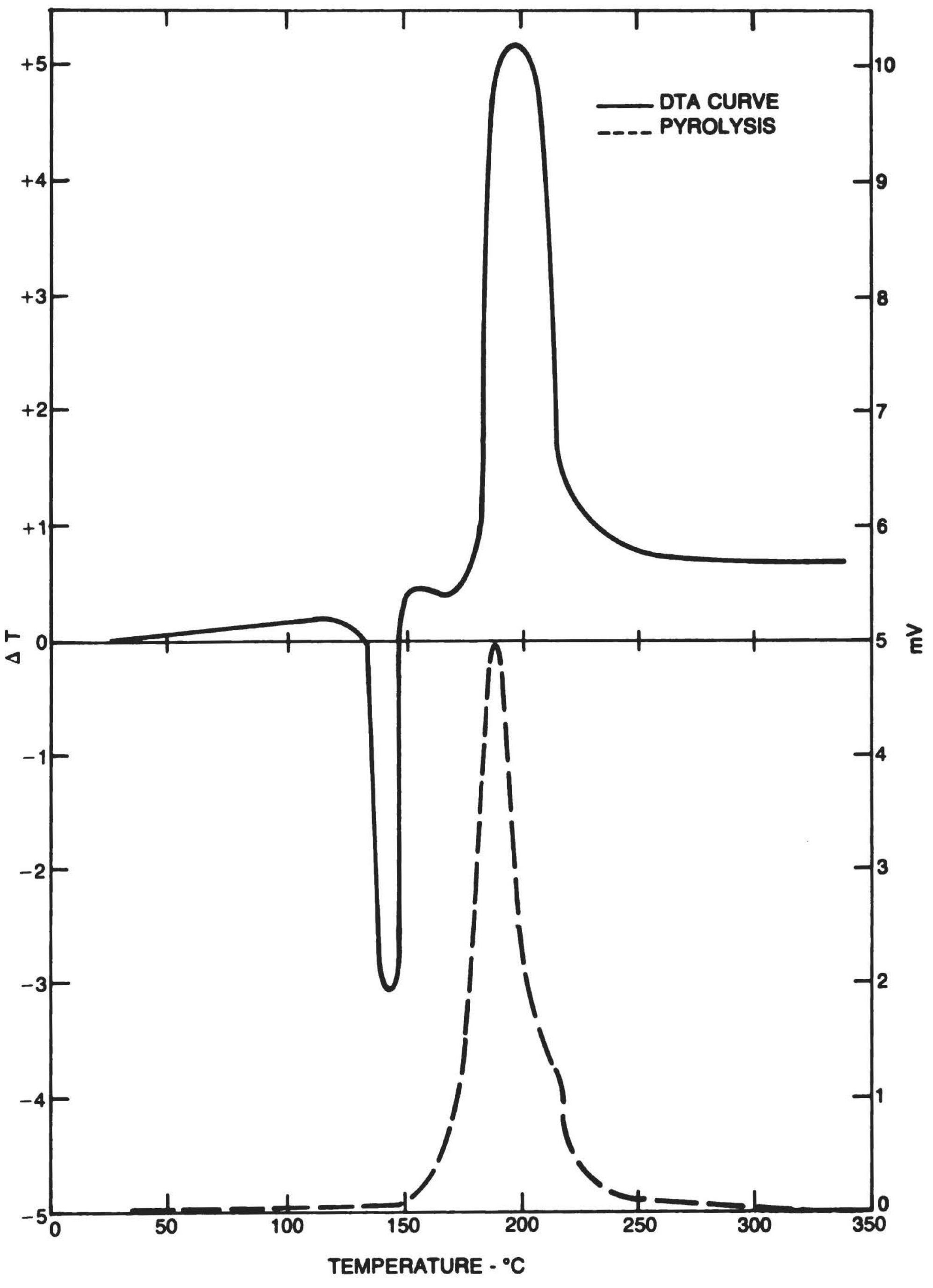


Figure 8-11. DTA curve for PETN.

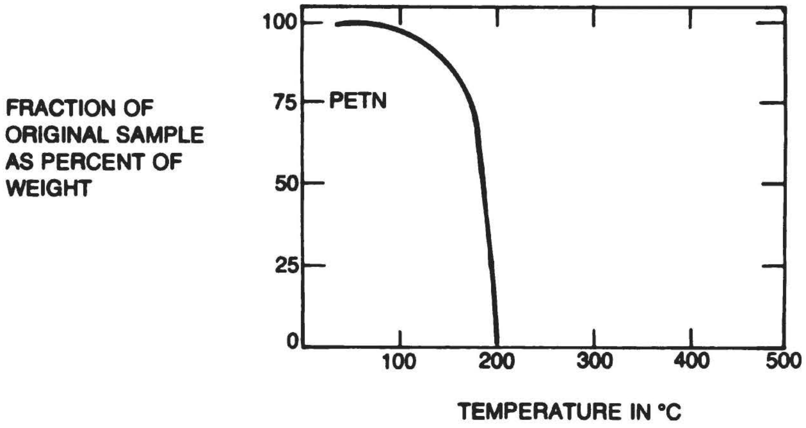


Figure 8-12. TGA curve for PETN.

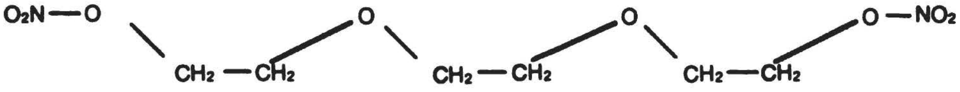


Figure 8-13. Structural formula for TEGN.

(2) TEGN is prepared by the nitration of triethylene glycol. The laboratory procedure for the production of TEGN is given here. The actual manufacturing procedure is by the Biazzi process, discussed under nitroglycerin. The triethylene glycol is purified by fractional distillation under vacuum in an 18 inch Vigeaux fractionating column. The assembly as a whole is equivalent to 4.5 theoretical plates. The distillation is conducted using a 5 to 1 reflux ratio, at a pot temperature of approximately 180°C and a take-off temperature of approximately 120°C. The purified triethylene glycol is carefully stirred into a mixed acid that consists of 65 percent nitric acid, 30 percent sulfuric acid, and 5 percent water that is maintained at 0 ± 5°C. The mixture is stirred and held at 0 ± 5°C for 30 additional minutes and then drowned by pouring over a large quantity of ice. The TEGN is extracted three times with ether and the combined extract is water washed until the pH is about four, then shaken with an excess solution of sodium bicarbonate, and further washed with a 1 percent sodium bicarbonate solution until the washings are colorless. The ether solution is then water washed until the pH is seven. The solution is then carefully separated from the excess water, treated with chemically pure calcium chloride to remove the dissolved water, and filtered. The ether is removed by bubbling with dry air. The yield is 1.34 grams of TEGN per gram of triethylene glycol, 84 percent of theoretical. The nitrogen content of different batches can vary from 11.60 to 11.69 percent with 11.67 percent the calculated value. A modification that allows continuous rather than batch nitration is to dissolve the triethylene glycol and mixed acid separately in dichloromonofluoromethane, $CHFCl_2$ or freon 21, and then mix the two solutions. A sufficient quantity of $CHFCl_2$ must be used to maintain the temperature at 11°C and to ensure a safe degree of dilution of the solution. The dispersant is evaporated and the TEGN is recovered. The yield of this process is 74 percent.

(3) TEGN is unaffected in the pendulum friction test with the metal and fiber shoe. The Bureau of Mines impact test indicates a sensitivity of over 100 centimeters and the Picatinny Arsenal impact test indicates 109 centimeters. The five second explosion temperature test value is 225°C.

(4) The 100°C heat test, with losses of 1.8 percent and 1.6 percent for the first and second 48 hour periods, respectively, indicates TEGN is much more stable than nitroglycerin but considerably less stable than all other standard explosives. No explosions occur in the 100 hour observation period. The vacuum stability test results, 45 milliliters of gas in 40 hours at 100°C and 0.80 to 0.99 milliliters of gas in eight hours at 120°C, indicate that TEGN is more stable than PETN, slightly less stable than RDX, and much less stable than TNT.

(5) TEGN is insensitive to detonation. No detonation occurs in samples placed in relatively light steel tubing with a diameter of 3.175 centimeters at a density of 1.33 grams per cubic centimeter. When heavily confined, the detonation velocity is less than 2,000 meters per second, or 30 percent of TNT. The 200 gram sand test indicates a brisance of 30.6 percent of TNT, with 14.7 grams of sand crushed. TEGN's deflagration point is 195°C.

(6) TEGN is extremely toxic and should be considered a potent poison when absorbed through the skin or ingested. Tests with rabbits indicate 21 millimoles per kilogram of body weight causes death in two to three weeks when absorbed through the skin. A level of intraperitonal exposure of 995 milligrams per kilogram of body weight causes death within 24 hours to 50 percent of the rats treated. TEGN, when selectively applied, can also inhibit the nerve functions in rats.

h. *1,1,1 - Trimethylolethane Trinitrate (TMETN).*

(1) This explosive is also known as metriol trinitrate and is sometimes referred to as MTN. The compound (figure 8-14) is a slightly turbid, viscous oil with a nitrogen content of 16.41 percent and a molecular weight of 255.15. TMETN has a melting point of −3°C and an apparent boiling point of 182°C, but this is merely the temperature at which decomposition becomes vigorous enough to resemble boiling. Other properties of the liquid are a density of 1.47 grams per cubic centimeter at 22°C and a refractive index of 1.4752 at 25°C. TMETN is practically insoluble in water. Less than 0.015 grams dissolved per 100 grams of water at up to 60°C. TMETN is soluble in alcohol and many other organic solvents. At 60°C TMETN's volitility is 24 milligrams per square centimeter. The heat of formation is 422 calories per gram at constant volume and 446 calories per gram at constant pressure. The heat of combustion is 2,642 calories per gram at constant volume with the water being liquid. In an acid bath, TMETN is hydrolyzed to the extent of 0.018 percent in 10 days at 22°C and 0.115 percent in 5 days at 60°C. TMETN can be used as a flash and errosion reducing additive in propellants and an ingredient of commercial explosives. TMETN alone does not gelatinize nitrocellulose unless the temperature is raised to 100°C, which would be dangerous. But if mixed with only 8 percent of metriol triacetate, gelatinization takes place at 80°C. When TMETN is mixed with nitroglycerin, the mechanical properties of double-base cast propellants are improved. Combinations with triethylene glycol dinitrate are used as plasticizers for nitrocellulose.

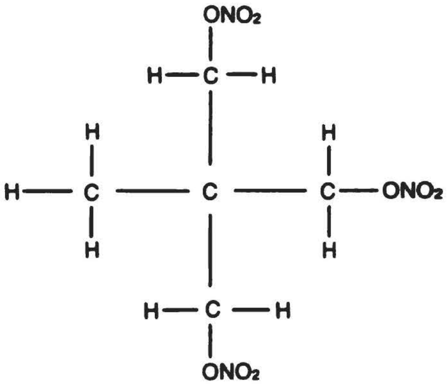


Figure 8-14. Structural formula for TMETN.

(2) One method for the manufacture of TMETN is to feed 50 kilograms of finely powdered metriol into a nitrator provided with cooling coils and an agitator. The nitrator contains 175 kilograms of mixed acid that consists of 65 percent nitric acid and 35 percent sulfuric acid. The nitration time is about 20 minutes at 20°C after which the contents of the nitrator are allowed to set for 15 minutes. The TMETN separates from the spent acid and is decanted and then washed at 40°C with an aqueous solution of soda and then with water. The yield is almost 100 kilograms of TMETN with a nitrogen content of 16.32 to 16.36 percent.

(3) The Bureau of Mines impact apparatus indicates TMETN is as sensitive as nitroglycerin, with a drop height of four centimeters for a two kilogram weight. The five second explosion temperature test value is 235°C and TMETN detonates with both the metal and fiber shoe in the pendulum friction test.

(4) TMETN is 91 percent as brisant as TNT with 43.7 grams of sand crushed in the sand test. The Trauzl test and ballastic mortar test indicate TMETN to be 140 percent and 136 percent, respectively, as powerful as TNT.

(5) The stability of TMETN is not very satisfactory as indicated by the vacuum stability and heat tests. In the 100°C heat test, a 2.5 percent weight loss is reported in the first 48 hours and 1.8 percent in the second 48 hours. No explosions occur in the first 100 hours. In the 100°C vacuum stability test, 1.9 cubic centimeters of gas are evolved in the first 40 hours. At 25°C TMETN is hygroscopic to the extent of 0.07 percent with 90 percent relative humidity and 0.14 percent at 100 percent relative humidity.

8-3. Nitramines. Compounds in this class are prepared by *N-type* nitration in which a nitro group is attached to a nitrogen atom of the compound being nitrated.

a. *Cyclotetramethylenetetranitramine (HMX).*

(1) HMX is also known as: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane; cyclotetramethylene tetranitramine; or octogen. HMX (figure 8-15) is a white, crystalline solid with a nitrogen content of 37.84 percent, a theoretical maximum density of 1.905 grams per cubic centimeter, a nominal density of 1.89 grams per cubic centimeter, a melting point of 285°C, and a molecular weight of 296.17. There are four polymorphs of HMX: an alpha, beta, gamma, and delta form. Each polymorph has a range of stability and there are differences among them in physical properties such as density, solubility, and refractive index. The most common polymorph is the beta form. The term HMX without an alpha, gamma or delta qualifier refers to the beta form throughout the rest of this text. The crystalline structure of beta HMX is monoclinic with a density of 1.903 grams per cubic centimeter. The unit cell dimensions are a=6.54 Angstroms, b=11.05 Angstroms, and c=8.70 Angstroms. Beta HMX is stable to about 102°C to 104.5°C,when the crystalline structure is converted to the alpha form. The crystals of the alpha form are orthorhombic with a density of 1.82 grams per cubic centimeter. The unit cell dimensions are a=15.14 Angstroms, b=23.89 Angstroms, c=5.91 Angstroms. At approximately 160°C to 164°C the meta stable gamma form exists. The crystals of the gamma form are monoclinic with a density of 1.76 grams per cubic centimeter. The unit cell dimensions are a=10.95 Angstroms, b=7.93 Angstroms, and c=14.61 Angstroms. Above the 160°C to 164°C range to the melting point, the delta form exists. The crystals of the delta form are hexagonal with a density of 1.80 grams per cubic centimeter. The unit cell dimensions are a=7.71 Angstroms and b=32.55 Angstroms. The polymorphs may also be prepared by precipitation from solution under various conditions. The beta form is precipitated from a solution of HMX in acetic acid, acetone, nitric acid, or nitrometrane with very slow cooling. The alpha form is precipitated from the same solution with more rapid cooling and the gamma form is precipitated with even more rapid cooling. The delta form is crystallized from solution such as acetic acid or betachloroethyl phosphate, in which HMX is only slightly soluble. Very rapid chilling of the solution is required. This is usually accomplished by pouring small quantities of the solution over ice. Military grade HMX consists only of the beta polymorph. HMX is insoluble in water, but is soluble in the solvents listed in table 8-11 to the degree shown.

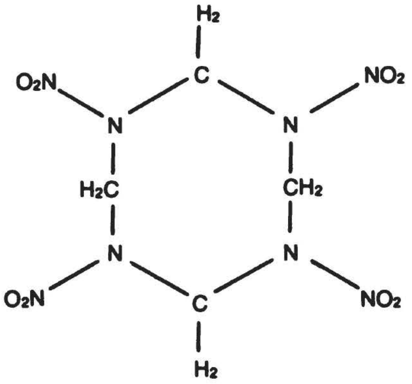


Figure 8-15. Structural formula for HMX.

Table 8-11. Solubility of HMX

Solvent	Grams of HMX dissolved per 100 grams of solution	Temperature °C
Dimethylformamide	4.4	25
Nitrobenzene	0.129	25
1,2-Dichlorethane	0.125	70
Acetic acid	0.0375	25
Acetone	0.96	25
Acetonitrile	1.98	25
Cyclohexanone	2.11	25
Ethylacetate	0.02	25
Ethylbromide	0.02	25
Methylethylketone	0.46	25
Nitroethane	0.172	25
Nitromethane	0.778	25
Triethylphosphate	1.75	25

Table 8-12 lists the solubility of HMX by volume for various solvents.

Table 8-12. Solubility of HMX by Volume

Solvent	Grams of HMX dissolved per 100 milliliters of solution
Gamma-butyrolactone	21.0
Cyclopentanone	1.3
Cyclohexanone	5.2
Acetone	2.2
Acetonitrile	2.0
Nitromethane	1.1
Nitroethane	0.03
Methylisobutylketone	1.8

HMX will also dissolve to the extent of 0.003 grams, 0.002 grams, and 0.144 grams in 100 milliliters of chloroform, carbon tetrachloride, and dioxane, respectively. Carbon disulfide will not dissolve HMX. Table 8-13 lists specific heat values for HMX at various temperatures.

Table 8-13. Specific Heat of HMX

Temperature °C	Calories per gram per degree centigrade
−75	0.153
0	0.228
25	0.248
50	0.266
75	0.282
85	0.288
90	0.290
100	0.295
125	0.307
150	0.315

HMX has a hardness of 2.3 on the Moh's scale, a heat of combustion of 660.7 to 667.4 kilocalories per mole, a heat of formation of 11.3 to 17.93 kilocalories per mole, a heat of detonation of 1.62 kilocalories per gram with liquid water and 7.48 kilocalories per gram with gaseous water. The vapor pressure of HMX in torr is given by the following equations for the temperature ranges indicated:

$$\log p = 16.18 - 9154/T(\mathrm{K}) \text{ for } 97.6°\mathrm{C} < T < 129.3°\mathrm{C}$$
$$\log p = 15.17 - 8596/T(\mathrm{K}) \text{ for } 188°\mathrm{C} < T < 213°\mathrm{C}$$

HMX and RDX are chemically very similar except that HMX is not easily decomposed by alkaline hydroxide. Concentrated sulfuric acid liberates a little more than one third of nitric acid with HMX while with RDX a little more than two thirds is liberated. HMX is used as an explosive charge when desensitized, as a booster charge in admixtures with TNT called octols, and as an oxidizer in solid rocket and gun propellants.

(2) Two grades of HMX are used for military applications. Both grades consist of only the beta polymorph and must meet the following requirements:

	Grade A	Grade B
Purity, minimum:	93 percent	98 percent
RDX content, maximum:	7 percent	2 percent
Melting point, minimum:	277°C	277°C
Acetone insoluble material, maximum:	0.05 percent	0.05 percent
Inorganic insoluble material, maximum:	0.03 percent	0.03 percent
Insoluble particles on US standard 40 sieve:	none	none
US standard 60 seive:	5	5
Acidity	0.02 percent	0.02 percent

In addition the HMX must meet the following granulation requirements:

Through US Standard Sieve No.	Class 1 Percent	Class 2 Percent	Class 3 Percent	Class 4 Percent	Class 5 Percent	Class 6 Percent
8				100		
12			99 min	85 min		99 min
35				25 ±15		
50	90 ± 6	100	40 ± 15			90 min
100	50 ± 10		20 ± 10	15 max		65 ± 15
120		90 min				
200	20 ± 6		10 ± 10			30 ± 15
325	8 ± 5	75 min			98 min	15 ± 10

(3) To manufacture HMX, a solution of 785 parts glacial acetic acid, 13 parts acetic anhydride, and 17 parts paraformaldehyde is maintained at a temperature of 44°C ±1°C. All part measurements in this discussion are by weight. The solution is held at that temperature throughout the subsequent steps of the process. Two more solutions are prepared. One consists of 101 parts hexamine and 165 parts acetic acid. The other is prepared by dissolving 840 parts ammonium nitrate in 900 parts of 99 percent or stronger nitric acid. Over a 15 minute period with constant stirring, the hexamine-acetic acid solution, 180 parts of the nitric acid-ammonium nitrate solution, and 320 parts acetic anhydride are added simultaneously, continuously, and equivalently. The mixture is aged for 15 minutes. In the second stage of the reaction, 320 parts of acetic anhydride and 271 parts of the nitric acid-ammonium nitrate solution are added proportionately, then 160 parts of acetic anhydride are added in bulk. The mixture is allowed to age for 60 minutes. Then 350 parts hot water are added and the solution is refluxed for 30 minutes. After cooling to 20°C by adding ice, the water insoluble precipitate is collected and washed with three portions of cold water. The yield of 200 parts HMX is 95 percent of the theoretical and the purity is higher than 90 percent. The product is alpha HMX which is converted to beta HMX by crystallization from boiling acetone, acetonitrile, or cyclohexanone, using equivalent parts of solid and solvent. The recrystallized HMX has a melting point of 278° to 279°C. The recrystallization process also removes any RDX that was formed during manufacturing.

(4) HMX has similar sensitivity to impact and friction as RDX. The Bureau of Mines impact apparatus with two kilogram weight measures 32 centimeters for a 20 milligram sample. In the pendulum friction test, HMX explodes with the steel shoe but is unaffected by the fiber shoe. Table 8-14 shows the gap test results for HMX.

Table 8-14. Gap Test Results for HMX

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.814	4.7	8.71
	1.517	20.3	11.28
LANL small scale gap test	1.840 (pressed)	3.2	3.43
	1.790 (pressed)	5.8	4.27
	1.20 (coarse)	36.8	8.53
	0.7 (fine crystals)	63	6.45
LANL large scale gap test	1.07	43.7	70.7

The minimum charge of lead azide required for detonation to obtain maximum brisance is 0.30 grams. Explosion temperature test values are 306°C in 10 seconds, 327°C in five seconds, and 380°C in 0.1 second. When HMX is under a compression of 93,082 kilopascals (13,500 pounds per square inch), the explosive can be reliably detonated by a Q-switched laser operating at 6,943 Angstroms. As measured in a differential thermalgraph analysis study, the auto ignition temperature of HMX is 234°C. In the spark sensitivity test with a brass electrode and a sample size of 66.9 milligrams, the energy required for a 50 percent probability of explosion for lead foil thicknesses of 3 and 10 mils is 0.2 joules and 1.03 joules respectively. For a steel electrode, the energy required is 0.12 joules and 0.87 joules for lead foil thicknesses of 1 and 10 mils, respectively.

(5) The sand test indicates HMX is 125 percent as brisant as TNT or about 96 percent as brisant as RDX. The ballistic pendulum test indicates 170 percent of TNT, the ballistic mortar test indicates 150 percent, and the Trauzl test indicates a power of 159 to 165 percent of TNT. The detonation velocity of HMX at a density of 1.89 grams per cubic centimeter is 9,110 meters per second. The following critical diameters were measured for HMX:

HMX/Wax, percent	Density grams per cubic centimeter	Critical diameters
90/10	1.10	$6.0 < d_c < 7.0$
78/22	1.28	$7.0 < d_c < 8.0$
70/30	1.42	$8.0 < d_c < 9.0$

The diameters are given in millimeters. A gelled aqueous slurry of 30 percent HMX will detonate high order. At 25 percent HMX concentration detonation would be partially propagated and at 20 percent concentration the detonation would not propagate. Settled slurries propagate high order detonation at and above 10 percent HMX concentration. At the five percent level, the settled slurry will detonate about one third of the time.

(6) The 150°C vacuum stability test indicates HMX is comparable to TNT in stability, with test values of 0.6 and 2.5 milliliters of gas evolved. The 100°C heat test loss in the first 48 hours is 0.05 percent and in the second 48 hours 0.03 percent. No explosions occur in 100 hours. At 30°C and 95 percent relative humidity, HMX is nonhygroscopic. In the LLNL reactivity test, less than 0.01 cubic centimeters of gas are evolved. The DTA curve is shown in figure 8-16 and the TGA curve is shown in figure 8-17.

b. *Cyclotrimethylenetrinitramine (RDX).*

(1) This explosive is also known as: hexahydro-1,3,5-trinitro-1,3,5-triazine; 1,3,5-trinitro-1,3,5-triazacyclohexane; cyclotrimethylene trinitramine; hexogen; cyclonite; or 1,3,5-trinitrotrimethylene-triamine. The compound (figure 8-18) is a white solid with a density of 1.806 grams per cubic centimeter, a nitrogen content of 37.84 percent, and a molecular weight of 222.13. RDX has orthorhombic crystals with a wide variety of habits; from needles when precipitated from HNO_3, to plates when precipitated from acetic acid, to a massive form when precipitated from nitroethane or acetone. The unit cell dimensions are a = 13.18 Angstroms, b = 11.57 Angstroms, and c = 10.71 Angstroms, and there are eight molecules per cell unit. On the Moh's scale RDX has a scratch hardness of 2.5. Other properties of pure RDX include a specific heat as shown in table 8-15 and a heat of combustion at constant pressure of 2,307.2 calories per gram. The heat of formation value is + 14.71 kilocalories per mole. RDX has an extremely low volatility.

Table 8-15. Specific Heat of RDX

Temperature °C	Calories per gram per degree
20	0.298
40	0.331
60	0.360
88	0.384
100	0.406
120	0.427
140	0.446

Packing density as a function of pressure is shown in table 8-16.

Table 8-16. RDX Packing Density

Pressure kilopascals	Pressure pounds per square inch	Density grams per cubic centimeter
34,475	5,000	1.52
68,950	10,000	1.60
137,900	20,000	1.68
172,375	25,000	1.70
206,850	30,000	1.72

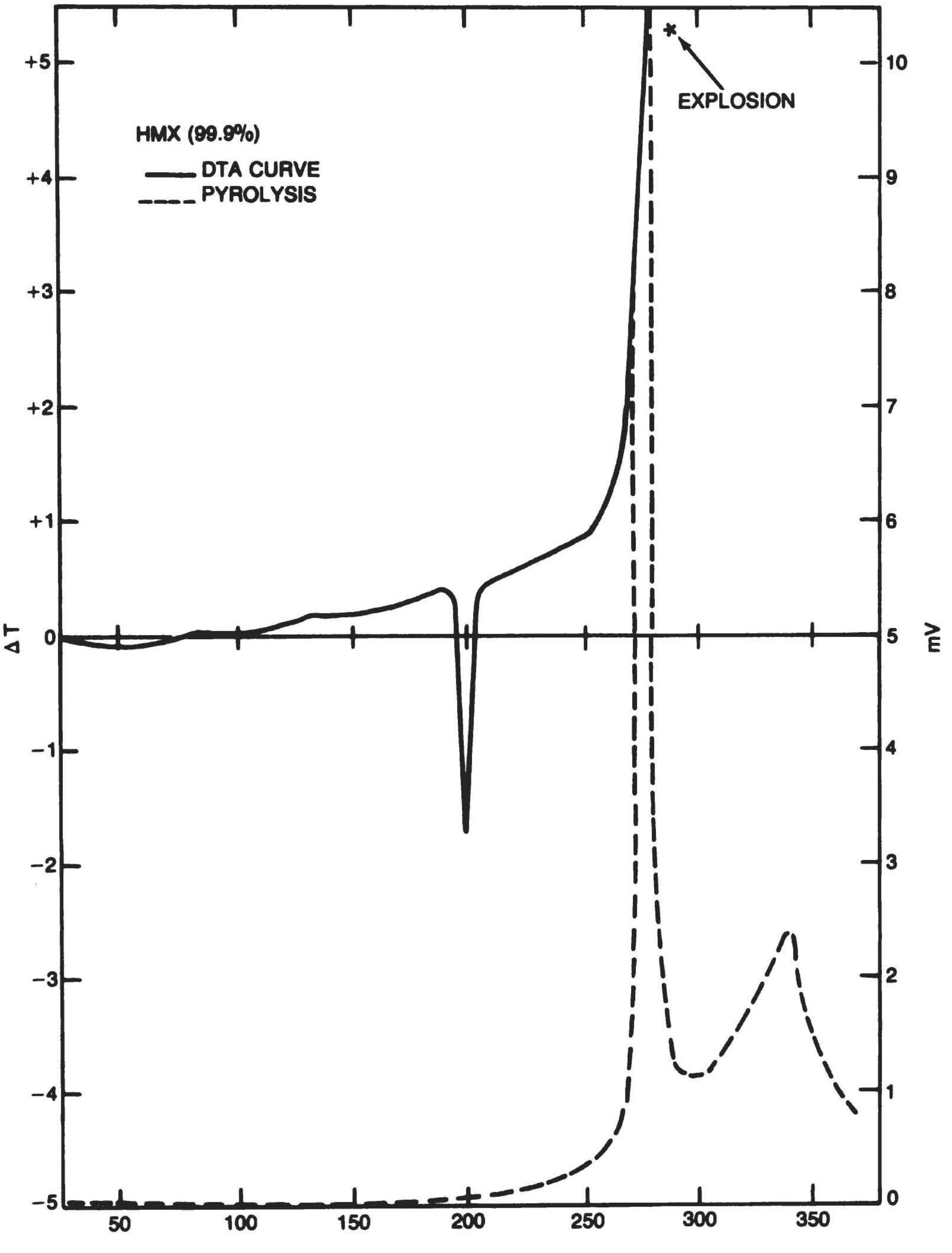


Figure 8-16. DTA curve for HMX.

RDX does not blend with or gelatinize nitrocellulose. With nitroglycerin, RDX forms an explosive plastic mass. Table 8-17 lists the solubility characteristics with TNT.

Table 8-17. RDX-TNT Solubility

Temperature °C	Grams of RDX dissolved per 100 grams of TNT
81	4.5
85	4.7
90	5.0
95	5.8
100	6.5
105	7.3
110	8.2

The eutectic mixture is 4.16 percent RDX at 79°C. Table 8-18 lists the solubility of RDX in various solvents. There is considerable divergence in the solubility data for RDX taken from different sources in the literature, probably due to the different methods and conditions used in making the determinations, the difference in purity, and the difference in physical state of the RDX tested. Therefore, the values given in table 8-18 are only approximate. The coefficient of cubical expansion between 20°C and 100°C is 0.00025 cubic centimeters per gram per degree centigrade. RDX has a heat combustion of 501.8 to 507.3 kilocalories per mole at constant volume with liquid water. The heat of formation is 14.7 kilocalories per mole. The heat of detonation is 1.62 kilocalories per gram with liquid water and 1.48 kilocalories per gram with gaseous water. RDX detonates according to the empirically determined equation:

$$(CH_2.NNO_2)_3 \longrightarrow 2CO + CO_2 + 2H_2O + H_2 + 3N_2$$

The temperature developed on explosion is 3380°C. There are two grades specified for RDX: types A and type B. Type A contains no HMX and type B has a constant impurity of from 8 to 12 percent HMX. Types A and B are produced by different manufacturing processes. Type A RDX melts between 202°C and 203°C; type B RDX melts between 192°C and 193°C. The vapor pressure of RDX is given by the equation:

$$\log p = 11.87 - 5850/T(\mathrm{K}) \quad \text{for } 55.7°\mathrm{C} < T < 97.7°\mathrm{C}$$

Pure RDX is used in press loaded projectiles but not in cast loaded projectiles because of extensive decomposition at the melting point. Cast loading is accomplished by blending RDX with a relatively low melting point substance. Compositions in which the RDX particles are coated with wax are called Composition A, in mixtures with TNT, Composition B, and blends with a nonexplosive plasticizer, Composition C. Straight RDX is used as a base charge in detonators and in some blasting caps, and as an oxidizer in specialized gun propellant.

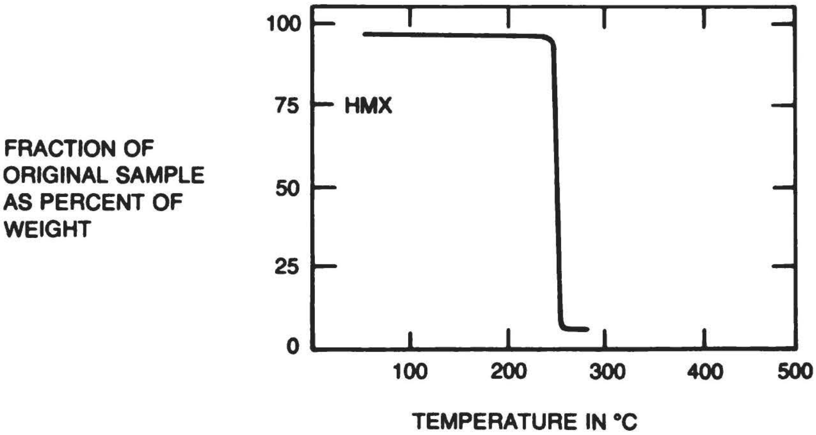


Figure 8-17. TGA curve for HMX.

Table 8-18. Solubility of RDX in Various Solvents

Solvent	Grams RDX per 100 grams of solution at:						
	0°C	20°C	30°C	40°C	60°C	80°C	100°C
Acetic acid (50%)	-	-	0.12	-	0.50	1.25	-
Acetic acid (100%)	-	-	0.41	-	1.35	2.60	-
Acetic anhydride	-	4.0	4.80	6.0	9.30	-	-
Acetone	4.2	6.8	8.40	10.3	15.3	(at 58)	-
Acetonitrile	-	-	12.0	16.2	24.6	33.0	-
Alcohol, ethyl	0.04	0.10	-	0.24	0.60	1.20	-
Benzene	-	0.05	0.06	0.09	0.20	0.40	-
Carbon tetrachloride	-	0.0013	0.0022	0.0034	0.007	-	-
Chlorobenzene	0.20	0.33	0.44	0.56	-	-	-
Chloroform	-	0.015	-	-	-	-	-
Cyclohexanone	-	12.7 (at 25°)	-	-	-	-	25 (at 97°)
Cyclopentanone	-	-	11.5 (at 28°)	-	-	-	37 (at 90°)
Dimethylformamide	-	25.5	27.3	29.1	33.3	37.7	42.6
Ether, dethyl	-	0.055	0.075	-	-	-	-
Beta-ethoxylethyl acetate	-	1.48	1.55	1.9	3.4	-	-
Isoamyl alcohol	0.02	0.026	0.04	0.06	0.21	0.50	1.33
Methanol	0.14	0.235	0.325	0.48	1.06	-	-
Methyl acetate	-	2.95	3.30	4.10	6.05 (at 52°)	-	-
Toluene	0.016	0.02	0.025	0.05	0.125	0.295	0.64
Trichloroethylene	-	0.20	0.21	0.22	0.23 (at 52°)	-	-
Trinitrotoluene (TNT)	-	-	-	-	-	4.4	7.0
Water	-	0.005	-	0.025 (at 50°)	-	-	0.28

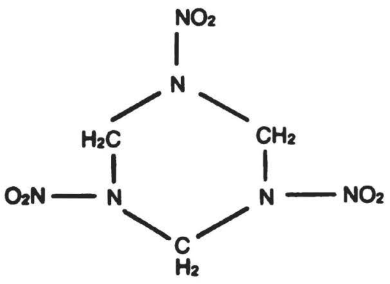


Figure 8-18. Structural formula for RDX.

(2) RDX is hydrolyzed slowly when treated with boiling, dilute sulfuric acid or sodium hydroxide according to the reaction:

$$C_3H_6N_6O_6 + 6H_2O \longrightarrow 3NH_3 + 3HCHO + 3HNO_3$$

In sulfuric acid solution the nitric acid oxidizes the formaldehyde to formic acid while being reduced to nitrous acid. RDX dissolved in cold, concentrated sulfuric acid decomposes when the solution is allowed to stand. Reduction of RDX dissolved in hot phenol yields methylamine, nitrous acid, and hydrocyanic acid; but if solid RDX is suspended in 80 percent ethanol and reduced, both hydrolysis and reduction take place and the products are methylamine, nitrous acid, ammonia, and formaldehyde. With diphenylamine and sulfuric acid, RDX gives a strong blue color. RDX dissolves, without decomposing, in concentrations of up to 70 percent nitric acid and may be recovered from solution by dilution with water. Hot or cold hydrochloric acid does not attack RDX. Complete decomposition can be obtained by heating RDX with equal parts of $Ca(OH)_2$ for four hours at 60°C. RDX decomposes slowly when heated at 60°C with a one tenth normal solution of sodium hydroxide for five hours, but rapidly when heated with a normal solution of sodium hydroxide. When RDX is placed in an alkaline solution, decomposition occurs. The products of that decomposition which have been isolated are: nitrogen gas, ammonia, nitrates, nitrites, formaldehyde, heramine, and organic acids such as formic. When mixed with oxides of heavy metals, such as iron or copper, RDX forms unstable compounds which may undergo decomposition and cause ignition of mixtures at temperatures as low as 100°C.

(3) Type A RDX is manufactured by the nitration of hexamethylenetetramine which is obtained by the reaction of formaldehyde and ammonia. The process is accomplished by slowly adding one part by weight of hexamethylenetetramine to 11 parts of 100 percent nitric acid, the temperature of which is maintained at 30°C or less while being stirred vigorously. The reaction proceeds according to the equation:

$$C_6H_{12}N_4 + 3HNO_3 \longrightarrow 3HCHO + NH_3 + (CH_2NNO_2)_3$$

The formaldehyde, HCHO, liberated by the reaction is oxidized by the nitric acid if the mixture is allowed to stand or is warmed. After being cooled to 0°C, the mixture is stirred for 20 minutes more and then drowned in ice water. As a result of the rupture and degradation of the hexamethylenetetramine molecule, numerous aliphatic and cyclic nitrocompounds are formed that are present in crude RDX. The crude RDX is caught on a filter and washed with water to remove most of the acid. Removal of all but a trace of acid is important and purification is accomplished by grinding the wet material then treating with boiling water or by recrystallizing from cyclohexanone or acetone. Production of type B RDX is based on the following reaction:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \longrightarrow 2(CH_2NNO_2)_3 + 12CH_3COOH$$

The hexamethylenetetramine is nitrated to RDX by the nitric acid and, as indicated for the production of type A RDX, three moles of formaldehyde are produced. The formaldehyde reacts with the ammonium nitrate in the presence of the acetic anhydride, $(CH_3CO)_2O$, to form hexamethylenetetramine, which is nitrated by the nitric acid to form the second mole of RDX. The HMX impurity is not shown. The yield of the type B reaction is greater than for the reaction using nitric acid alone. Other methods for producing RDX include a process of nitrating hexamethylenetetramine by nitric acid in the presence of phosphorous pentoxide with a yield of 90 percent of theoretical. Nitration by some processes in the presence of ammonium salts such as $(NH_4)_2SO_4$ can increase yields. Yields of 65 percent, 80 percent and 91 percent were obtained using no ammonium salt, ammonium nitrate, and ammonium sulfate, respectively. Another possible method of manufacture uses nitrogen pentoxide dissolved in inert, nonaqueous solvents such as hydrocarbons or chlorinated hydrocarbons to nitrate hexamethylenetetramine. The equation for the reaction would be:

$$C_6H_{12}N_4 + 3N_2O_5 \longrightarrow (CH_2NNO_2)_3 + 3HCHO + 2N_2O_3$$

The yield for this method is claimed to be 89 percent. A proposed method for the production of type A RDX consists of oxidizing the compound 1,3,5-trinitroso-1,3,5-triazacyclohexane, which is obtained from hexamethylenetetramine, HCL, and $NaNO_2$. Oxidization with hydrogen peroxide and nitric acid yields as an intermediate 1-nitroso-3,5 dinitroso-1,3,5 triazacyclohexane which is converted on further treatment with hydrogen peroxide and nitric acid into RDX having a melting point of 205°C.

(4) Type A and type B RDX are equally sensitive to impact, friction, heat, and initiation. This is due to the fact that HMX, the chief impurity in type B RDX, has sensitivity characteristics that are very similar to those of RDX. Impact tests indicate RDX is 300 percent as sensitive as TNT. Temperature has a marked effect on the sensitivity of RDX. Impact tests of a sample of type A RDX at 20°, 88°, and 105°C gave values of 9, 8, and 5 inches, respectively. Granulation also affects sensitivity; the height of fall increases with decreasing particle size. In pendulum friction tests, RDX explodes with the steel shoe but is unaffected by the fiber shoe. When rubbed in an unglazed porcelain mortar, partial deflagration occurs. RDX displays great sensitivity in the rifle bullet impact test, but the test samples partially deflagrate rather than detonate. RDX can be initiated by lead azide or mercury fulminate. Gap test results for RDX are shown in table 8-19.

Table 8-19. Gap Test Results for RDX

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.717	4.7	7.90
	1.546	14.2	12.01
	1.188	34.1	11.18
LANL small scale gap test	1.735 (hot-pressed)	4.1	4.8 - 5.6
	1.11 (bulk coarse)	38.7	8.86
	1.00 (bulk fine)	44.8	7.82
	0.7 (fine crystalline)	61	6.77

RDX is much less sensitive to an electric spark than tetryl, TNT, or PETN. Using a circuit with a capacitance of 0.0003 millifarads and a test sample of pulverized or crystalline RDX, no ignitions occur at 12,300 volts but local ignitions do occur at 14,950 volts. At elevated temperatures RDX either fumes off and ignites or deflagrates when unconfined. There are no explosions. Some elevated temperature test results are: at 255° to 260°C, five seconds; at 316°C, one second; at 405°C, 0.1 second. Held at 290°C RDX fumes. The flammability index is 278 versus 100 for TNT and 244 for tetryl. The presence of more than 14 percent moisture prevents detonation by a number 6 blasting cap.

(5) Reported sand test results indicate RDX is from 125 to 145 percent as brisant as TNT. Fragmentation tests, with 51 grams of explosive at a density of 1.50 loaded in a 40 millimeter shell, indicate a brisance of 141 percent of TNT. Plate cutting tests indicate RDX is 125 percent as brisant as TNT, while plate dent tests indicate 135 to 141 percent. The equation for detonation velocity is:

$$D = 2.56 + 3.47p$$

where D is in meters per second and p, the density, is in grams per cubic centimeter. Upon detonation, the pressure developed is 12,600 kilograms per square centimeter or 156 percent of TNT. The following were measured for RDX at the densities shown:

RDX/Wax percent	Density grams per cubic centimeter	Critical diameter
95/5	1.05	$4.0 < d_c < 5.0$
90/10	1.10	$4.0 < d_c < 5.0$
80/20	1.25	$3.8 < d_c < 5.0$
72/28	1.39	$3.8 < d_c < 5.0$

The diameters are given in millimeters. The volume of gas produced at 0°C and 760 millimeters of pressure is 908 liters per kilogram or 132 percent of TNT. Trauzl tests indicate RDX is 151 to 170 percent as powerful as TNT. However, tests against earthworks, masonry, and in underwater explosions indicate a power of close to 200 percent that of TNT. In one test a 25 kilogram charge of RDX in a shell produced a crater in packed earth 12.60 cubic meters in volume. The same amount of TNT under the same conditions produced a crater 6.75 cubic meters in volume. This indicates a power for RDX of 186.5 percent of TNT. The ballistic mortar test indicates a power of 150 to 161 percent that of TNT. These test results indicate RDX is the second most powerful military explosive.

(6) RDX is highly stable. In a one year surveillance test no decomposition occurred at either 65°C or 85°C. When heated for two months at 100°C no decomposition occurred. The 82.2 KI test results are 60 minutes. In the heat tests, the results were: at 75°C, .03 percent weight loss in 48 hours; at 100°C, 0.04 percent weight loss in the first 48 hours, no weight loss in the second 48 hours and no explosions after 100 hours; at 132°C no change occurred in eight hours of heating; and at 135°C there was no acid and no explosion in 300 minutes. A sample of five grams of RDX subjected to the vacuum stability test yielded the following results: in 40 hours at 120°C, 0.9 cubic centimeters of gas evolved and at 150°C, 2.5 cubic centimeters of gas evolved. A sample of five grams of type B RDX with a melting point of 192°C evolved 3.95 cubic centimeters of gas in 40 hours. In the LLNL reactivity test 0.02 to 0.025 cubic centimeters of gas were evolved. The DTA curve for RDX is shown in figure 8-19 and the TGA curve is shown in figure 8-20.

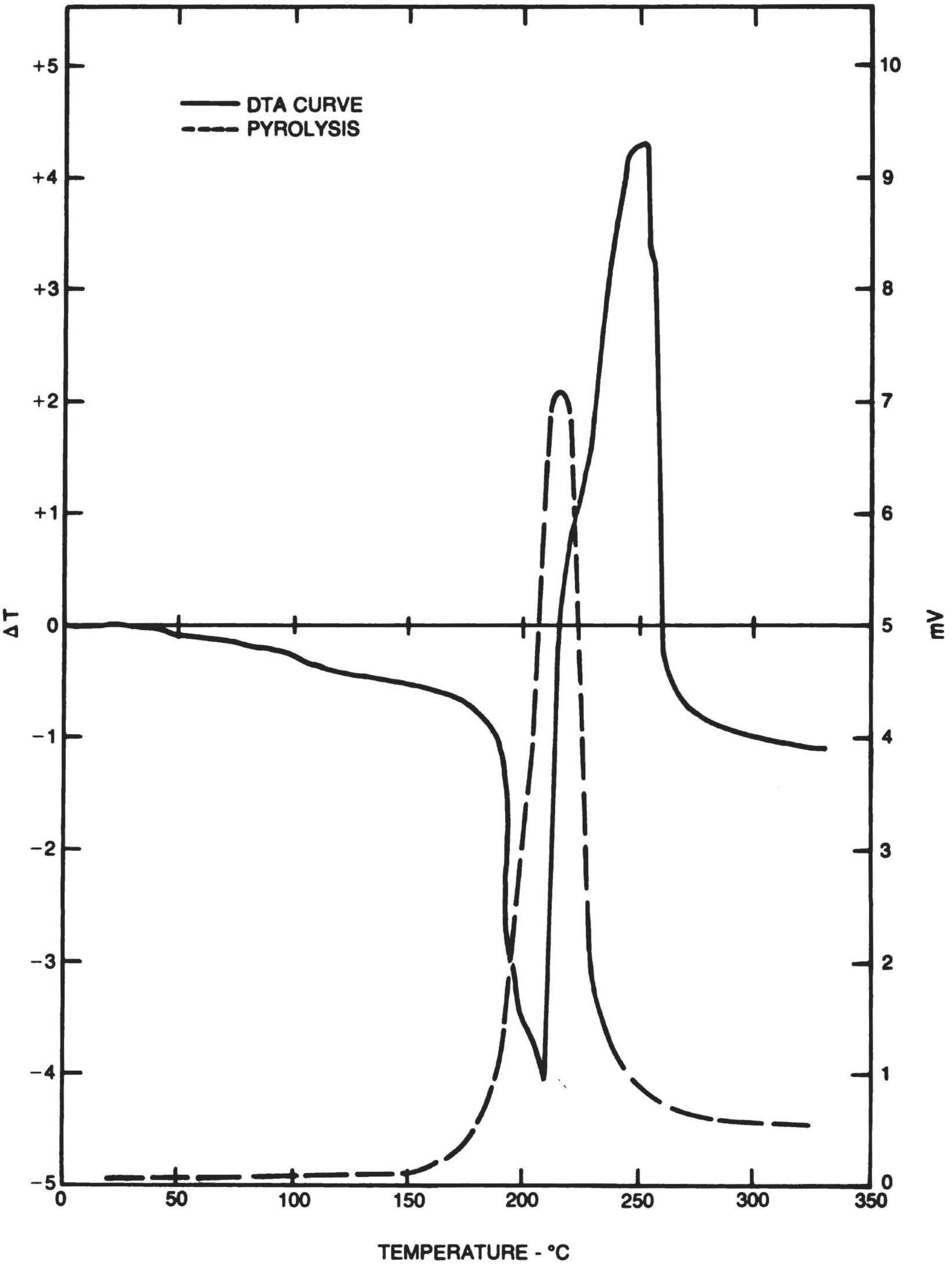


Figure 8-19. DTA curve for RDX.

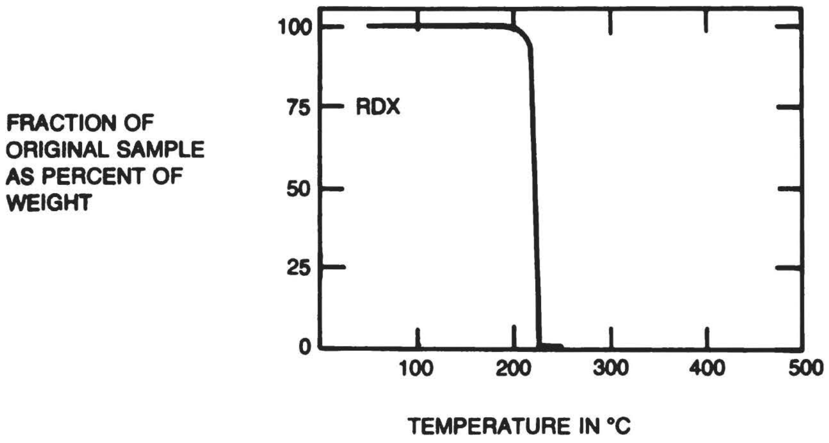


Figure 8-20. TGA curve for RDX.

(7) In the United States and England, RDX is stored wetted with water. In Germany and Japan it is stored dry. RDX does not cause corrosion of aluminum or stainless steel, even in the presence of moisture. Dry RDX causes no corrosion of and RDX with 0.5 percent moisture causes only slight corrosion of nickel or zinc. Dry or damp RDX causes very slight corrosion of copper, brass, mild steel, or cadmium.

(8) Table 8-20 lists the requirements for military grade RDX for the United States government.

Table 8-20. Types of RDX

Properties	Type A	Type B
Melting point, °C (min)	200.0	190.0
Acetone insoluble (max)	0.05	0.05
Inorganic insoluble (max)	0.03	0.03
Insoluble particles retained on US standard sieve No. 60, particles (max)	5	5
Acidity, percent (max)	0.05	0.02

Type A RDX is produced by the nitric acid process: type B is produced by the acetic anhydride process. Granulation requirements are listed in table 8-21.

Table 8-21. Granulation Requirements for RDX

Through US standard sieve No.	Class (% of material passing sieve)							
	A	B	C	D	E	F	G	H
8	-	-	-	100	-	-	-	-
12	-	-	99*	-	-	-	-	-
20	98	-	-	-	-	-	-	-
35	-	99	-	20	-	-	-	100
50	90	95	40	-	-	-	98	98*
60	-	-	-	-	-	99	-	-
80	-	-	-	-	-	97	-	-
100	60	65	20	-	-	-	90	90*
120	-	-	-	-	-	83	-	-
170	-	-	-	-	-	65	-	-
200	25	33	10	-	-	-	46	70
230	-	-	-	-	-	36	-	-
325	-	-	-	-	97*	22	-	50

*Minimum Percent

(9) The suggested uses of RDX based on class and granulation are as follows:

(a) Class A, for use in Composition A3, Composition B, Composition C4, and cyclotol

(b) Class B, for use in Composition A3 and Composition C4

(c) Class C, for use in the preparation of RDX booster and detonator pellets

(d) Class D, for use in cyclotols

(e) Class E, for use in Composition C4 and plastic bonded explosives (PBX's)

(f) Class F, for use in Composition B3

(g) Class G, for use in PBX's

(h) Class H, for use in Composition C4

c. *Ethylenediamine Dinitrate (EDDN).*

(1) This explosive is also designated EDD or EDAD. The compound (figure 8-21) is composed of white crystals with a specific gravity of 1.595 at 25/4°, a nitrogen content of 30.10 percent, an oxygen balance to CO_2 of −25.8 percent, a melting point of 185° to 187°C, and a molecular weight of 186.13. The compound is soluble in water, but insoluble in alcohol or ether. EDDN has a heat of combustion of 374.7 kilocalories per mole at constant pressure, a heat of formation of 156.1 kilocalories per mole, and a heat of explosion of 127.9 to 159.3 kilocalories per mole. Eutectics are formed with ammonium nitrate, but EDDN is immiscible with molten TNT. An aqueous solution of EDDN is distinctly acidic. EDDN has been used to a limited extent as a bursting charge pressed in shells and as a cast charge in eutectic mixtures with ammonium nitrate. Mixtures with wax were used in boosters during World War II by the Germans.

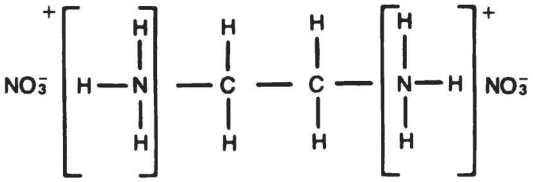


Figure 8-21. Structural formula for EDDN.

(2) EDDN is produced by neutralization of ethylenediamine dihydrate with concentrated nitric acid. This is followed by the concentration and crystallization of the salt formed.

(3) EDDN is more sensitive to shock than TNT, having impact test values of nine inches and 75 centimeters, respectively, with the Picatinny and Bureau of Mines apparatuses. In rifle bullet impact tests with a charge of specific gravity 1.0 no detonations occurred on the impact of bullets with velocities below 960 meters per second and incomplete detonations occurred with bullet velocities around 1,000 meters per second. EDDN is less sensitive to initiation than TNT, requiring a minimum detonating charge of 0.10 gram of tetryl according to the sand test. Two grams of mercury fulminate are required for the initiation of a 50 gram sample pressed to a specific gravity of 1.23 in a paper cylinder 30 millimeters in diameter. In a gap test a minimum separation of 3.75 centimeters was found with paper cartridges each containing a 50 gram sample pressed to a density of 0.75. The explosion temperature test value of EDD is 445°C, as compared with 475°C for TNT. A small sample placed in a test tube ignites in six seconds when plunged into a bath preheated to 370°C, and in one second when the temperature of the bath is increased to 430°C. EDDN is ignited by open flame after one minute and continues to burn at the rate of 1.5 centimeters per minute.

(4) The sand test indicates EDDN is 96 percent as brisant as TNT, and plate dent test values are practically the same for the two explosives. The detonation velocity for a sample of EDDN with a specific gravity of 1.00 is 4,650 meters per second, 6,270 meters per second at a specific gravity of 1.33, and 6,915 meters per second at a specific gravity of 1.50. EDDN is indicated to be 114 percent and between 120 and 125 percent as powerful as TNT by the ballistic pendulum and Trauzl lead block tests, respectively.

(5) When heated in vacuum EDDN vaporizes and condenses without noticeable decomposition. When heated at 10 millimeters of pressure in an atmosphere of nitrogen or air, autocatalytic decomposition occurs between 230°C and 360°C. EDDN is hygroscopic to the extent of 1.24 percent at 90 percent relative humidity and 25°C. In the 120°C vacuum stability test, five milliliters of gas are evolved. Because of poor solubility, hygroscopicity, and acidity characteristics, EDDN is not very satisfactory for use as a military explosive and is an inferior substitute for TNT.

d. *Ethylenedinitramine (Haleite).*

(1) This compound is also known as N, N'-dinitroethylene diamine; ethylene dinitramine; or 1,2-dinitrodiaminoethane, and is sometimes designated EDNA. The name Haleite is in recognition of the development of this compound as a military explosive by the late Dr. G. C. Hale of Picatinny Arsenal. The compound (figure 8-22) is white with an orthorhombic crystal structure, a nitrogen content of 37.33 percent, an oxygen balance to CO_2 of −32 percent, an oxygen balance to CO of −10.5 percent, and a molecular weight of 150.10. The density of the crystals vary from 1.66 to 1.77 depending on the solvent from which the crystallization took place. Packing density as a function of pressure is shown in table 8-22.

Table 8-22. Haleite Packing Density

Pressure grams per cubic kilopascals	Pressure pounds square inch	Density grams per cubic centimeter
34,475	5,000	1.28
68,950	10,000	1.38
82,740	12,000	1.41
103,425	15,000	1.44
137,900	20,000	1.49

Haleite melts with decomposition at 177.3°C, but does not extrude. The solubility of Haleite in water at 10°, 20°, 50°, 75°, and 95°C is 0.10, 0.25, 1.25, 5.0, and 16.4 grams, respectively, per 100 grams of solvent. In 95 percent ethanol at 10°, 20°, 50°, 75°, and 78.5°C, Haleite is soluble to the extent of 0.55, 1.00, 3.50, 10.07, and 11.5 grams, respectively, per 100 grams of solvent and is soluble in methanol. Haleite is insoluble in ether, but in actetone at 20°C, Haleite is soluble to the extent of 8.2 grams per 100 grams. Haleite is soluble in nitromethane, nitrobenzene, and dioxane, which can be used to recrystallize the explosive. The heat of combustion of Haleite at constant pressure is 2,477 calories per gram, from which a heat of formation value of 20.11 kilogram-calories per mole is derived. The heat of explosion is 1,276 calories per gram.

$$\begin{array}{l} CH_2.NH.NO_2 \\ | \\ CH_2.NH.NO_2 \end{array}$$

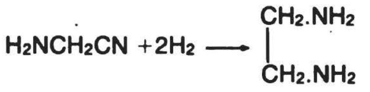
Figure 8-22. Structural formula for Haleite.

(2) Haleite is an explosive that combines the properties of a high explosive like TNT and an initiating agent like mercury fulminate or lead azide, possessing a high brisance and comparatively low sensitivity. No other high explosive is known which has such a low sensitivity to impact and at the same time so readily explodes by heat. Another important characteristic of Haleite is a relatively low explosion temperature, approaching that of mercury fulminate or nitroglycerin. Haleite lacks oxygen for complete combustion to CO_2. Mixtures with oxidizing agents such as ammonium nitrate, potassium chlorate, and ammonium perchlorate yield a series of explosive mixtures more powerful than Haleite.

(3) The first step in the manufacture of Haleite is the production of ethylene diamine. One reaction employed is:

$$CH_2O + HCN \longrightarrow HOCH_2CN$$

$$HOCH_2CN + NH_3 \longrightarrow H_2NCH_2CN + H_2O$$



$$H_2NCH_2CN + 2H_2 \longrightarrow \begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array}$$

The yield of the second reaction is 82 percent. The third reaction is carried out under high pressure. The ethylene diamine is converted to ethyleneurea, 2-imidazolidinone, by either reacting with diethylcarbonate or carbon dioxide. The reaction with diethylenecarbonate is not generally used because the yield is only 42 percent of theoretical and the reaction requires the use of high pressure and high temperature for an extended period of time. The reaction with carbon dioxide is carried out under 820 atmospheres of pressure at 220°C. The reactions are shown in figure 8-23. The ethyleneurea can be nitrated with either concentrated nitric acid or a mixture of nitric and sulfuric acids. In the latter case, 10 parts of mixed acid containing 74.0 percent sulfuric acid, 15.4 percent nitric acid, and 10.6 percent water are cooled to 10°C or less and agitated. One part of ethyleneurea is added at such a rate that the temperature does not rise above 10°C. After the last portion of the ethyleneurea has been added, stirring is continued for five minutes. A variation of this process is to dissolve 1 part of ethyleneurea in 7.5 parts of 95 percent sulfuric acid, while maintaining the temperature at 20°C. This solution then is added slowly, while maintaining the temperature of the mixture at 0°C or less, to 3.33 parts of a mixed acid containing 15.8 percent sulfuric acid, 66.7 percent nitric acid, and 17.5 percent water. When addition is complete, the temperature is increased to 10°C and maintained at that value for two hours. The dinitroethyleneurea is caught on a filter and

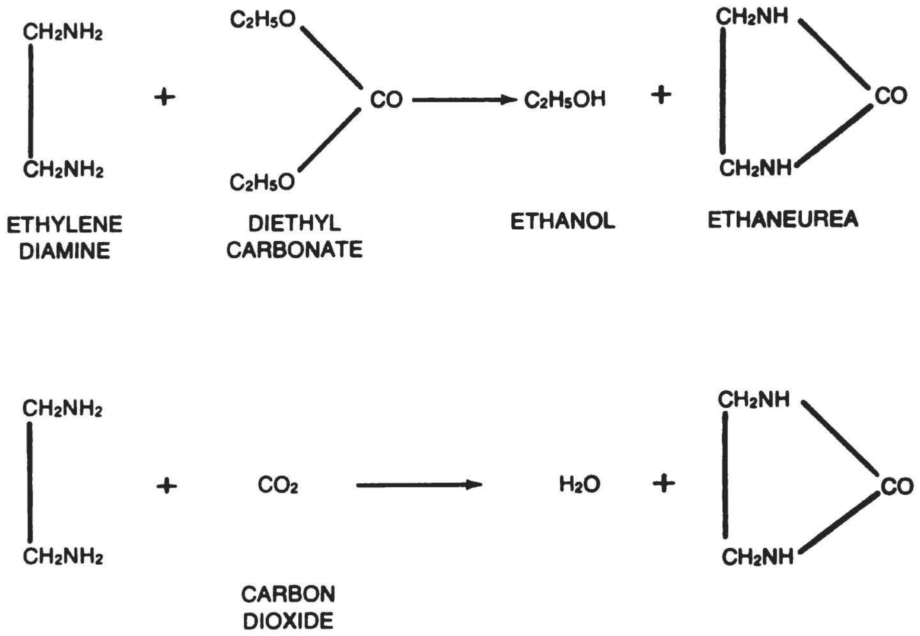


Figure 8-23. Production of ethyleneneurea.

washed with ice water until the washings are almost neutral. Additional dinitroethyleneurea is recovered by drowning the spent acid in ice water. A total yield of 97 percent of the theoretical is obtainable. One part dinitroethyleneurea, by weight, is suspended in seven parts water and boiled until the evolution of carbon dioxide ceases. The reaction is shown in figure 8-24. Haleite separates as shining crystals when the solution is cooled to room temperature. This is caught on a filter, washed with cold water, and dried. The total yield of Haleite from ethyleneurea is approximately 92 percent of the theoretical. Another method of producing Haleite is by treating dinitroethylenediurethane with an alcoholic solution of ammonia followed by acidifying with hydrochloric acid. This reaction is shown in figure 8-25.

(4) One grade of Haleite is specified for military purposes. This complies with the following requirements:

Color: White to buff.
Moisture: Maximum, 0.10 percent.
Melting point: Minimum, 174.0°C.
Purity: Minimum, 99.0 percent.
Water insoluble matter: Maximum, 0.10 percent.
Grit: None.
120°C vacuum stability test: Maximum, 5.0 milliters of gas in 40 hours.
Granulation:

	Percent
Through US No. 10 sieve, minimum	100
Through US No. 100 sieve, maximum	20

(5) Impact tests show Haleite to be slightly more than twice as sensitive as TNT, with a 48 centimeter drop height versus 100 centimeters for TNT. In the rifle bullet impact test for 100 trials, there were 60 partial detonations, 20 burnings, and 20 unaffected. Haleite is unaffected by either the fiber or steel shoe in the pendulum friction test. A minimum initiating charge of 0.21 grams of mercury fulminate or 0.13 grams of lead azide are required for initiation. In the gap test, a minimum separation of 14 centimeters was found for two paper cartridges, each containing 50 grams of Haleite at a density of 0.80. This value is 64 percent of that for tetryl at a density of 0.94. The explosion temperature test value is 190°C. The 0.1 second explosion temperature test value is 265°C. Haleite flammability index is 138 seconds.

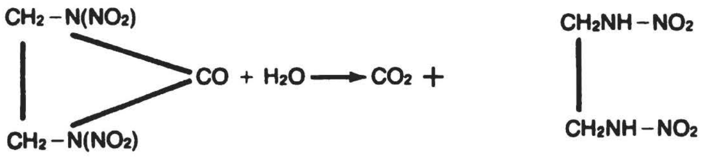


Figure 8-24. Boiling of dinitroethyleneurea.

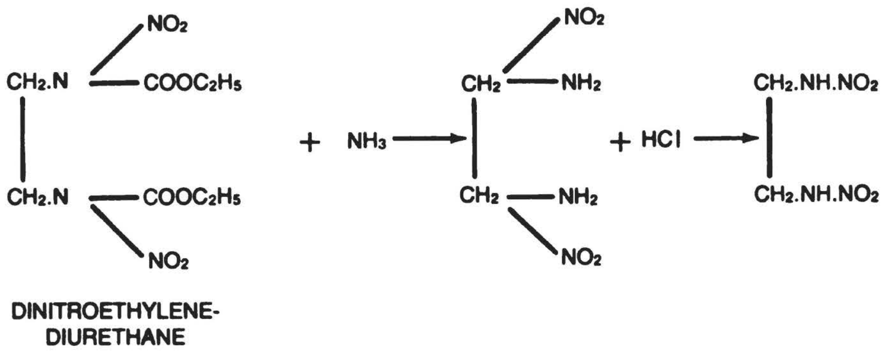


Figure 8-25. Production of Haleite.

(6) As measured by the sand test, Haleite has a brisance of 109 to 119 percent of that for TNT. The plate dent test indicates a brisance value of 113 to 122 percent of TNT. The plate cutting test indicates a brisance equal to that of PETN. A fragmentation test using a three inch, high explosive, M42A shell with a charge of 95 percent Haleite and 5 percent wax at a density of 1.56 was found to produce 117 percent as many fragments as TNT. Other fragmentation test values varied from 136 to 147 percent of TNT. The detonation velocity for a sample at a density of 1.55 grams per cubic centimeter is reported as 7,883 meters per second. For a sample of density 1.50, a detonation velocity of 7,580 meters per second was reported and a velocity of 5,650 meters per second for a sample of density 1.0. The ballistic mortar tests indicate Haleite is 136 to 140 percent as powerful as TNT. The Trauzl test indicates a power of 122 to 143 percent of TNT.

(7) In the 100°C heat test, a 0.2 percent weight loss was reported in the first 48 hours, and 0.3 percent was lost in the second 48 hours. No explosions occurred. The 135°C heat test results are satisfactory. The 75°C international heat test result is that a 0.01 percent loss occurs in 48 hours. Decomposition temperatures are 170°C in 20 seconds, 173°C in 15 seconds, 178°C in 10 seconds, 189°C in 5 seconds. At higher temperatures, Haleite darkens to a red brown with the evolution of NO_2. Haleite is hygroscopic to the extent of 0.01 percent at 90 percent relative humidity. In the vacuum stability test at 100°C with a five gram sample, 0.5 cubic centimeters of gas are evolved in 48 hours. At 120°C, 1.5 to 2.4 cubic centimeters of gas are evolved, and at 135°C more than 11 cubic centimeters are evolved. Tests have shown Haleite to be volatilized at the rate of 0.05 percent per hour when heated at 100°C in an open dish. Storage tests have shown dry Haleite to be of unimpaired stability after storage at 65°C for five months or 50°C for 30 months. Therefore, Haleite is considered to be of satisfactory stability at the normal exposure temperatures for storage and handling. Dry Haleite does not cause corrosion of aluminum, brass, copper, mild steel, stainless steel, cadmium, nickel, or zinc. Magnesium and magnesium alloys are slightly affected by dry Haleite. Stainless steel is not corroded by wet Haleite, but copper, brass, mild steel, cadmium, nickel, and zinc are heavily corroded in the presence of as little as 0.5 percent moisture.

e. *Nitroguanidine (NQ).*

(1) This explosive is also known as picrite or guanylnitramine. The compound (figure 8-26) has a nitrogen content of 53.84 percent, an oxygen balance to CO_2 of −30.8 percent, a theoretical maximum density of 1.81 grams per cubic centimeter, a nominal density of 1.55 to 1.75 grams per cubic centimeter, and a molecular weight of 104.1. The melting point of nitroguanidine varies somewhat with the rate of heating. The pure material melts with decomposition at 232°C, but values from 220°C to 250°C are obtainable with various heating rates. At least two crystalline forms exist for nitroguanidine; alpha and beta. The alpha form is obtained when nitroguanidine is dissolved in concentrated sulfuric acid and then drowned with water. The crystals formed are long, thin, lustrous, flat needles that are tough and very difficult to pulverize. The needles have a double refraction value of 0.250. This is the form most commonly used in the explosive industry. The beta form crystallizes from hot water in fern-like clusters of small, thin, elongated plates. The plates have a double refraction value of 0.185. The beta form may be converted into the alpha by dissolving in concentrated sulfuric acid and drowning in water. Neither form, however, is converted into the other by recrystallization from water, and the two forms can be separated by fractional crystallization from water. The beta form may also be converted to the alpha form by decomposition of the nitrate or hydrochloride formed by beta nitroguanidine. When alpha nitroguanidine is decomposed by heat, some beta nitroguanidine is formed; but the beta compound generally is obtained by the nitration of the mixture of guanidine sulfate and ammonium sulfate, resulting from the hydrolysis of dicyandiamide, $H_2N.C(:NH).NH.CN$, by sulfuric acid. The alpha form is obtained by the reaction of guanidine and nitric acid to form the nitrate. The nitrate is dehydrated to form the nitrocompound. Both forms of nitroguanidine have the same melting point and are alike in most chemical and physical properties. The unit cell dimensions are 17.58 Angstroms, 24.84 Angstroms, and 3.58 Angstroms. There are 16 molecules per cell. The refractive index is; alpha equals 1.526, beta equals 1.694, and gamma equals 1.81. However, they differ slightly in solubility in water except at 25°C and 100°C, where their solubility curves cross, having values of 0.42 to 0.44 grams per 100 milliliters at 25°C and 8.25 grams per 100 milliters at 100°C. Solubility between 25°C and 100°C is slightly lower for the alpha than for the beta form. At 0°C the solubility for both forms is about 0.12. Both forms are slightly soluble in alcohol and nearly insoluble in ether. In a solution of one normal potassium hydroxide at 25°C the solubility is 1.2. Table 8-23 lists the solubility for nitroguanidine in sulfuric acid at various concentrations and temperatures.

Table 8-23. Solubility of Nitroguanidine in Sulfuric Acid

Sulfuric acid percentage in water	Temperature °C	Grams dissolved per 100 cubic centimeters
0	0	0.12
	25	0.42
15	0	0.3
	25	0.55
20	0	0.45
	25	1.05
25	0	0.75
	25	1.8
30	0	1.3
	25	2.9
35	0	2.0
	25	5.2
40	0	3.4
	25	8.0
45	0	5.8
	25	10.9

Nitroguanidine has a crystal density of 1.715, but because of the toughness and flexibility of the crystals, a density of only 0.95 is obtained when subjected to a pressure of 3,000 psi. The heat of combustion of nitroguanidine at constant pressure is 210.4 kilocalories per mole, and from this is derived a heat of formation value of 20.29 kilogram-calories per mole. The heat of detonation is 1.06 kilocalories per gram with liquid water and 880 calories per gram with gaseous water. The volume of gas produced is 1077 cubic centimeters per gram. Nitroguanidine is essentially nonvolatile. The vapor pressure is given by the equation:

$$\log pa = 13.01 - 7014/T(°C)$$
$$\text{for } 70.7°C < T < 174.2°C$$

One torr equals 133 pa. The specific heat, in calories per gram per degree centigrade, for high bulk density nitroguanidine is:

$$0.269 + (7.0 \times 10^{-4})T \text{ for } 37°C < T < 167°C$$

The specific heat for low bulk density nitroguanidine is:

$$0.242 + (11.1 \times 10^{-4})T \text{ for } 37°C < T < 167°C$$

Because of the low temperature of explosion, about 2,098°C, nitroguanidine is used in triple-base propellants that are practically flashless and less erosive than nitrocellulose-nitroglycerin propellant of comparable force. When used by the Germans in World War II in antiaircraft guns, a nitroguanidine propellant increased the barrel life from 1,700 firings to about 15,000 firings.

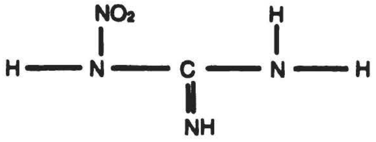


Figure 8-26. Structural formula for nitroguanidine.

(2) Nitroguanidine is chemically reactive because of a free amino group as well as a nitro group and a tendency toward dearrangement. With hot concentrated nitric acid, nitroguanidine forms a nitrate that melts at 147°C and, with strong hydrochloric acid, yields a crystalline hydrochloride. On reduction, nitroguanidine yields nitrosoguanidine, $H_2N.C(NH).NH.NO$, and then aminoguanidine, $H_2N.C(:HN).NH.NH_2$. With a solution of diphenylamine in sulfuric acid, nitroguanidine gives a blue color. When tested with ferrous ammonium sulfate and sodium hydroxide, a fuchsine color is developed. When warmed with water and a large excess of ammonium carbonate, nitroguanidine forms guanidine carbonate. With an aqueous solution of hydrazine, nitroguanidine reacts to form N-amino, N'-nitroguanidine, $N_2N.HN.C(:NH).NH.NO_2$, which melts at 182°C. On being heated or undergoing reaction in sulfuric acid solution, nitroguanidine appears to undergo dearrangement according to two modes:

$$H_2N.C.(:NH).NH.NO_2 \longrightarrow NC.NH_2 + H_2N.NO_2$$

Cyanamide
Nitramide

$$H_2N.C(:NH).NH.NO_2 \longrightarrow NH_3 + NC.NH.NO_2$$

Ammonia
Nitrocyanamide

When decomposed by heating above the melting point, the products obtained from nitroguanidine are water, nitrous oxide, cyanamide, melamine, ammonia, cyanic acid, cyanuric acid, ammeline, and ammelide. These are the products to be anticipated from the dearranged compound. The reaction and decomposition of the primary products of decomposition form carbon dioxide, urea, melam, melem, mellon, nitrogen, hydrocyanic acid, cyanogen, and paracyanogen. In aqueous solution, nitroguanidine dearranges in both of the above modes, but this is only to a small degree, unless another compound is present to react with one of the products of dearrangement. As a result of this, nitroguanidine is relatively stable in aqueous solution. A saturated aqueous solution at 25°C has a pH value of 5.5. After being heated at 60°C for two days, such a solution has a pH value of 8.5. In the absence of ammonia and in the presence of a primary aliphatic amine, nitroguanidine reacts to form an alkylnitroguanidine as if the amine reacted with nitrocyanamide present by dearrangement. A solution of either form of nitroguanidine in concentrated sulfuric acid acts chemically as if the nitroguanidine had dearranged into nitramide and cyanamide, although alpha nitroguanidine is precipitated if the solution is poured into water. When such a solution is warmed, nitrous oxide and a little nitrogen are evolved at first from the dehydration of nitramide. Later and more slowly, carbon dioxide is liberated resulting from the hydrolysis of cyanamide. After standing for some time, a sulfuric acid solution of nitroguanidine no longer gives a precipitate of nitroguanidine when diluted with water. Although a freshly prepared solution contains no nitric acid, this is formed by the hydration of nitramide, if a material that can react with nitric acid is present. Consequently, nitroguanidine splits off the nitro group quantitatively and the purity of the material can be determined by the nitrometer method.

(3) The specification for military nitroguanidine covers two types of material and two classes with respect to granulation. The requirements with which the explosive must comply are as follows:

	Type I, %		Type II, %	
Properties	Min	Max	Min	Max
Purity (assay)	98.0	-	99.0	-
Ash content	-	0.30	-	0.30
pH value	4.5	7.0	4.5	7.0
Acidity (as sulfuric acid)	-	0.60	-	0.06
Total volatiles	-	0.25	-	0.25
Sulfates (as sodium sulfate)	-	0.20	-	0.20
Water insoluble impurities	-	0.20	-	0.20

Granulation requirements are as follows:

Type	Class	Minimum in microns	Maximum in microns
I	1	4.3	6.0
	2	-	3.3
II	1	3.4	6.0
	2	-	3.3

(4) Several methods for the preparation of nitroguanidine are known. The earliest method was by the direct nitration of guanidine thiocyanate with mixed acids. Guanidine thiocyanate is one of the cheapest and easiest to prepare of the guanidine salts. However, this method of production also produced sulfur compound impurities which attacked nitrocellulose. This lowered the stability of propellent compositions to an unacceptable degree, thus precluding early use of the compound as an ingredient in nitrocellulose based propellents. A more pure form of nitroguanidine that does not contain the sulfur compound impurities can be prepared in one of several known ways. In one method equimolecular quantities of urea and ammonium nitrate are fused according to the equation:

$$H_2N.CO.NH_2+NH_4NO_3 \longrightarrow H_2N.C(:NH).NH.NO_2+2H_2O$$

The product is then recrystallized from boiling water. The yield of this method is approximately 92 percent of the theoretical. Another method of preparation involves heating a solution of equimolecular quantities of cyanamide and ammonium nitrate to 160°C at a pressure of 200 pounds. The reaction proceeds according to the equation:

$$H_2N.CN+NH_4NO_3 \longrightarrow H_2N.C(:NH).NH.NO_2+H_2O$$

The product is then recrystallized from boiling water. The yield of this method is approximately 88 percent. A third method involves the production of guanidine nitrate as a precursor to the nitroguanidine. Two reactions can be employed to produce guanidine nitrate. The first reaction:

$$H_2N.C(:NH).NH_2+HNO_3 \longrightarrow H_2N.C(:NH).NH_2.HNO_3$$

is simply the reaction between guanidine and nitric acid. The second reaction:

$$H_2NC(:NH).NH.CN+NH_4NO_3 \longrightarrow H_2N.C(:NH).NH_2HNO_3+NC.NH_2$$

is the reaction between dicyandiamide and ammonium nitrate. As the guanidine or dicyandiamide can be produced from the raw materials coke, limestone, atmospheric nitrogen, and water, the production of nitroguanidine does not involve the use of special natural resources. However, a very large amount of electrical energy is required for the production of dicyandiamide or guanidine. Dehydration of guanidine nitrate to nitroguanidine is affected by adding 1 part of the nitrate to 2.3 parts by weight of sulfuric acid (95 percent), so that the temperature does not rise above 10°C. The reaction proceeds according to the equation:

$$H_2N.C(:NH).NH_2.HNO_3 \longrightarrow H_2O+H_2N.C(:NH).NH.NO_2$$

As soon as all the nitrate has been dissolved, the milky solution is poured into seven and one-half parts of ice and water. The mixture is kept ice-cold until precipitation is complete, when the nitroguanidine is caught on a filter, washed with cold water, and redissolved in 10 parts of boiling water. The nitroguanidine recrystallizes when the solution cools. The yield is approximately 90 percent of the theoretical.

(5) Impact sensitivity test results are 47 centimeters using the standard two kilogram weight in the Bureau of Mines apparatus and 26 inches using a nonstandard weight of one pound in the Picatinny Arsenal apparatus. Even when a factor is applied to correct for the nonstandard weight, the values obtained are inconsistent. The preponderance of evidence, however, is that this explosive is considerably less sensitive than TNT to impact as well as friction and initiation. Gap test results for nitroguanidine are shown in table 8-24. Nitroguanidine is unaffected by the rifle bullet impact test and both the fiber and steel shoes in the pendulum friction test. The result of the five second explosion temperature test is 275°C. A minimum charge of 0.20 grams of lead azide or 0.10 grams of tetryl are required for initiation. Sensitivity to initiation varies somewhat with crystal size. Larger quantities can be detonated by a blasting cap containing 1.5 grams of mercury fulminate. Nitroguanidine, therefore, may be classified as one of the least sensitive of military explosives.

Table 8-24. Gap Test Results for Nitroguanidine

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
LANL small scale gap test	1.575 (pressed)	11.8	no explosions
LANL large scale gap test	1.715 (pressed)	3.5	no explosions
	1.609 (pressed)	9.6	5.00

(6) The sand test indicates nitroguanidine to be between 73.5 and 84 percent of TNT. At a density of 1.5 grams per cubic centimeter, the plate dent test indicates a brisance of 95 percent of TNT, and the lead block compression test indicates 73 percent of TNT. The critical diameter at a density of 1.52 grams per cubic centimeter is between 1.27 millimeters and 1.43 millimeters. At a density of 1.70 grams per cubic centimeter the detonation velocity is 8.100 meters per second. At a specific gravity of 1.5 the velocity is 7,650 and at a specific gravity of 1.0 the velocity is 5,360. At a density of 1.55 grams per cubic centimeter, nitroguanidine has a higher velocity of detonation than TNT at the same density; 7,650 compared to 6,900 for TNT. The detonation velocity as a function of density is given by the equation:

$$d = 1.44 + 4.015p$$

where d is in kilometers per second and p, the density, is in grams per cubic centimeter. By the Trauzl test, nitroguanidine is 78 to 101 percent as powerful as TNT, and by the ballistic mortar test, 104 percent as powerful. The temperature of explosion is about 2098°C as compared to 2820°C for TNT. The relatively small heat of explosion explains nitroguanidine's cooling effect when present in propellent compositions.

(7) Nitroguanidine begins to undergo decomposition at a higher temperature, 232°C, than does TNT, 80°C to 200°C. The results of the 75°C international test is a 0.04 percent weight loss in 48 hours. The 100°C heat test results are 0.48 percent weight loss in the first 48 hours, 0.09 percent in the second 48 hours and no explosions in 100 hours. Vacuum stability tests at 120°C show nitroguanidine and TNT to be of the same order of stability. As both are essentially nonhygroscopic and very slightly soluble in water, the impairment of stability by moisture is not a practical problem. In the LLNL reactivity test, 0.02 to 0.05 cubic centimeters of gas are evolved per 0.25 grams of sample. Propellent compositions containing nitroguanidine have been found to be of a high order of stability; indications are that the nitroguanidine acts to some extent as a stabilizer, since such compositions generally do not liberate red fumes when subjected to the 65.5°C surveillance test. The DTA curve for nitroguanidine is shown in figure 8-27. The TGA curve is shown in figure 8-28.

f. *2,4,6-Trinitrophenylmethylnitramine (Tetryl).*

(1) This explosive is also known as: 2,4,6-tetranitro-N-methyl aniline; N-methyl-N,2,4,6-tetranitro-benzenamine; 2,4,6-trinitrophenyl-methylnitramine; tetranitromethylamulene; or picryl-methylnitramine and is sometimes referred to as pyronite, tetrylit, tetralite, tetralita, or CE. The compound (figure 8-29) is colorless when freshly prepared and highly purified, but rapidly acquires a yellow color when exposed to light. Tetryl has a nitrogen content of 24.4 percent, an oxygen balance to CO_2 of -47 percent, a nominal density of 1.71 grams per cubic centimeter with a theoretical maximum density of 1.73 grams per cubic centimeter, and a molecular weight of 287.15. The melting point of the pure substance is 129.45°C and of the technical grade, 129°C. Melting is accompanied by partial decomposition. Repeated solidification and melting rapidly increase the degree of decomposition. Tetryl has a scratch hardness of less than one on the Mohs' scale and therefore the crystals are slightly softer than talc. The crystals are monoclinic with unit cell dimensions of a = 14.13 Angstroms, b = 7.37 Angstroms, c = 10.61 Angstroms. There are four molecules per unit cell. The refractive index is: alpha, 1.546; beta, 1.632; gamma, 1.74. Table 8-25 lists the density of tetryl as a function of loading pressure.

Table 8-25. Density as a Function of Loading Pressure for Tetryl

Loading pressure in kilopascals	Loading pressure in pounds per square inch	Density in grams per cubic centimeter
20,685	3,000	1.40
34,475	5,000	1.47
68,950	10,000	1.57
82,740	12,000	1.60
103,425	15,000	1.63
137,900	20,000	1.67
206,850	30,000	1.71
	cast	1.62

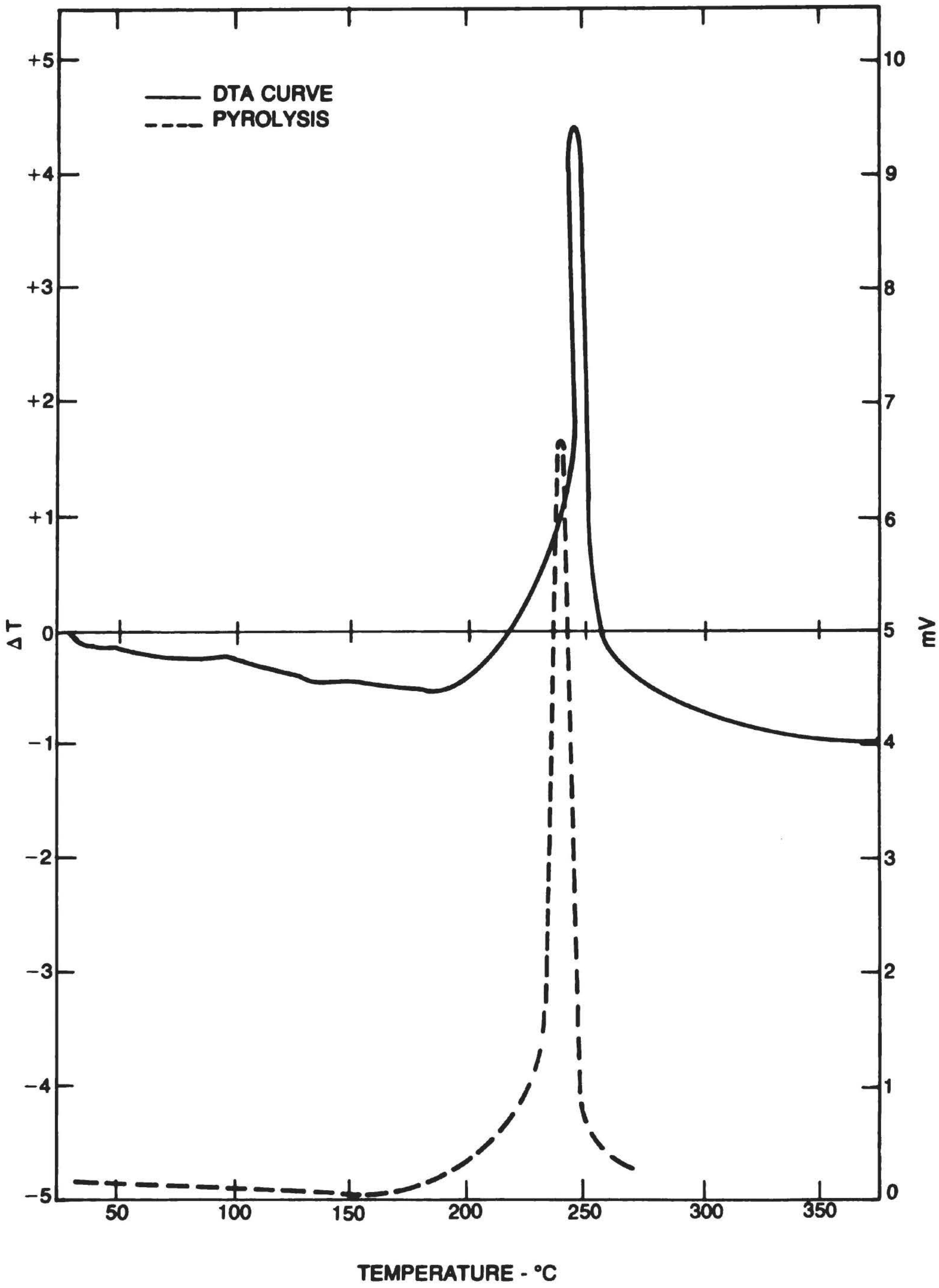


Figure 8-27. DTA curve for nitroguanidine.

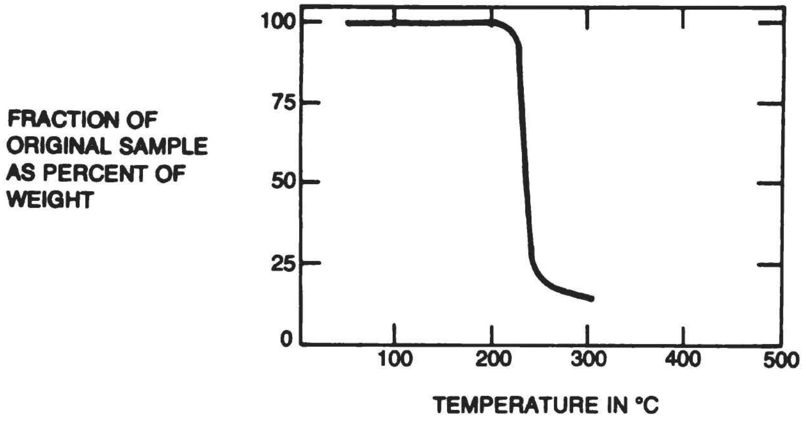


Figure 8-28. TGA curve for nitroguanidine.

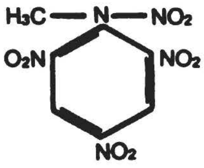


Figure 8-29. Structural formula for tetryl.

Over the temperature range of 200° to 403° Kelvin, the specific heat of tetryl as a function of temperature has been found to be

$$\text{Specific heat} = 0.213 + (2.18 \times 10^{-4})T - (3.73 \times 10^{-7})T^2$$

where T is in degrees Kelvin and the specific heat is in units of calories per gram per degree centigrade. Table 8-26 lists the dielectric constant for tetryl at various densities.

Table 8-26. Dielectric Constant of Tetryl

Density grams per cubic centimeter	Dielectric constant measured at 35 giga cycles
0.9	2.059
1.0	2.163
1.4	2.782
1.5	2.905
1.6	3.097
1.7	3.304

Tetryl has a heat of fusion of 5.9 kilocalories per mole and entropy of fusion of 13.7 eu. The heat of vaporization value is 26 kilocalories per mole, the coefficient of thermal expansion is 0.32×10^{-3} per degree, and the thermal conductivity in cgs units is 6.83×10^{-4} at a density of 1.53 grams per cubic centimeter. Tetryl's heat of combustion at constant pressure is 2,914 calories per gram. The heat of formation value is 4.67 to 7.6 kilogram-calories per mole. The vapor pressure in torr of tetryl is given by the equation:

$$\log p = 13.71 - 6776/T(\mathrm{K}) \qquad \text{for } 85°\mathrm{C} < T < 106°\mathrm{C}$$

Tetryl dissolves readily in concentrated nitric acid and moderately well in other mineral acids but is soluble to the extent of only 0.3 percent in the spent acid after manufacture. Table 8-27 lists tetryl solubility in various solvents at the temperatures given. Benzene holds more tetryl in solution if a solution with solid tetryl present is cooled to a given temperature than if a mixture of benzene and an excess of tetryl is heated to and maintained at a given temperature. At 15°C, 25°C, 35°C, 45°C, and 55°C, tetryl has respective supersolubility values of 10.2, 12.2, 14.9, 18.25, and 22.5 and subsolubility values of only 3.9, 5.5, 7.4, 9.7, and 13.25 grams per 100 grams of benzene.

Table 8-27. *Solubility of Tetryl in Various Solvents*

Solvent	Grams per 100 grams of solvent											
	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C	120°C
Water	0.0050	-	0.0075	-	0.0110	-	-	-	0.810	-	0.184	-
Carbon tetrachloride	0.007	-	0.015	-	0.058	-	0.154	-	-	-	-	-
Ether	0.188	0.330	0.418	0.493	-	-	-	-	-	-	-	-
95% Ethanol	0.320	0.425	0.563	0.76	-	1.72	-	5.33 at 75°C	-	-	-	-
Chloroform	0.28	-	0.39	-	1.20	-	2.65	-	-	-	-	-
Carbon disulfide	0.009	0.015	0.021	0.030	-	-	-	-	-	-	-	-
Ethylene dichloride	-	4.5 at 25°C	-	-	-	-	-	45 at 75°C	-	-	-	-
Acetone	-	-	75	95	116	138	-	-	-	-	-	-
Trichloroethylene	0.07	-	0.12	-	0.26	-	-	-	1.50	1.76 at 86°C	-	-
Ethyl acetate	-	-	40 approx.	-	-	-	-	-	-	-	-	-
Toluene	-	-	8.5	-	-	-	-	-	-	-	-	-
Xylene	-	-	3.3	4.4	5.4	6.0	-	-	-	-	-	-
TNT	-	-	-	-	-	-	-	-	82	-	149	645

(2) Tetryl is highly resistant to attack by dilute mineral acids, but does react with concentrated acid or weak basic solutions. Trinitrophenyl methylamine (figure 8-30) is formed when tetryl reacts with concentrated sulfuric acid or with phenol. Prolonged boiling with dilute sulfuric acid has no effect. When tetryl is boiled with a solution of sodium carbonate, dilute aqueous sodium hydroxide, or dilute aqueous potassium hydroxide, the nitramino group is hydrolized as shown in figure 8-31. If this reaction is carried out in a nitrometer in the presence of mercury, the nitric acid is reduced to nitric oxide and can be measured. In benzene solution at ordinary temperatures, tetryl reacts with aniline to form 2,4,6-trinitrodiphenylamine and methylnitramine as shown in figure 8-32. Aqueous sodium sulfide decomposes tetryl completely into nonexplosive, water soluble products. The reaction is relatively slow unless the solution is heated to 80° to 90°C. Prolonged heating of tetryl at 120°C yields picric acid. Tetryl is reduced and hydrolized to 2,4,6-triaminophenol by the action of tin and hydrochloric acid. Tetryl and TNT form an addition compound with a mole ratio of one to two, respectively. An addition compound is also formed with naphthalene with a mole ratio of one to one. Tetryl forms a eutectic mixture with 76.5 percent trinitro-m-xylene that has a melting point of 118.8°C, and with 29.5 percent trinitroanisole that has a melting point of 22.8°C.

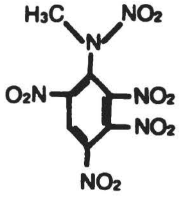


Figure 8-30. *Trinitrophenyl methylamine.*

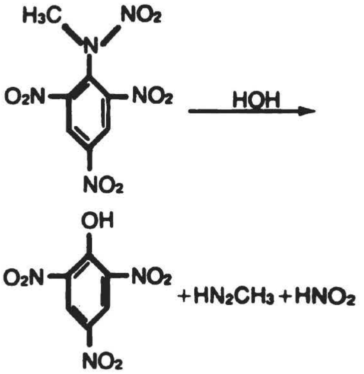


Figure 8-31. *Hydrolysis of tetryl.*

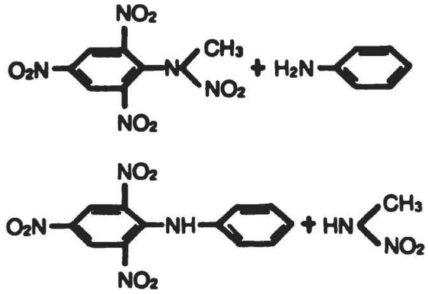


Figure 8-32. Reaction of tetryl with aniline.

(3) A number of homologs and analogs of tetryl are known. Figure 8-33 shows some examples.

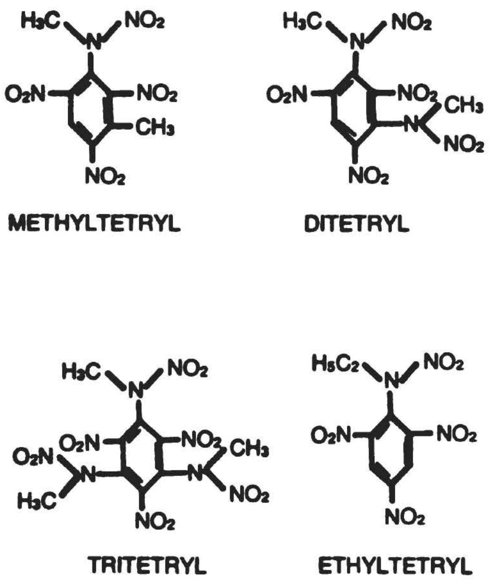


Figure 8-33. Homologs and analogs of tetryl.

(4) Tetryl is fairly resistant to degradation by gamma radiation. Exposure to a 10^4 Curie Co^{60} source, which emits gamma rays at 1.173 and 1.332 million electron volts, produced some erratic results, but on the whole the changes induced by this exposure were not great. A sample exposed to 1.4×10^7 R passed the 120°C vacuum stability test, but a sample exposed to 1.2×10^8 R could only pass the 100°C test and failed in the 120°C test. Weight loss increased dramatically when exposure levels were increased from 1.3×10^8 R to 10^9 R. Irradiated samples did not show much change over control samples in the DTA test until exposure levels reached 1.2×10^8 R, and even at 10^9 R changes were moderate. The impact sensitivity, detonation velocity, and explosion temperature are only slightly affected by exposure to gamma radiation.

(5) Tetryl shows negligible reaction with: Adhesive EC 1099, Dapon resin, Delrin, Epoxy 907 adhesive, Galvanoplast, conductive paint, Glastimat No. 1, Lexan, Loctite 404, Molylube No. 18, Permacel PN 112 tape, Polyesters, polysulfide rubber sealant, polyurethane EP 626/628, RTV 102 and 732 vulcanizing rubbers, Silastic RTV 731 or 732 (uncured), Silicone No SE 1201 and No Q 95-011, urea-formaldehyde. Tetryl is also compatible with the following adhesives: Adiprene L-10Q, L-167 and LD-213, and Eastman 910.

(6) As of 1979 the United States has discontinued the use of tetryl. No new components are being designed with tetryl, and all components that contained tetryl are being redesigned to eliminate the tetryl. The reason for this action is the relative instability of tetryl after storage at elevated temperatures. Various NATO nations have not discontinued tetryl's use in boosters and lead charges.

(7) Two methods have been used extensively for the manufacture of tetryl. The first method uses methylamine (CH_3NH_2), a cheap commercial bulk chemical, in the production of dinitrophenylmethylamine from 2,4- or 2,6-dinitrochlorobenzene by the reaction:

$$C_6H_3(NO_2)_2Cl + CH_3NH_2 \longrightarrow HCl + C_6H_3(NO_2)_2NH.CH_3$$

This can be nitrated to tetryl with relative ease. A considerable amount of tetryl was prepared by this method in the United States during World War II. A variation on this method is used at the present time in Germany. The reaction between the 2,4- or 2,6-dinitrochlorobenzene and methylamine is carried out in the presence of sodium hydroxide. The dinitrophenylmethylamine is then dissolved in sulfuric acid, which is made up from spent acid and contains some nitric acid, oxides of nitrogen and 16 percent water. This solution is then added to mixed acid containing 78 percent nitric acid, 6 percent sulfuric acid, and 16 percent water. The second method uses dimethylaniline as the starting material. The use of dimethylaniline has the disadvantage of requiring nitric acid for the removal of one methyl group by oxidation according to the equation:

$$C_6H_5N(CH_3)_2 + 10NHNO_3 \longrightarrow (NO_2)3C_6H_2N(NO_2)CH_3 + 6NO_2 + CO_2 + 8H_2O$$

This disadvantage is not shared by the first process described above. Direct nitration of dimethylaniline proceeds so violently that the reaction can be carried out only under specialized conditions. The dimethylaniline is converted to dimethylaniline sulfate by dissolving one part of the chemical in 14.4 parts of 96 to 99 percent sulfuric acid at 20°C to 30°C. Many years experience in tetryl manufacture has shown that the ratio of sulfuric acid to dimethylaniline should not be lower than 3:1, since a smaller amount of sulfuric acid may be detrimental to the nitration process. However, the ratio of sulfuric acid to dimethylaniline must not be too high, otherwise tetryl yield is decreased. Sulfonation of the benzene ring will occur if the temperature is not maintained between 20°C and 40°C. A quantity of 15.4 parts of the solution of dimethylaniline sulfate is added in a nitrator to 9.2 parts of mixed acid which contains 66.7 percent nitric acid, 15.8 percent sulfuric acid, and 17.5 percent water. The contents of the nitrator are heated to 68°C then heating is discontinued. This step involves a reaction that oxidizes a methyl group and is highly exothermic. The temperature of the reaction must be maintained at 60°C to 72°C by external means, if necessary. For safe and efficient nitration, very vigorous stirring is essential to ensure that the reacting liquids are mixed almost instantaneously. The mixture is kept in this nitrator for a very short period, so the reaction may be incomplete. The contents of the nitrator are discharged via an overfall to a larger reactor that is also equipped with a stirrer. In this reactor, which is maintained at 70°C, the reaction is completed. Commercial dimethylaniline contains some methylaniline which is nitrated to 2,3,4,6-tetranitrophenylnitramine (also called m-nitroethyl) which in turn is readily hydrolyzed to 2,4,6-trinitro-3-hydroxyphenylmethylnitramine. The nitration and hydrolysis are shown in figure 8-34. The compound formed is readily soluble in water and easily removed. If the water content of the mixed acid is too high, benzene insoluble impurities are formed which are benzidine derivatives. The derivatives are shown in figure 8-35. After the reaction is completed in the reactor, the liquid which contains partially crystallized tetryl is allowed to run into a crystallizer which is maintained at 20°C. The crystallized product is discharged to a vacuum filter where the tetryl is collected and the spent acid is passed on to be renitrated. Tetryl must then be purified carefully to remove any tetranitrocompound and occluded acidity, which have adverse effects on the stability of tetryl. Most of the acidity is removed by washing with cold water. Treatment with boiling water decomposes any tetranitrocompound present and removes any products. If benzene is used as a solvent, the crude tetryl is dissolved, the solution is washed with water to remove residual acidity, and filtered to remove insoluble matter. Upon cooling the solution, the tetryl is precipitated, separated, and dried. If acetone is used as the solvent, the solution is neutralized and filtered and the tetryl is precipitated by mixing the solution with water. The acetone purification process is carried out on a continuous basis, while that with benzene is operated as a batch process. In the lab, high purity tetryl can be obtained by nitrating dimethylaniline with nitric acid, not mixed acid, in the presence of inert solvents such as dichloromethane, chloroform, or carbon tetrachloride.

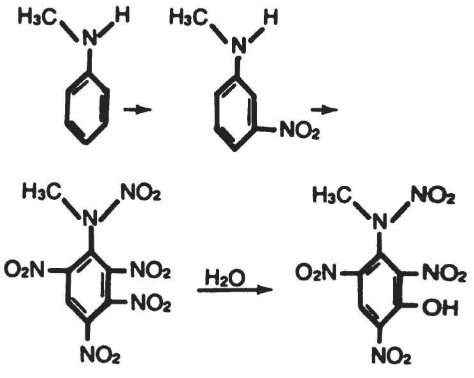


Figure 8-34. Nitration and hydroylsis of methylaniline.

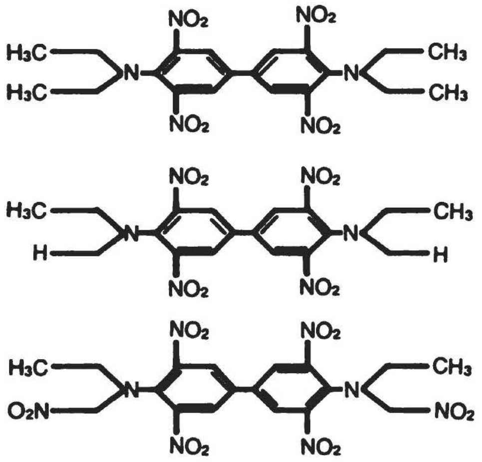


Figure 8-35. Benzidine derivatives during tetryl manufacture.

(8) One grade of tetryl is specified for military purposes. This complies with the following requirements:

Color:	Light yellow
Moisture and volatiles:	Maximum, 0.10 percent
Toluene insoluble matter:	Maximum, 0.10 percent
Grit:	3 particles
Acidity:	Maximum, 0.02 percent
Melting point:	Minimum, 128.8°C; maximum, 129.5°C

Granulation: Percent through US standard sieve:

No. 12, minimum	100
No. 16, minimum	95
No. 30, minimum	-
No. 40, maximum	-
No. 60, maximum	30
No. 100, maximum	5

A requirement also exists for an infrared spectrum with only certain specified peaks and no extraneous peaks. The requirement with respect to insoluble matter is included because of the marked desensitizing effect of such impurities. Freedom from grit is required because of the affect of grit on sensitivity to impact and friction.

(9) Impact and rifle bullet tests indicate tetryl is more sensitive than TNT. The pendulum friction test, however, produces no detonations with the steel shoe. The explosion temperature test value of tetryl is much lower than that of TNT. For tetryl dropped on a heated copper surface the results in table 8-28 were reported.

Table 8-28. Heat Initiation of Tetryl

Temperature in °C	Time to explosion in seconds
302	0.4
280	1.1
260	2.0
236	6.2

Slightly different results were obtained with confined samples of tetryl. The explosion times for 25 milligrams of tetryl in copper shells of 0.635 millimeter diameter submerged in a hot woods metal bath are shown in table 8-29.

Table 8-29. Heat Initiation of Confined Tetryl

Temperature in °C	Time to explosion in seconds
360	0.325
346	0.425
329	0.582
285	1.45
269	2.22
264	Does not detonate

When a 0.5 gram sample of tetryl is heated at a rate of 20°C per minute, ignition occurs between 190°C and 194°C. If the temperature of a sample is held at 180°C ignition occurs in 40 seconds. The minimum primary charges necessary for reliable detonation of tetryl with mercury fulminate is 0.20 to 0.29 grams and with lead azide is 0.025 to 0.10 grams. Tetryl containing 60 percent water cannot be detonated by a commercial detonator. Shock sensitivity as measured by the gap tests are summarized in table 8-30.

Table 8-30. Gap Test Results for Tetryl

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.687	2.5	7.80
	1.434	17.1	11.96
LANL small scale gap test	1.684 (pressed)	2.7	3.84
	1.676 (pressed)	3.1	4.04
	0.93 (bulk)	46.2	7.44
LANL large scale gap test	1.690 (not pressed)	2.3	59.82
	1.666 (pressed)	3.7	60.60
	0.85 (bulk)	50.9	69.2

The shock sensitivity of a lightly confined sample decreases as temperature decreases, but confined samples show only a slight tendency toward reduced shock sensitivity. Particle size has an effect on shock sensitivity. As the particle size decreases, the shock sensitivity increases. Deflagration can also be initiated by shock. For coarse tetryl with a density of 1.65 grams per cubic centimeter in a 21 millimeter diameter plexiglas tube, the deflagration threshold pressure is 12.1 to 14 kilobar, as compared to 18 kilobar for detonation. Tetryl's sensitivity to shock initiation by an explosive bridge wire is dependent on particle size and crystal habit. The sensitivity decreases as packing density increases. In studies of tetryl's sensitivity to initiation by laser beams, no initiation occurred upon direct exposure to the beam. But if the tetryl sample was coated with a thin metal film, initiation was observed at a density of 1.08 grams per cubic centimeter. With higher density tetryl no initiation occurred.

(10) At a density of about 1.60 grams per cubic centimeter, the sand test indicates a brisance of 113 to 123 percent of TNT, the copper cylinder compression test indicates 117 to 125 percent, the lead block compression test indicates 112 percent, the plate dent test indicates 115 percent, and the fragmentation effect test indicates 121 percent. The ideal detonation velocity as a function of density is given by the equation:

$$D=5600+3225(p-1)$$

where D, the detonation velocity, is in units of meters per second and p, the density, is in grams per cubic centimeter. This equation yields slightly higher values than have been observed by other researchers. Low velocity detonation has been observed when coarse tetryl is weakly initiated. Below a certain diameter, which varies with particle size, low velocity detonation can be stable for lengths up to 25 charge diameters. Above this diameter low velocity detonation is stable for only distances of 2 to 4 charge diameters, at which point there is a transition to normal detonation velocity. Table 8-31 summarizes the dependence of transition diameter, minimum diameter for low velocity detonation, minimum diameter for normal detonation, and the approximate speed for low velocity detonation on particle size for 0.9 grams per cubic centimeter tetryl. Low velocity detonation is not affected by the initiating power of the detonator, provided the detonator is weak enough not to initiate normal detonation. For charge diameters between the minimum diameter for low velocity detonation and minimum diameter for normal detonation, even powerful initiators will produce only steady, low velocity detonation, provided the charge is of sufficient strength. Low velocity detonation is maximum at the transition diameter. This velocity is virtually independent of particle size and even type of explosive. TNT, PETN, RDX, and tetryl all have the same maximum low velocity detonation. Experiments with oil coated or crushed particles suggest that the main reaction in low velocity detonation is surface combustion. The power of tetryl by the ballistic pendulum test is 145 percent that of TNT, by the ballistic mortar test 126 to 132 percent of TNT, and by the Trauzl test 125 to 145 percent of TNT. The heat of detonation as a function of density is given by the equation:

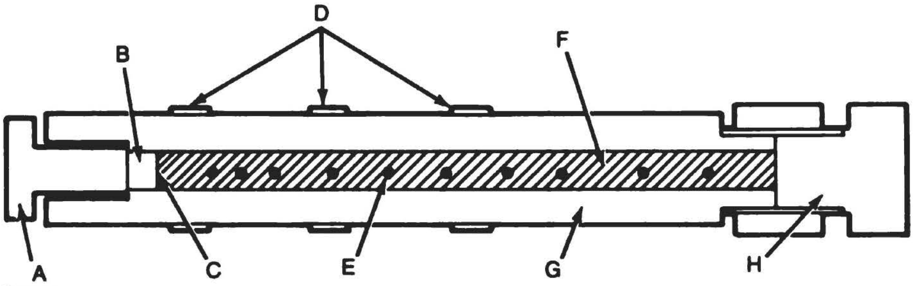
$$Q=680+282p$$

where Q is in units of calories per gram and p, the density, is in grams per cubic centimeter. The values given by the above equation fall short of the computed values for an ideal detonation. Point initiation studies with tetryl at a density of 1.51 grams per cubic centimeter indicate that the radius of curvature of the detonation front increases with charge length in the manner expected for spherical expansion of the front. The radius of curvature is also a function of the particle size and packing density of the explosive. The apparatus shown in figure 8-36 was used to study the deflagration to detonation transfer in tetryl. After ignition, the length of the column before detonation occurs is determined by the markings on the tube fragments recovered. This result is checked with the ionization probe and strain gage records for consistency. The results for coarse tetryl with a particle size of 470 microns and fine tetryl with a particle size of 20 microns are plotted in figure 8-37. According to the graph, both fine and coarse tetryl show the same effects of compaction on predetonation column length, which is nearly constant at low density, with increasing values at 75 percent density. At a given density, the fine tetryl has a greater predetonation column length than the coarse, as well as longer relative time to detonation. In the experiments with tetryl, the ionization probes frequently failed to respond because the decomposition products formed shortly after ignition have such a high electrical resistance. Another unique characteristic of tetryl is that the onset of accelerated burning is located nearer to the onset of detonation than the ignition region. Both of these effects are attributed to the low temperature of decomposition of tetryl. The addition of 3 percent wax to a sample changes the initial low temperature decomposition to behavior typical of other explosives, with accelerated burning starting sooner. The burning rate of tetryl is not greatly affected by the initial temperature of the sample; the rate increasing by less than a factor of two for a temperature difference of 100°C. The burning rate decreases with additions of small amounts of water, and increases with increasing ambient pressure.

(11) Figure 8-38 shows the amount of gas evolved by tetryl as a function of temperature and time. The presence of picric acid tends to accelerate the evolution of gas, while trinitroanisole or trinitroaniline tend to slow the evolution of gas. Table 8-32 shows the composition of the gaseous products of tetryl decomposition.

Table 8-31. Low Velocity Detonation in Tetryl

Particle size in millimeters	Minimum diameter for low velocity detonation	Minimum diameter for normal detonation in millimeters	Transition diameter in millimeters	Minimum low velocity detonation in kilometers per second	Maximum low velocity detonation in kilometers per second
0.5	7	13	13	1.4	2.1
0.8	9	15	16	1.3	2.3
1.3	12	20	21	1.3	2.2



A - IGNITER BOLT
B - IGNITER
C - IGNITER/EXPLOSIVE INTERFACE
D - STRAIN GAGES
E - IONIZATION PROBE LOCATION
F - EXPLOSIVE CHARGE
G - TUBE
H - BOTTOM CLOSURE

INNER DIAMETER = 16.3MM

OUTER DIAMETER = 50.8MM

DISTANCE FROM IGNITER/EXPLOSIVE INTERFACE TO BOTTOM CLOSURE = 295.4MM

Figure 8-36. Deflagration to detonation transfer apparatus.

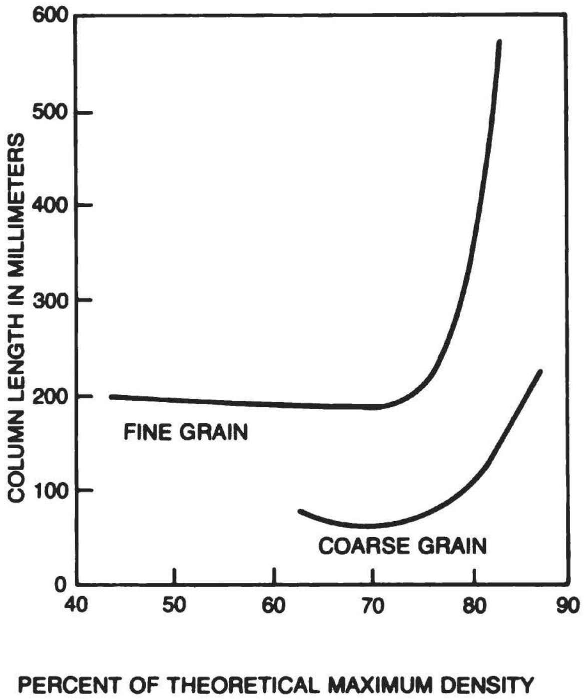


Figure 8-37. Effect of compaction on predetonation column length in tetryl.

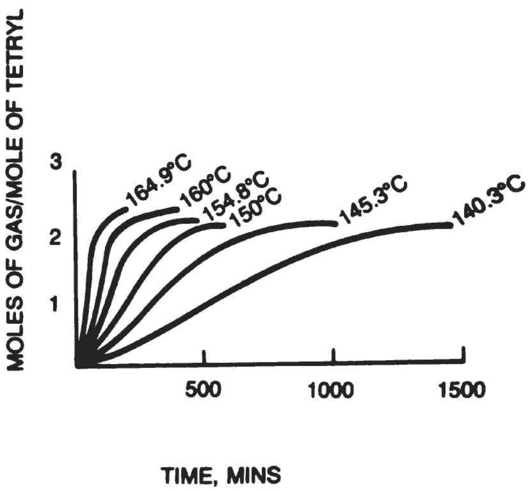


Figure 8-38. Kinetic gas-evolution curves in the decomposition of tetryl.

Table 8-32. Composition of Gaseous Products of Tetryl Decomposition

Time mins	Moles of gas per mole of tetryl	Composition of dry gas, volume %				Composition of gas, moles per mole of tetryl				
		CO_2	CO	NO	N_2	CO_2	CO	NO_2	NO	N_2
221	0.650	23.6	10.6	4.3	61.5	0.134	0.060	0.016	0.024	0.348
1530	2.208	25.9	12.0	5.3	56.8	0.493	0.229	0.000	0.101	1.080
40	0.450	25.1	10.9	5.0	59.0	0.087	0.035	0.021	0.017	0.204
50	0.667	24.5	11.3	6.3	57.9	0.124	0.057	0.018	0.032	0.282
80	1.338	23.9	11.1	8.2	56.8	0.243	0.113	0.031	0.084	0.578
110	1.808	24.3	10.8	8.1	56.8	0.358	0.158	-	0.118	0.838
140	2.010	25.2	11.5	8.5	54.8	0.420	0.193	0.016	0.143	0.925
200	2.149	25.1	11.8	8.6	54.5	0.448	0.210	0.004	0.153	0.972
422	2.304	25.7	12.1	8.2	54.0	0.491	0.231	0.001	0.156	1.030
1440	2.674	27.8	13.4	8.4	50.4	0.624	0.302	0	0.190	0.130
40	1.950	24.5	11.6	8.8	55.1	0.397	0.188	0.023	0.142	0.892
382	2.572	27.7	12.7	9.6	50.0	0.584	0.268	0.003	0.202	1.060

Table 8-33 shows the composition of the condensed phase as a function of time for tetryl that has been heated at 160°C.

Table 8-33. Composition of Condensed Phase Tetryl

Time mins	Weight of residue as % of initial quantity of tetryl	Moles per mole of tetryl			
		Tetryl	2,4,6-trinitro-anisole	Picric Acid	N-methyl-2,4,6-trinitroaniline
25	95.6	0.832	0.073	0.037	0.030
45	90.0		0.195		0.034
55	86.9	0.494	0.265	0.094	0.045
70	83.8		0.295	0.113	
90	80.5	0.227	0.412	0.131	0.072
111	78.2		0.503		
145	75.9	0.029	0.525	0.160	0.065
300	74.2	0.019	0.478	0.204	0.047
400	73.2		0.463		
1440	69.0	0	0.110	0.524	0.031

The heat of reaction for the slow decomposition of tetryl is 328 to 341 calories per gram. Vacuum stability tests show tetryl to be less stable than TNT. The DTA curve for tetryl is shown in figure 8-39 and the TGA curve is shown in figure 8-40. Ammunition that has been loaded with tetryl cannot be stored at temperatures greater than 125°. This is specifically why the United States has discontinued the use of this explosive. Tetryl corrodes steel heavily. Slight corrosion is reported for iron, zinc, zinc plated steel, tin plated steel, parkerized steel, brass, and monel metal. Tetryl does not react with copper, tin, nickel, lead, copper plated steel, bronze, stainless steel, cadmium, aluminium, silver, and titanium. Tetryl frequently is used with one to two percent of a binding agent or lubricant, such as graphite, stearic acid, or magnesium stearate; and has been found to be compatible with such materials as well as black powder.

8-4. Nitroaromatics. Compounds in this class are prepared by *C-type* nitration in which a nitrogroup is attached to a carbon atom of the compound being nitrated.

a. *Ammonium Picrate.*

(1) This explosive is also known as ammonium 2,4,6-trinitrophenolate, explosive D, and Dunnite. The compound (figure 8-41) has a nitrogen content of 22.77 percent, an oxygen balance to CO_2 of −52 percent, a maximum crystal density of 1.717 grams per cubic centimeter, a nominal density of 1.63 grams per cubic centimeter, a melting point with decomposition of about 280°C and a molecular weight of 246. Ammonium picrate exists in a stable form as yellow, monoclinic crystals and a meta stable form as red, orthorhombic crystals. The unit cell dimensions are a = 13.45 Angstroms, b = 19.74 Angstroms, and c = 7.12 Angstroms. The compound manufactured for military use is yellow to orange in color. Table 8-34 lists the density of ammonium picrate as a function of loading pressure.

Table 8-34. Density of Ammonium Picrate

Pressure in kilopascals	Pressure in pounds per square inch	Density in grams per cubic centimeter
20,685	3,000	1.33
34,475	5,000	1.41
68,950	10,000	1.47
82,740	12,000	1.49
103,425	15,000	1.51
137,900	20,000	1.53
344,750	50,000	1.59
689,500	100,000	1.64

The refractive index at 20°C is: alpha, 1.508; beta, 1.870; and gamma, 1.907. The heat of combustion of ammonium picrate at constant pressure is 2,745 calories per gram, from which is derived a heat of formation value of 95.82 kilogram-calories per mole. The heat of explosion is 706 calories per gram. Table 8-35 lists the solubility of ammonium picrate in various solvents as a function of temperature.

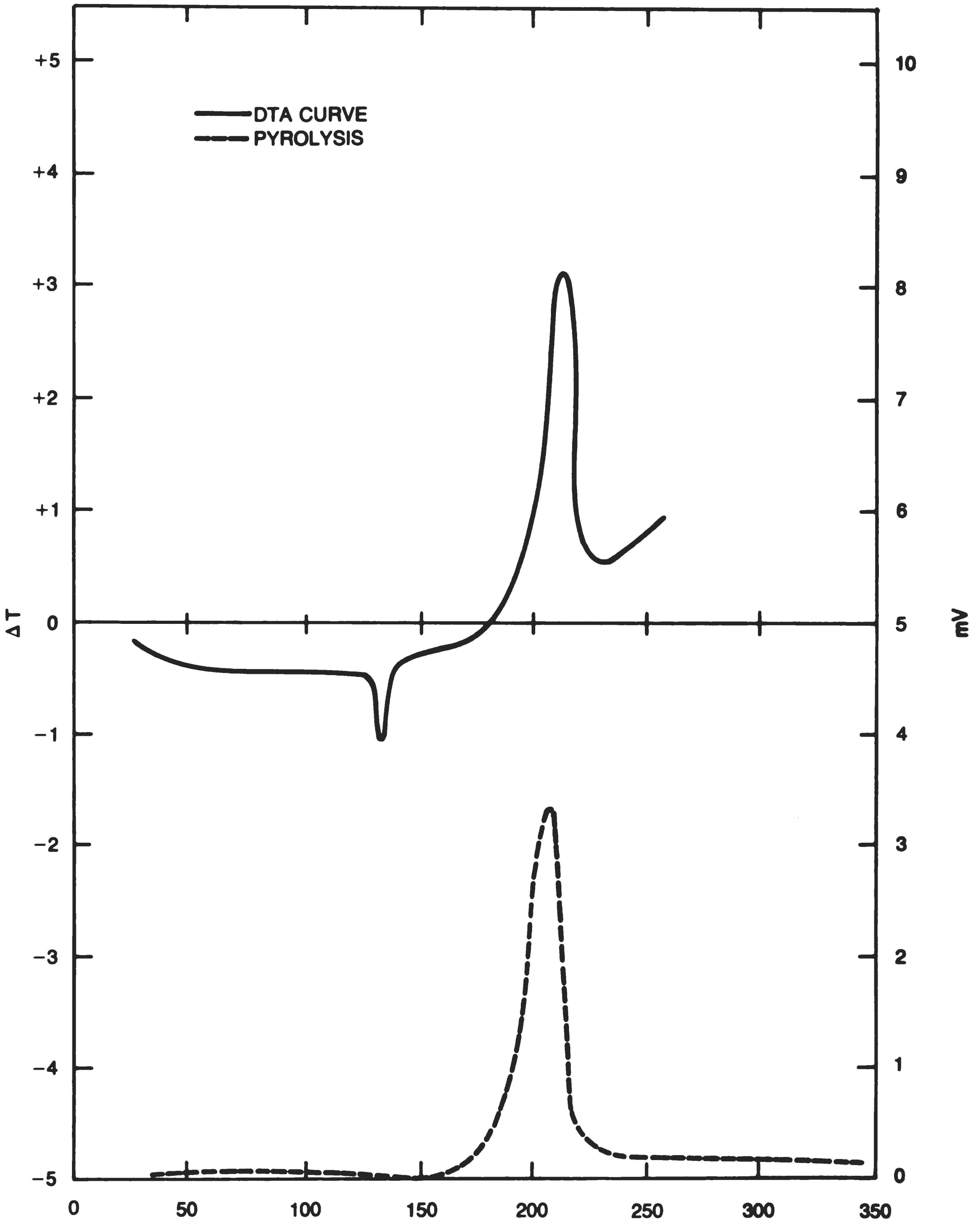


Figure 8-39. DTA curve for tetryl.

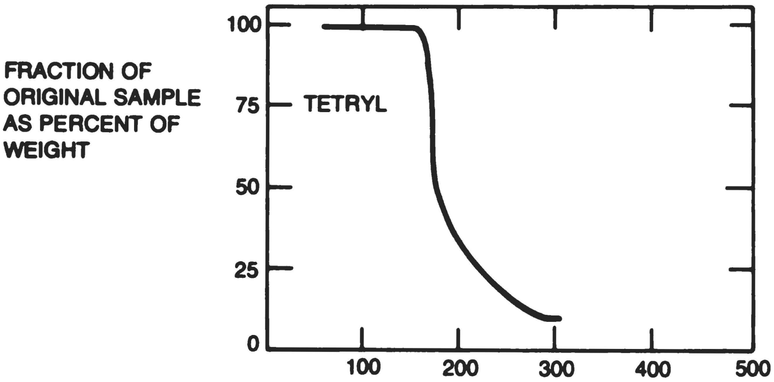


Figure 8-40. TGA curve for tetryl.

Table 8-35. Solubility of Ammonium Picrate

Solvent	Solubility in grams per 100 grams of solvent						
	0°C	10°C	20°C	30°C	50°C	80°C	100°C
Water	-	0.70	102	-	-	-	75
Ethanol	0.51	0.69	0.86	1.05	1.89	3.62	-
Ethyl acetate	0.29	0.30	0.34	0.38	0.45	0.56	-
Acetone	-	-	-	2.85	-	-	-
Octyl alcohol	-	-	0.2 at 25°C	-	-	-	-

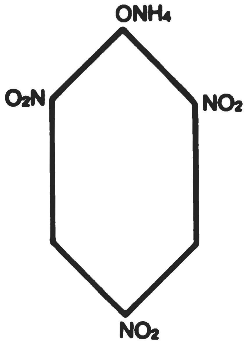


Figure 8-41. Structural formula for ammonium picrate.

In ethanol, ammonium picrate dissolves very slowly and slow separation occurs when the solution is left standing. The solubility in ether is very slight. Ammonium picrate, because of an extreme insensitivity to shock, is used in armor piercing projectiles. The compound is also used in jet assisted takeoff units for aircraft.

(2) Chemically, ammonium picrate is not very reactive. Decomposition by alkalies yields picric acid and ammonia. This reaction is the basis of one of the methods for determining the purity of the material. When maintained at the melting point, ammonium picrate decomposes to the same products. At 0°C an equimolecular amount of ammonia is absorbed, but at 26°C this is lost by volatilization.

(3) The manufacture of ammonium picrate is relatively simple. Picric acid, which is only partially soluble in water, is suspended in hot water and neutralized by the addition of gaseous or aqueous ammonia. The picrate, which is more soluble in water, is formed and immediately goes into solution. The reaction is slightly exothermic. On cooling the solution, the ammonium picrate separates out. If a marked excess of ammonia is used, the red form is obtained so care must be taken to avoid this and obtain the yellow form. The yellow form has a higher bulk density than the red and can be pressed better. The separated crystals are washed with cold water to remove any free ammonia present and then dried.

(4) The specifications for ammonium picrate cover one grade of material representing two classes with respect to granulation. Class 1 material, which is the coarser of the two classes, is intended for use in the press-loading of shells, while class 2 is used for the manufacture of picratol and other compositions. The requirements are as follows:

	Class 1	Class 2
Surface moisture and volatile content (%), maximum:	0.10	-
Total moisture content (%), maximum:	-	0.2
Ammonium picrate purity (%), minimum:	99	99
Sulfates (as sulfuric acid) (%), maximum:	0.10	0.10
Chloroform insoluble impurties (%), maximum:	0.10	-
Water insoluble material (%), maximum:	0.10	0.10
Irritant contaminants as parts chlorine per million, maximum:	50	-
Ash (%), maximum:	0.1	0.1
Acidity and alkalinity (as picric acid or ammonia (%), maximum:	0.025	0.025
Color	Yellow to orange	Yellow to orange
Granulation (US standard sieves)		
Percent through No. 12 sieve, minimum	99.9	-
Percent through No. 40 sieve, minimum	-	99.5
Percent retained on No. 70 sieve, minimum	60	-
Percent retained on No. 70 sieve, maximum	-	20
Percent through No. 200 sieve, maximum	5	-

The picric acid used to make class 2 ammonium picrate shall be made by the nitration of phenol and shall contain no material salvaged from trimmings or from loading operations. Class 2 ammonium picrate shall contain no reworked ammonium picrate made by way of any process other than the phenol nitration process. The irritant contaminants requirement is not applicable to ammonium picrate made from picric acid produced by the nitration of phenol. The color requirement is intended to cover the unavoidable presence of a small amount of the red form of ammonium picrate in admixture with the yellow form. The requirement with respect to irritant contaminants represents a control of the purity of picric acid used in manufacture when this is made by the dinitrochlorbenzene process. The chloroform soluble matter requirement also represents a control of the nature of impurities present in picric acid manufactured by a process other than the nitration of phenol.

(5) Ammonium picrate is distinctly less sensitive to impact than TNT and is unaffected by the steel shoe in the pendulum friction test. A slightly greater sensitivity is indicated by the rifle bullet impact test with three partially burned samples in ten trials. This is attributed to the lower temperature required for explosion for ammonium picrate, 318°C in the five second test, as opposed to 457°C for TNT. The time to explosion as a function of temperature is shown in table 8-36.

Table 8-36. Ammonium Picrate Explosion Temperature

Time in seconds	Temperature in degrees centigrade
0.1	405
1	367
5	318
10	314
15	299
20	295

The low degree of sensitivity of ammonium picrate to impact is paralleled by a relative insensitivity to initiation. In the sand test, ammonium picrate is not detonated completely by either lead azide or mercury fulminate. A booster charge of 0.06 gram of tetryl is required for complete detonation. In this test, a minimum charge of 0.28 gram of diazodinitrophenol detonates ammonium picrate but a charge of only 0.15 gram is required for the detonation of TNT. The minimum charge of mercury fulminate required to initiate 0.4 grams of ammonium picrate loaded at about 200 atmospheres of pressure is 0.85 grams versus 0.26 grams of mercury fulminate necessary to initiate 0.4 grams of TNT. Moisture has a marked effect on the sensitivity of ammonium picrate to initiation. The presence of 0.5, 1.0, and 2.0 percent of moisture requires increases in the minimum detonating charge of tetryl to 0.09, 0.11, and 0.14 gram, respectively. Storage of either the yellow or red form at 50°C for two years causes such an increase in sensitivity that initiation by mercury fulminate alone is possible. Subsequent storage of the yellow form at magazine temperatures for two years causes desensitization to such an extent that a booster charge to tetryl is required for complete detonation and four years of such storage is required for return to the original condition of insensitivity. Storage at 50°C has the same effect on the sensitivity of red ammonium picrate but subsequent storage at magazine temperatures for four years merely increases the minimum detonating charge of mercury fulminate from 0.23 to 0.29 gram. The changes in sensitivity are not accompanied by any change in brisance or in color. In an electrostatic sensitivity test for material that passes through a 100 mesh sieve, an energy of 6.0 joules was required for confined material and 0.025 joules for unconfined material. Ammonium picrate which has been pressed into and removed from projectiles or other ammo is much more sensitive to shock than new or unused material. Therefore, reclaimed material should not be pressed or loaded into ammo items until after recrystallization.

(6) In the sand test, 37.5 grams to 39.5 grams of sand are crushed, which indicates a brisance of 78 to 82.5 percent of TNT. The plate dent test indicates a brisance of 91 percent of TNT for a charge of ammonium picrate with a density of 1.50 grams per cubic centimeter. Fragmentation tests indicate a brisance of 91 percent, 96 percent and 99 percent of TNT for charges that have been pressed to density values of 1.50, 1.53, and 1.55, respectively. The approximate velocity of detonation as a function of density is given by the equation:

$$V = 960 + 3800d$$

where V is in meters per second and d, the density, is in grams per cubic centimeter. A charge diameter of 2.54 centimeters was used to determine the above equation. The critical diameter for a sample with density of 1.65 grams per cubic centimeter is greater than 25.4 millimeters. When exploded adiabatically at constant volume, ammonium picrate produces a pressure of 8956 kilograms per square centimeter when pressed to a density of 1.5 grams per cubic centimeter, and 9553 kilograms per square centimeter when pressed to a density of 1.6 grams per cubic centimeter. These values are 113 percent of the corresponding values for TNT. Although the heat of explosion of ammonium picrate is only 86 percent that of TNT, the ballistic pendulum test indicates a power of 98 percent of TNT. This combination of brisance and power, almost equal to those of TNT, together with relative insensitivity, has made ammonium picrate suitable for use in armor piercing projectiles. However, the impracticality of melt-loading ammonium picrate has led to partial replacement by picratol, which can be melt-loaded. When ignited in an unconfined state, ammonium picrate burns slowly without detonation emitting dense, black smoke. However, when confined and heated to the ignition temperature, an explosion occurs. Complete detonation produces a dense, black cloud of smoke with sooty deposits and an odor of ammonia. When incomplete detonation occurs, yellow smoke is produced along with unburned ammonium picrate particles.

(7) Ammonium picrate is of a very high order of stability. In the 100°C heat test, 0.1 percent is lost in the first 48 hours and 0.1 percent in the second 48 hours. No explosions occur in 100 hours. In the 130°C heat test there is no acidity or explosion in 300 minutes. The vacuum stability test at 100°C produced 0.2 cubic centimeters of gas in 40 hours, at 120°C, 0.4 cubic centimeters of gas are produced, and at 150°C, 0.4 cubic centimeters of gas are produced. The material has been found to withstand storage at ordinary temperatures for a period of twenty years with no evidence of deterioration, and at 50°C for more than five years without marked deterioration. Moisture increases ammonium picrate's reactivity with metals such as lead, potassium, copper, and iron. The compounds produced are extremely sensitive. This reactivity requires that all projectiles loaded with this material have contact areas covered with acid proof paint. At 100°C ammonium picrate is compatible with TNT or black powder but undergoes reactions with nitroglycerin, nitrocellulose, PETN, or tetryl. Figure 8-42 shows the DTA curve for ammonium picrate.

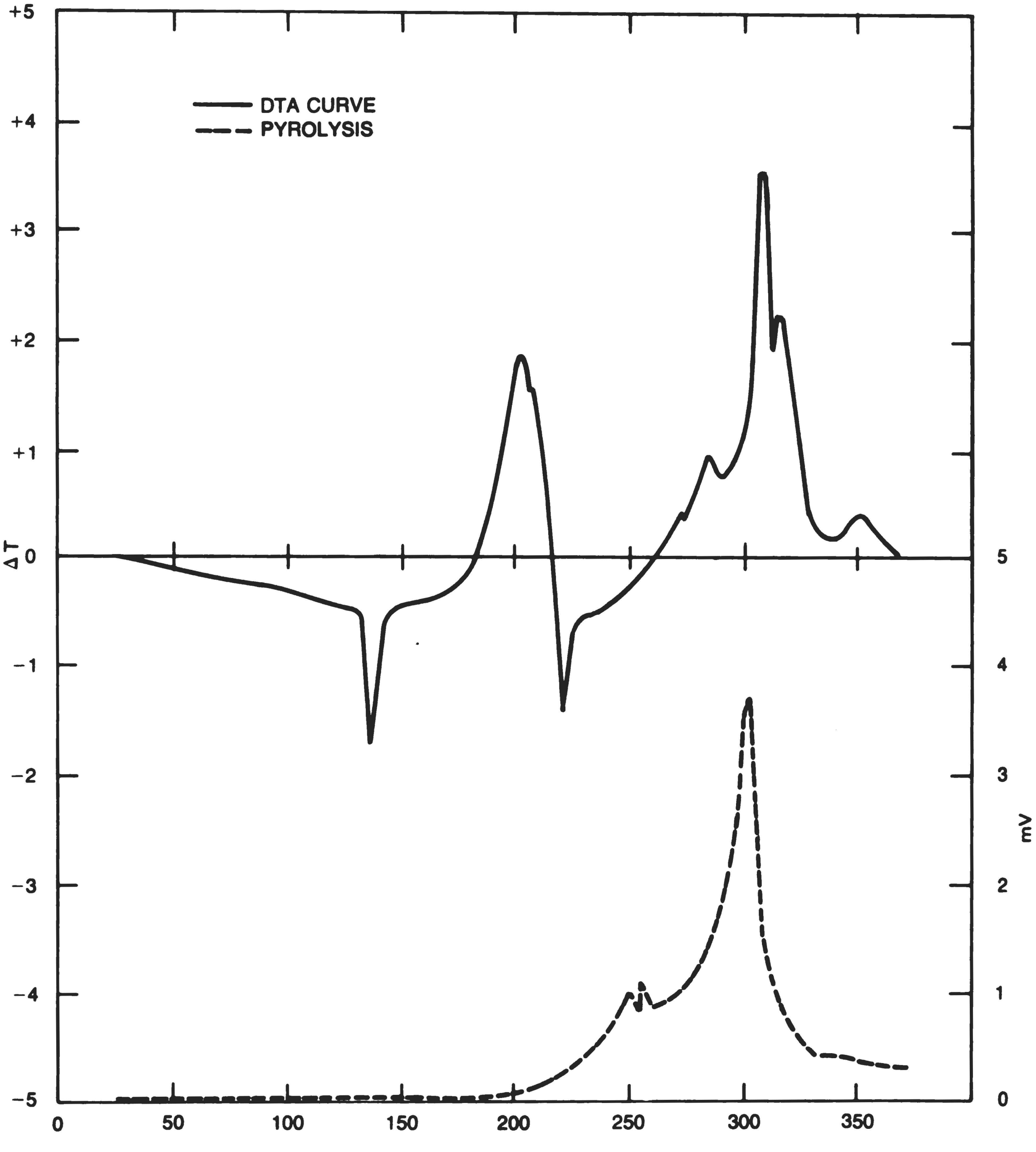


Figure 8-42. DTA curve for ammonium picrate.

b. *1,3-Diamino-2,4,6-Trinitrobenzene (DATB).*

(1) This explosive is also known as 2,4,6-trinitro-1,3-diaminobenzene; 2,4,6-trinitro-7,3-benzenediamine trinitro-m-phenylenediamine; or 2,4,6-trinitro-1,3-diaminobenzol and may be referred to as DATNB. The compound (figure 8-43) is a yellow, crystalline solid with a nitrogen content of 28.81 percent, a melting point of 286°C to 301°C with decomposition, and a molecular weight of 243.14. Two polymorphs of DATB have been identified. Form I, which is stable to 217°C, has two molecules per unit cell and unit cell lengths of a=7.30 Angstroms, b=5.20 Angstroms, c=11.63 Angstroms. Form II has four molecules per unit cell and unit cell lengths of a=7.76 Angstroms, b=9.04 Angstroms, c=12.84 Angstroms. The maximum density of form I is 1.837 grams per cubic centimeter and the density of form II is 1.815 grams per cubic centimeter. The nominal density of DATB is 1.79 grams per cubic centimeter. DATB is slightly soluble in acetic acid and only very slightly soluble in other solvents. The vapor pressure is given by the equation:

$$\log p = 12.75 - 7492/T\,(^{\circ}\mathrm{C}) \quad \text{for } 92.8^{\circ}\mathrm{C} < T < 176.8^{\circ}\mathrm{C}$$

The heat of formation is −97.1 to −119 calories per gram, the heat of combustion is −7115 kilocalories per mole, the heat of detonation with liquid water was experimentally determined as 980 calories per gram and with gaseous water, 910 calories per gram. The computed maximum values for the heat of detonation are 1260 calories per gram and 1150 calories per gram for gaseous and liquid water, respectively. The specific heat is given by the equation:

$$C_p = 0.20 + (1.11 \times 10^{-3})T - (1.81 \times 10^{-6})T^2 \quad \text{for } 47^{\circ}\mathrm{C} < T < 200^{\circ}\mathrm{C}$$

The heat of sublimation is 138 calories per gram. DATB can be used as a pressed explosive or as a ballistic modifier in some rocket propellents.

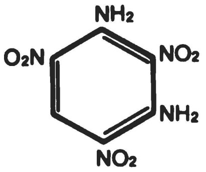


Figure 8-43. Structural formula for DATB.

(2) DATB can be prepared by nitrating m-dichlorobenzene to 2,4,6-trinitro-1,3-dichlorobenzene and aminating in methanol solutions. Another method of preparation is by the amination of 2,4,6-trinitro-3-aminoanisole. In a third method of preparation phosphorous oxytrichloride and dipyridinium styphnate are reacted directly at steam bath temperature and a suspension of the resulting 2,4,6-trinitro-1,3-dichlorobenzene in methanol is treated with gaseous ammonia. Impact sensitivity is 200 percent that of TNT. Table 8-37 shows the gap test results for DATB.

Table 8-37. Gap Test Results for DATB

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.775	3.5	3.28
	1.233	33	5.18
LANL small scale gap test	1.801 (hot pressed)	2.0	0.36
	1.714 (pressed)	6.7	1.27
LANL large scale gap test	1.786 (pressed)	2.8	41.68
	1.705 (pressed)	7.2	45.36
	0.81 (bulk)	56	49.3
PX gap test	1.781	3.2	17.86
	1.446	21.3	19.94

(3) The detonation velocity is given by the equation:

$$D = 2.480 + 2.852p$$

where D is in kilometers per second and p, the density, is in grams per cubic centimeter. The failure diameter of unconfined DATB at a density of 1.816 grams per cubic centimeter is 5.3 millimeters. The detonation pressure is 251 and 259 kilobars for samples with densities of 1.780 and 1.790 grams per cubic centimeter, respectively. The plate dent test indicates a brisance of 120 percent of TNT.

(4) In the vacuum stability test, less than 0.03 cubic centimeters of gas are evolved in 48 hours at 120°C. In the LLNL reactivity test, less than 0.03 cubic centimeters of gas are evolved per 0.25 grams of sample in 22 hours at 120°C. Figure 8-44 shows the DTA curve for DATB.

c. *2,2'4,4',6,6'-Hexanitroazobenzene (HNAB).*

(1) This explosive is also known as bis (2,4,6-trinitrophenyl)-diazene. HNAB forms blood red prisms when crystallized from nitrobenzene, glacial acetic acid, or concentrated nitric acid. The compound (figure 8-45) has a melting point of 215°C to 216°C, a molecular weight of 452, and a density of 1.79 grams per cubic centimeter. HNAB has a heat of formation of −58 to −67.9 calories per mole and a heat of detonation of 1.47 kilocalories per gram for liquid water and 1.42 kilocalories per gram for gaseous water. The specific heat is 0.3 calories per gram per degree centigrade. Table 8-38 shows the gap test results for HNAB.

Table 8-38. Gap Test Results for HNAB

	Density in grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.774	-	6.38
	1.383	-	12.04
LANL small scale gap test	1.601 pressed	-	5.6

(2) One method of obtaining HNAB is to treat picryl chloride, $(NO_2)_3.C_6H_2.Cl$, with hydrazine, $H_2N.NH_2$, to obtain hexanitrohydrazobenzene. The hexanitrohydrazobenzene is then oxidized by nitric acid or nitrogen oxide gas in a glacial acetic acid solution to HNAB. The nitrogen oxide gas is obtained from the reaction of nitric acid and As_2O_3. Another method of obtaining HNAB also involves two steps. The first step is to suspend a mixture of dinitrochlorobenzene, $(NO_2)_2.C_6H_3.Cl$, with hydrazine in hot water that contains sodium or calcium carbonate to form tetranitrohydrazobenzene, $(NO_2)_2.C_6H_3.NH.HN.C_6H_3(NO_2)_2$. The second step is to treat the tetranitrohydrazobenzene with concentrated nitric acid. The nitric acid introduces the two required NO_2 groups and also oxidizes the -NH.HN- group to an -N:N- group to form HNAB.

(3) HNAB is a very powerful and brisant high explosive. At a density of 1.77 grams per cubic centimeter, the detonation velocity is 7250 meters per second. Power, by the Trauzl test, is 123 percent of TNT. The DTA curve for HNAB is shown in figure 8-46.

d. *Hexanitrostilbene (HNS).*

(1) This explosive is also known as hexanitrodiphenylethylene or 1,2 bis-(2,4,6-trinitrophenyl)-ethylene or 1,1'-(1,2-ethenediyl) bis-(2,4,6-trinitrobenzene). The compound (figure 8-47) forms yellow needles when crystallized from nitrobenzene. HNS has a nitrogen content of 18.67 percent, a molecular weight of 450.24, and a melting point of 316°C. The theoretical maximum density of type I HNS is 1.740 grams per cubic centimeter with a nominal density of 1.72 grams per cubic centimeter. The crystals are orthorhombic with unit cell dimensions of a=22.13 Angstroms, b=5.57 Angstroms, c=14.67 Angstroms. At the melting point decomposition and explosions occur. The heat of formation is 13.9 to −18.7 kilocalories per mole, the heat of sublimation is 94.9 calories per gram, the heat of detonation with liquid water is 1.42 kilocalories per gram, and the heat of detonation with gaseous water is 1.36 kilocalories per gram. The specific heat is given by the equation:

$$C_p = 0.201 + (1.27 \times 10^{-3})T - (2.39 \times 10^{-6})T^2 \text{ for } 47°C < T < 220°C$$

where C_p is in calories per gram per degree centigrade.

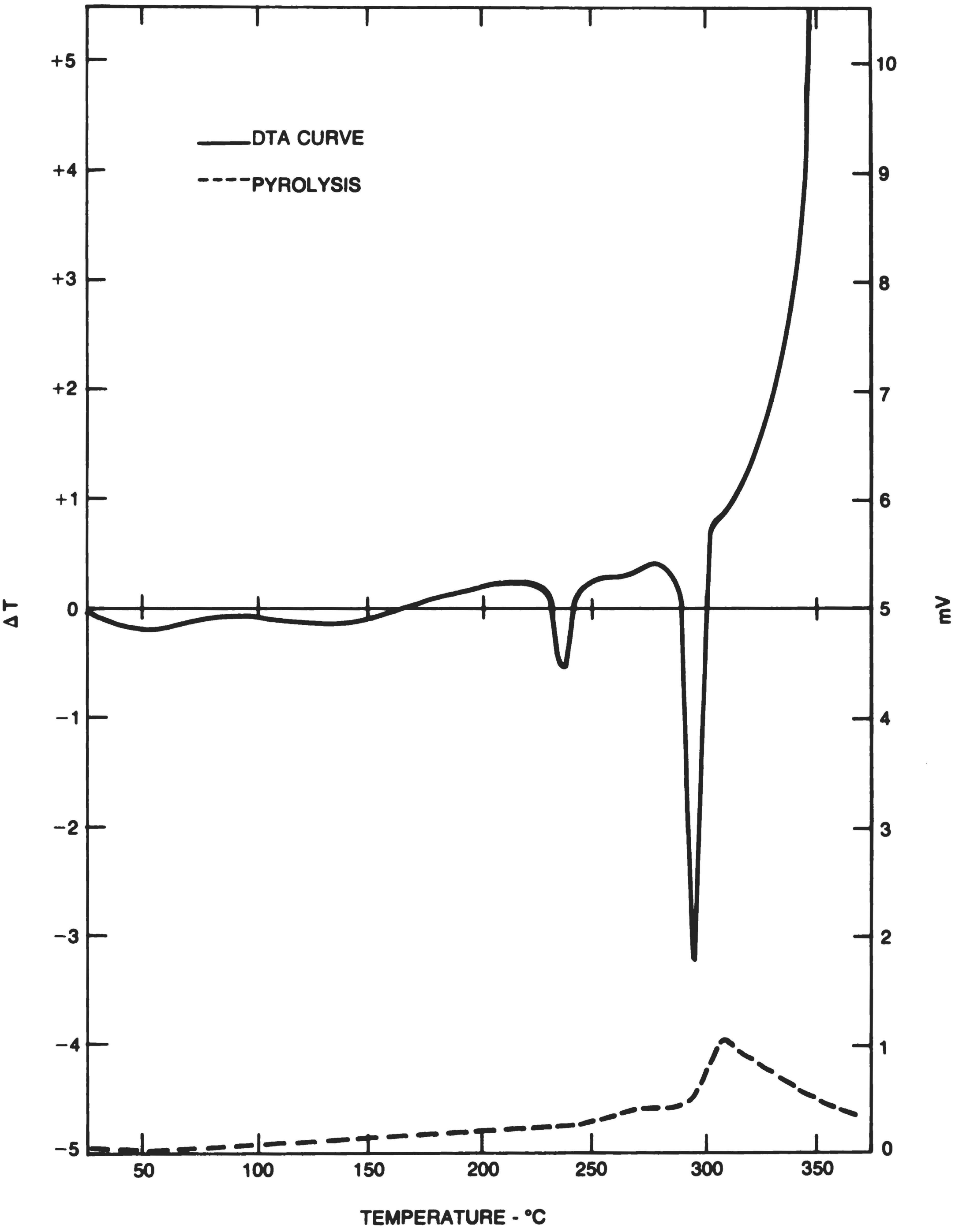


Figure 8-44. DTA curve for DATB.

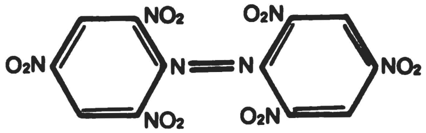


Figure 8-45. Structural formula for HNAB.

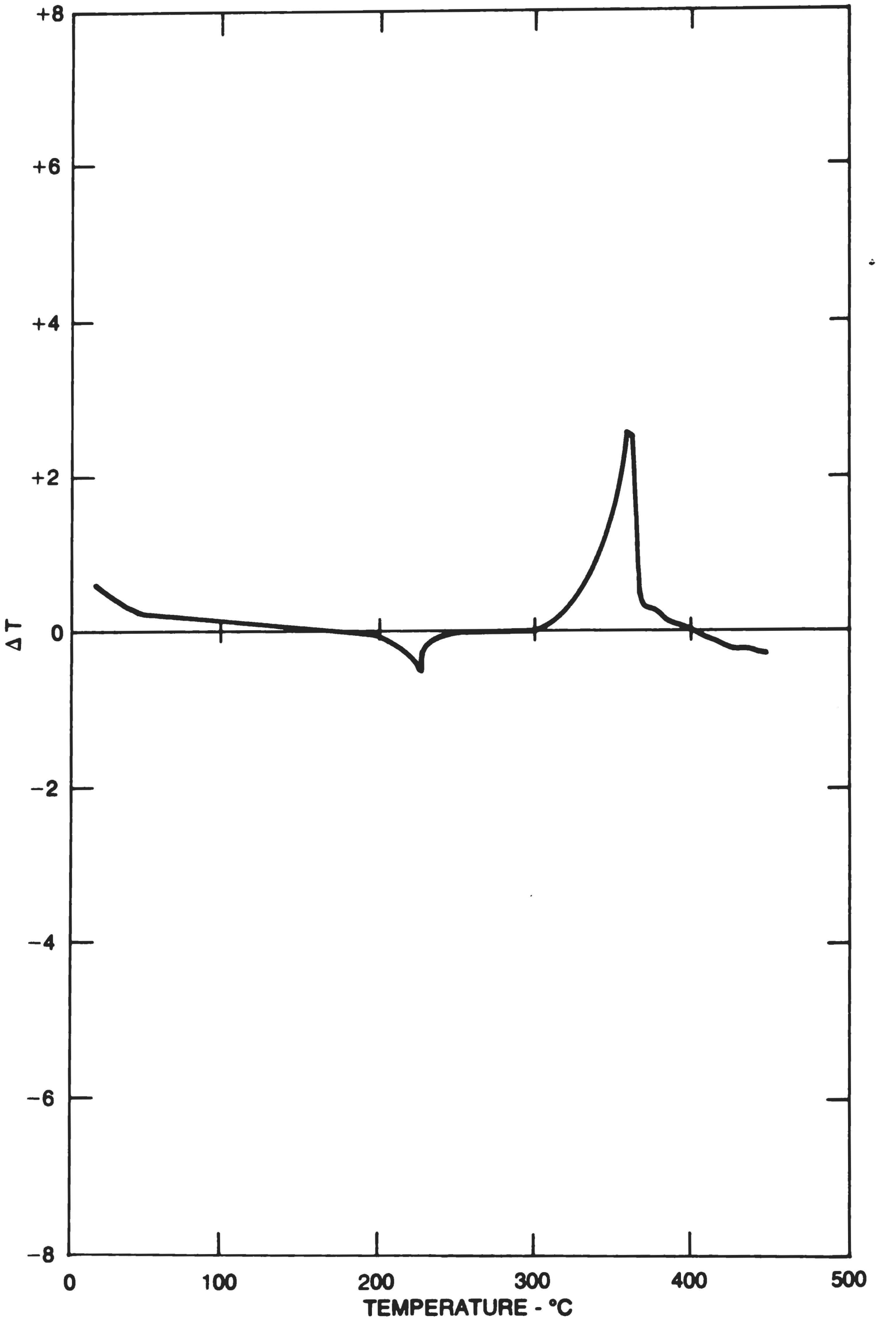


Figure 8-46. DTA curve for HNAB.

HNS is soluble in dimethyl formamide and slightly soluble in hot acetone, methylethyl ketone, and glacial acetic acid. HNS is used as a heat resistant booster explosive and has excellent properties for use in PBXs and mild detonating fuse end couplers and end boosters.

(2) HNS can be prepared from 2,4,6-trinitrobenzyl chloride by heating on a steam bath with methanol containing potassium hydroxide. HNS has a uniquely small critical diameter of about 0.5 millimeters (0.020 inch), is practically insensitive to electrostatic spark, is less sensitive to impact than tetryl, and is radiation resistant.

(3) Two types of HNS are manufactured, as shown in table 8-39.

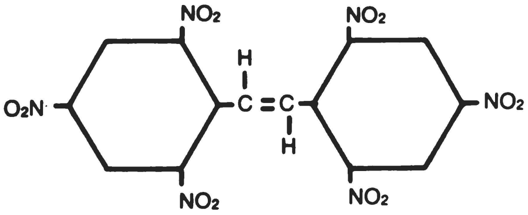


Figure 8-47. Structural formula for HNS.

Table 8-39. Properties of HNS

Property	Type I	Type II
Melting point, °C with decomposition	316	319
Particle size in microns	1-5	100-300
Bulk density in grams per cubic centimeter	0.32-0.45	0.45-1.0
Differential thermal analysis, onset of exotherm	315°C	325°C
Electrostatic spark sensitivity, fires above, in micro farads	0.001 at 8kv	0.0001 at 17kv
Friction sensitivity in kilograms per centimeter	440	440
Impact sensitivity in centimeters, Naval Ordnance Laboratory machine	44	61
Vacuum stability at 260°C in cubic centimeters per gram per hour:		
1st 20 minutes	1.8	0.3
Additional two hours	0.6	0.2
At 280°C	2.7	2.7
Velocity of detonation in meters per second at a density of 1.70 grams per cubic centimeter	7000	7000
Autoignition point	325°C	325°C
Decomposition rate at 260°C	0.1%/hour	0.1%/hour
Heat of combustion, calories per gram	3451	3451
Mean firing voltage for an explosive bridge wire with a one microfarad capacitor	12,950 at 0.9 grams per cubic centimeter	12,950 at 0.9 grams per cubic centimeter
Vapor pressure	2.9×10^{-8} torr at 160°C	2.9×10^{-8} torr 160°C

(4) HNS is half as sensitive to impact as TNT. Gap test results for HNS are shown in table 8-40.

Table 8-40. Gap Test Results for HNS

	Density in grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test			
HNS I	1.694	2.6	5.18
	1.122	35.5	7.06
HNS II	1.725	0.9	5.46
	1.644	-	7.52
	1.322	24	9.53
LANL small scale gap test			
HNS I	1.669	4.1	5.28
	1.566	10	5.84
	1.376	20.9	6.71
	1.840 (pressed)	2.1	2.31

(5) At a density of 1.70 grams per cubic centimeter, the velocity of detonation is 7,000 meters per second and the detonation pressure is 262 kilobars. The plate dent test indicates a power of 120 percent of TNT.

(6) In the 100°C heat test, HNS loses less than 1 percent weight in 48 hours. Less than one cubic centimeter of gas is evolved in the 100°C vacuum stability test. Figures 8-48 and 8-49 show the DTA and TGA curve for HNS, respectively.

e. *1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB).*

(1) This explosive is also known as 2,4,6-trinitro-1,3,5-benzenetriamine and may be referred to as TATNB. TATB (figure 8-50) has a nitrogen content of 32.56 percent, an oxygen balance to CO_2 of −55.78 percent, and a molecular weight of 258.18. TATB is yellow but exposure to sunlight or ultraviolet light causes a green coloration which, with prolonged exposure, turns brown. The compound has a theoretical maximum density of 1.937 grams per cubic centimeter and a nominal density of 1.88 grams per cubic centimeter. An instantaneous hot bar decomposition temperature of 450°C to 451°C was reported with rapid thermal decomposition above 320°C. The structure of the crystalline lattice of TATB (figure 8-51) contains many unusual features. Some of these are the extremely long C-C bonds in the benzene ring, the very short C-N bonds, amino bonds, and the six furcated hydrogen bonds. Evidence of a strong intermolecular interaction, hydrogen bonds, in TATB is indicated by the lack of an observable melting point and very low solubility. The intermolecular network results in a graphite-like lattice structure with the resulting properties of lubricity and intercalaction. Physical properties of the triclinic unit cell, which consists of two molecules, are a=9.010 Angstroms, b=9.028 Angstroms, c=6.812 Angstroms, and alpha=108.59°, beta=91.82°, and gamma=119.97°. Continuous monitoring of the cell constants of TATB between 214°K and 377°K allowed for the calculation of a volume change of +5.1 percent for this molecular system. Expansion of the pure material is almost exclusively a function of a 4 percent linear increase in the c axis, which is the perpendicular distance between sheets of hydrogen-bonded TATB molecules. The solubility of TATB is greater than 20 percent by weight per volume of solution in super acids such as concentrated sulfuric acid, chlorosulfonic acid, fluorosulfonic acid, and trifluoromethane sulfuric acid. Table 8-41 lists the solubility of TATB in various solvents.

Table 8-41. Solubility of TATB in Various Solvents

Solvent	Solubility, in parts per million
Methanesulfonic acid	820
Hexamethylphosphortriamide	150
Ethanesulfonic acid	120
DMSO	70
Hexafluoroacetone sesquihydrate	68
N-methyl-2-pyrrolidinone	58
N,N-dimethylacetamide	33
DMF	27
Tetramethylurea	26
Dimethyl methylphosphonate	22
N,N-dimethylpropionamide	16
Bis(dimethylamino)phosphochloridate	14
Gamma butyrolacetone	14
Concentrated nitric acid	14

Table 8-41. Solubility of TATB in Various Solvents (Cont)

Solvent	Solubility, in parts per million
3-Methylsulfolane	13
Pyridine	12
Trimethylphosphate	11
Dimethylcyanamide, vinyl sulfone	8
Methyl dichlorophosphate	7
N-methylformamide	6
Methyl methanesulfonate	5
Trimethylphosphite	4
Acetone	3
Dimethyl carbamoyl chloride	3
Acetonitrile	3
Acetic anhydride	3
Trifluoroacetic acid	3
Acetic acid	1
Hexamethyldisilazane	less than 1
Trifluoroacetic anhydride	less than 1
Hexafluorobenzene	less than 1
Pentafluoropyridine	less than 1
Perfluoro-2-butyltetrahydrofuran	less than 1
Basic solvents:	
Tetramethylguanidine	485
Bu_4NOH, 25% in methanol	390
N,N,N',N'-Tetramethylglycinamide	67

At 131.4°C and 171.3°C TATB has vapor pressures of 10^{-7} torr and 10^{-5} torr, respectively. At 344,750 and 441,280 kilopascals (50,000 and 64,000 pounds per square inch) the loading density of TATB is 1.80 and 1.89 grams per cubic centimeter, respectively. Thermochemical characteristics include a heat of combustion of 735.9 kilocalories per mole, a heat of detonation with gaseous water at 1.87 grams per cubic centimeter of 1018 calories per gram, a heat of detonation with liquid water of 2831 calories per gram, and a heat of formation of −33.46 to −36.85 kilocalories per mole. The heat of sublimation is 155.7 calories per gram and the heat of reaction during self-heating is 600 calories per gram. The heat capacity as a function of temperature is given by the equation:

$$\textit{Specific heat} = 0.215 + (1.324 \times 10^{-3})\,T - (2 \times 10^{-6})T^2 \quad \text{for } 0^\circ\text{C} < T < 300^\circ\text{C}$$

The effects of gamma radiation are shown in table 8-42.

Table 8-42. Effects of Gamma Radiation on TATB

Amount of cobalt 60 radiation R	Density before irradiation in grams per cubic centimeter	Density of kv irradiation in grams per cubic centimeter	Detonation velocity in meters per second	Detonation pressure in kilobars	Explosion temperature in °C
Control	1.84	-	7,510	260	403
1.0×10^7	1.84	1.84	7,520	260	394
9.0×10^7	1.85	1.84	7,525	261	370
7.4×10^8	1.82	1.81	7,435	250	345

TATB is suitable for use in plastic explosives and in explosives mixtures with TNT that can be cast. The major military use is in special applications in warheads of high speed guided missiles. In this application energy is sacrificed but handling safety is gained because the main charge remains inert under the service environments of high velocity impact and fire.

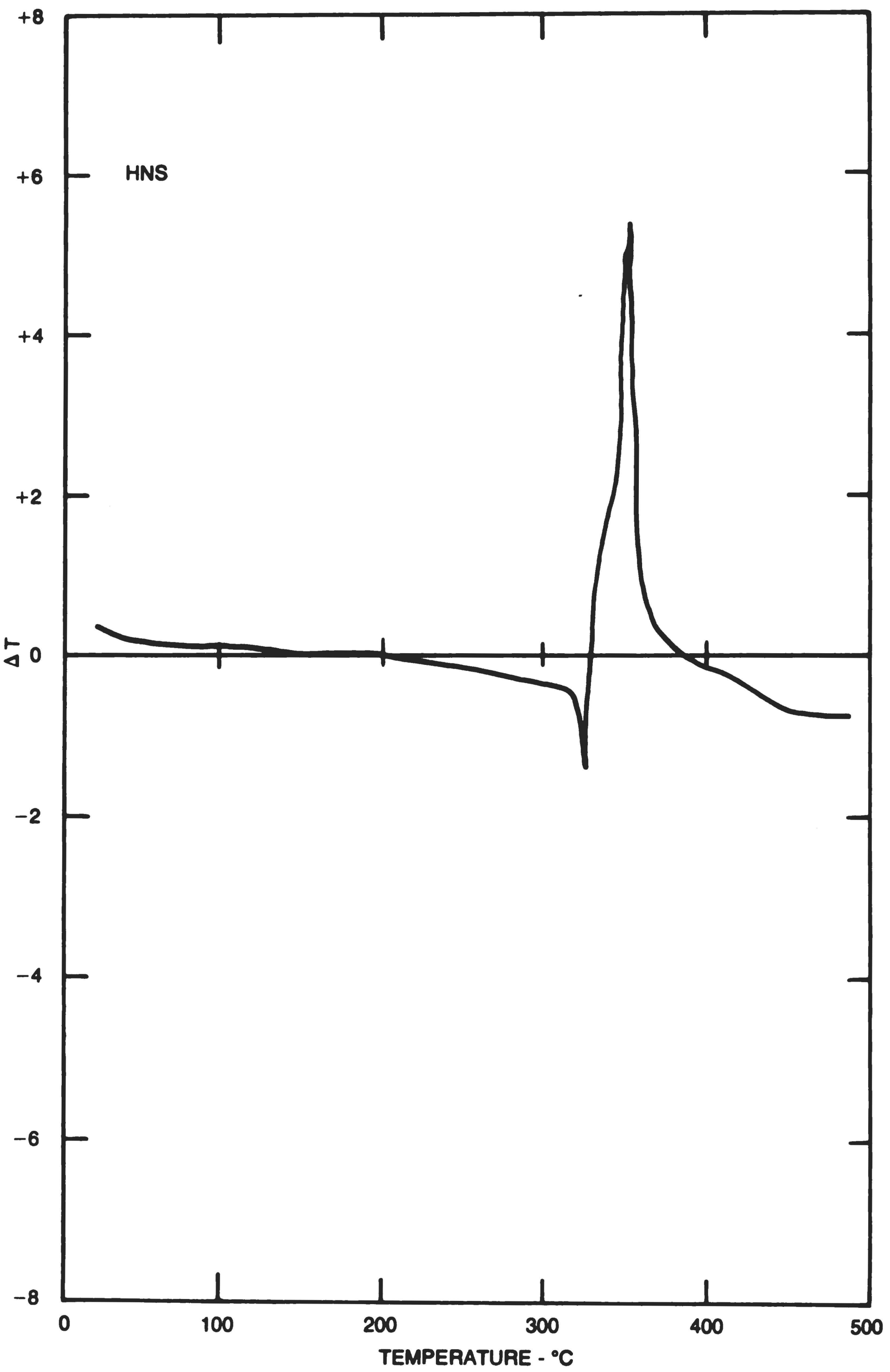


Figure 8-48. DTA curve for HNS.

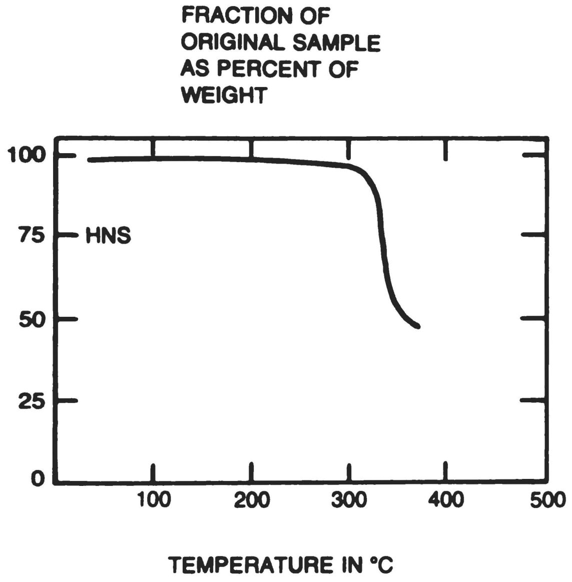


Figure 8-49. TGA curve for HNS.

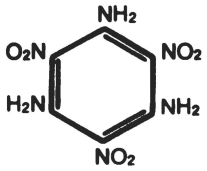


Figure 8-50. Structural formula for TATB.

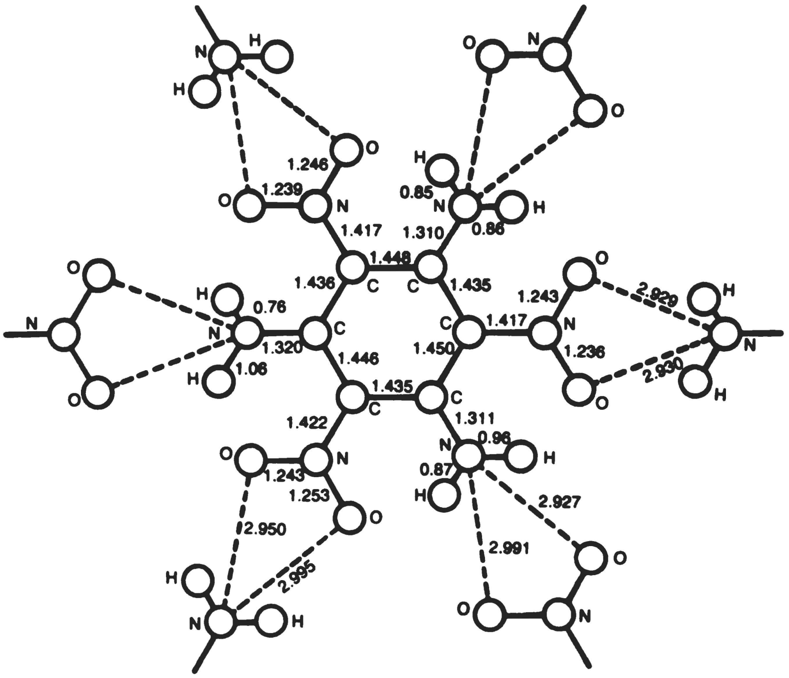


Figure 8-51. Configuration of the TATB molecule.

(2) The preferred method of preparation in the laboratory consists of the nitration of s-trichlorobenzene with a mixture of nitric acid and oleum at a temperature of 150°C for three hours. A toluene solution of the trinitrotrichlorobenzene (TCTNB) produced by the nitration is then aminated to yield TATB. The preferred manufacturing method to produce a particle size greater than 20 microns in 96 percent of the yield, suitable for PBXs and normal explosive compounds, is by the partially patented procedure that follows. The procedure is carried out in two steps; a nitration step and an amination.

(a) The equipment required is:

1 A 38 liter (10-gallon), glass-lined Pfaudler reactor capable of operation over a range of 20° to 150°C and pressure of 70 torr to 670 kilopascals (100 pounds per square inch), gauge, agitation provided by an anchor type blade at speeds of 20 to 200 revolutions per minute.

2 A glass-lined, concentric tube reflux condenser integral with the reactor.

3 A 189 liter (50-gallon), stainless steel reactor with agitator used in ice quenching of the nitration mixture.

4 Two 227 liter (60-gallon), stainless receivers used in filtrate storage and recovery.

5 A stainless steel, 28 centimeter × 28 centimeter × 5 centimeter plate and frame filter press, closed delivery washing type.

(b) The materials required for the nitration step are 2.5 kilograms of TCB with a melting point of 63°C to 64°C, 7.7 kilograms of $NaNO_3$ granular AR sodium nitrate, and 57.2 kilograms of 30 percent oleum. The oleum is charged to the glass-lined reactor, and the sodium nitrate is then added at a slow rate with full agitation. The reaction is quite exothermic, and jacket cooling is used to keep the temperature at 60° to 70°C. When the entire amount of sodium nitrate has been added and the exotherm peak has passed, the kettle contents are brought to a temperature of 100°C. The TCB is then charged to the reactor and steam is applied to the jacket to bring the temperature quickly to 145° to 155°C. The reactor contents are maintained at this temperature for a period of four hours. The small amounts of gas that are produced during the nitration are vented through the reflux condenser. At the end of the four hour reaction period, the contents are cooled to 40°C and discharged into the 50 gallon stainless steel reactor which contains approximately 113 kilograms of crushed ice. Full agitation is used during this quench step and the nitrous fumes are removed using a water sealed vacuum pump. The TCTNB product precipitates in the form of heavy, white crystals. With the stated quantity of ice, the temperature during dilution does not exceed 40°C, and hydrolysis of the product does not occur. The quenched reaction mixture is then pumped through the plate and frame press which discharges into a 60 gallon holding tank. Dynel cloth is used as the filtering medium. Only two frames are needed for the amount of cake produced. The cake is washed with several 20 gallon quantities of water, each followed with an air blow. This is continued until the wash water pH is 6 to 7. The cake is dried in open trays in a forced draft oven at 60°C for 16 hours. This completes the nitration step.

(c) The materials required for the amination step are 2724 grams of the TCTNB produced during the nitration step, 27.24 kilograms of technical grade toluene, 681 grams of water, 1044 grams of refrigeration grade anhydrous ammonia. The quantity of ammonia includes the amount for leakage and blow down. The TATB yield will be two kilograms. First, the TCTNB is dissolved in the toluene and the solution is clarified by filtration using Celite filter aid before transfer to the 10 gallon reactor. At this point 67 percent of the contaminating ammonium chloride by-product can be eliminated by adding 681 grams of water. The reactor system is then sealed and heating is continued until the contents are at 145°C. Since the amination step is moderately exothermic, the jacket steam is turned off at this time. Ammonia gas is then added to the reactor gas phase through an opening on the top of the kettle. The ammonia is metered through a rotameter at a rate of about 3632 grams per hour. When the ammonia overpressure reaches about 34.5 kilopascals (five pounds per square inch), the reactor system is purged of residual air by venting through the reflux condenser. The system is then resealed and the reaction is continued for approximately three hours. Moderate agitation is used during this period. During most of the three hour reaction period, conducted at 150°C, the pressure is maintained at 241.3 to 275.8 kilopascals (35 to 40 pounds per square inch, gauge). This represents an ammonia partial pressure of about 34.5 to 69 kilopascals (5 to 10 pounds per square inch). As the reaction progresses, a small amount of jacket heating may be necessary to maintain the 150°C temperature. The termination of the amination reaction is marked by a sharp rise in system pressure to about 413.7 kilopascals (60 pounds per square inch, gauge). After the pressure rise, the ammonia flow is shut off and the system is cooled to about 60°C. The system is then vented and approximately ten gallons of water is added to the reaction mixture with good agitation. The TATB product is recovered by filtration using the plate and frame press equipped with cotton cloths backed with filter paper. One frame is sufficient for the amount of product produced. The cake is washed three times with 20 gallon portions of water, interspersed with air blows. This is sufficient to remove by-product NH_4Cl. To dry the cake and remove volatile impurities, the cake is steamed for about ten minutes and air-blown before removal from the press. The cake is then dried in open trays in a forced draft oven at 100°C for 16 hours.

(d) The yield of this process is 89.0 percent of the theoretical with 4 percent of the particles below 20 microns in size. The crystal density of the product is 1.93 grams per cubic centimeter. If water was added during the amination process to remove the ammonium chloride contaminate the amount of chlorine impurities will be about 0.2 percent. If no water was added, the chlorine impurities will amount to about 0.6 percent. The process used for the manufacture of finely divided TATB suitable for use in booster pellets is slightly different. Using this process 82±.5 percent of the product will pass through a 20 micron sieve. In this process all the amination reactions are conducted in a 100 gallon stainless steel reactor heated with 517.125 kilopascals (75 pounds per square inch) steam to the jacket. The reactor is fitted with an ammonia inlet, a vent tube for azeotroping water from the system, and a thermowell. The TCTNB is first dissolved in toluene in a feed vessel and passed through a 1.5 micrometer in-line filter during transfer to the reactor. The solution is then heated to 140°C and the water azeotroped from the system. The ullage is then backfilled with ammonia and the temperature brought to 150°C. The reaction time varies between six and eight hours with completion indicated by a drop in ammonia flow as measured by the mass flow meter, an increase in system pressure approaching the 413.7 kilopascals (60 pounds per square inch, gauge) of the ammonia regulator and a decrease in the heat generated as indicated by the requirement of more steam to the reactor jacket. Product isolation involves cooling the reaction mixture to about 100°C, adding 40 liters of water, and vigorously stirring for half an hour. The warm mixture is isolated in a plate and frame press, washed with 85°C water for one hour, and steamed for one hour. The product is then dried for a minimum of 16 hours at a temperature of 115°C prior to sampling and packaging.

(3) TATB has an impact sensitivity of 11 inches by the Picatinny Arsenal apparatus for a seven milligram sample. By the ERL apparatus using a 2.5 kilogram weight with type 12 tools and without grit, the no detonation or reaction height is 200 centimeters. The point of 50 percent detonations is approximately 800 centimeters; the weight energy at this point is about 200 joules. The shock input to cause detonation has been determined to be 9500 joules per square meter. The five second explosion temperature test result is 520°C, and the auto ignition point is 320°C to 325°C. A charge of 0.30 grams of lead azide is required to initiate TATB. Table 8-43 lists the gap test results for TATB. Susan test results are shown in figure 8-52.

Table 8-43. Small Scale Gap Test Results for TATB

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.887	2.2	1.12
	1.519	21.3	4.12
LANL small scale gap test	1.872 (pressed)	3.4	0.13
LANL large scale gap test	1.786 (pressed)	2.8	41.68
	1.705 (pressed)	7.2	45.36
	0.81 (bulk)	56	49.3
PX gap test	1.883 (pressed)	-	approximately 5.3
	1.861 (pressed)	4.0	5.61
	1.700 (pressed)	12.3	14.10
	1.03 (bulk)	-	10.2 - 16.3

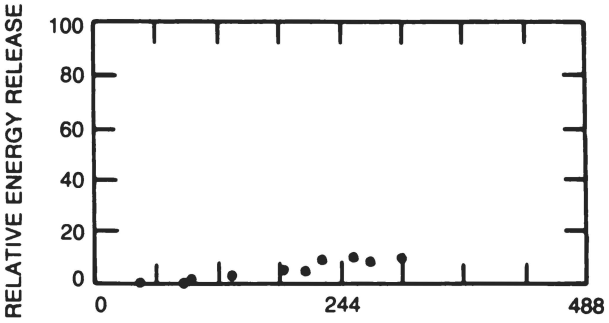


Figure 8-52. Susan test results for TATB.

(4) In the sand test, TATB crushes 42.9 grams of sand indicating a brisance of 90 percent of TNT. The detonation velocity as a function of density is given by the equation:

$$D=2.480+2.85p$$

where D is in kilometers per second and p, the density, is in grams per cubic centimeter. This equation yields slightly higher results than reported by other investigators. The detonation pressure for a sample with a density of 1.847 grams per cubic centimeter is 259 kilobars. Table 8-44 lists, as a function of density, the Chapman-Jouguet pressure, energy, and isentropic exponent from watershock measurements.

Table 8-44. Detonation Characteristics of TATB

Density in grams per cubic centimeter	Detonation velocity in meters per second	UH_2O in detonation meters per second	mH_2O meters per second	Pressure at explosive water interface in kilobars	Detonation pressure in kilobars	Isentropic exponent	**Detonation energy in calories per gram**
1.80	7,658	6,071	2,685	163.0	259.4	3.07	829
1.50	6,555	5,519	2,303	126.9	174.6	2.71	808

The Chapman-Jouguet pressure at crystal density is calculated to be 313 kilobars. Under oxygen deficient conditions the formation of detonation product gases proceeds according to the equation:

$$C_6H_6N_6O_6 \longrightarrow 3H_20(g)+3CO(g)+3N_2(g)+3C(s)$$

(5) TATB has excellent thermal stability. Differential Scanning Calorimeter measurements show exotherms at 330°C and 350°C when run at a heating rate of 10°C per minute. In the 100° heat test, approximately .17 cubic centimeters of gas are evolved in 48 hours. In the 200°C test for 48 hours 0.5 cubic centimeters of gas are evolved; at 220°C for 48 hours 2.3 cubic centimeters are evolved. At 260°C for one hour approximately 1.2 cubic centimeters of gas are evolved. At 280°C 2.0 cubic centimeters of gas are evolved. Figure 8-53 shows the DTA curve for TATB.

f. *2,4,6-Trinitrotoluene (TNT).*

(1) This explosive is also known as trotyl, tolit, triton, tritol, trilite, and 1-methyl-2,4,6-trinitrobenzene. TNT has been the most widely used military explosive from World War I to the present time. The advantages of TNT include low cost, safety in handling, fairly high explosive power, good chemical and thermal stability, favorable physical properties, compatibility with other explosives, a low melting point favorable for melt casting operations, and moderate toxicity. There are six possible ring nitrated TNT isomers. The alpha isomer, which is the one of military interest (figure 8-54) is symmetrical and will be referred to as TNT. The other five meta isomers will be identified by the Greek letters beta through eta excluding zeta. TNT is a yellow, crystalline compound with a nitrogen content of 18.5 percent, an oxygen balance to CO_2 of −73.9 percent, a molecular weight of 227.13, and a melting point of 80°C to 81°C. The freezing point, which is a more reproduceable quantity than the melting point, is used in the specification for the two military types of TNT that are procured. The freezing point is very sensitive to impurities. At atmospheric pressure, TNT boils at 345°C. Small amounts can be distilled rapidly at atmospheric pressure without an explosion, but explosions do occur with the longer heating periods required for larger quantities. TNT boils at 190°C, 210°C to 212°C, and 245°C to 250°C at 2 torr, 10 to 12 torr, and 50 torr, respectively. Unlike some other high explosives TNT does not undergo partial decomposition when melted. Samples of TNT have been melted and solidified at least 60 times with no significant decrease in the freezing point. The effect of moisture content on the freezing point is shown in table 8-45.

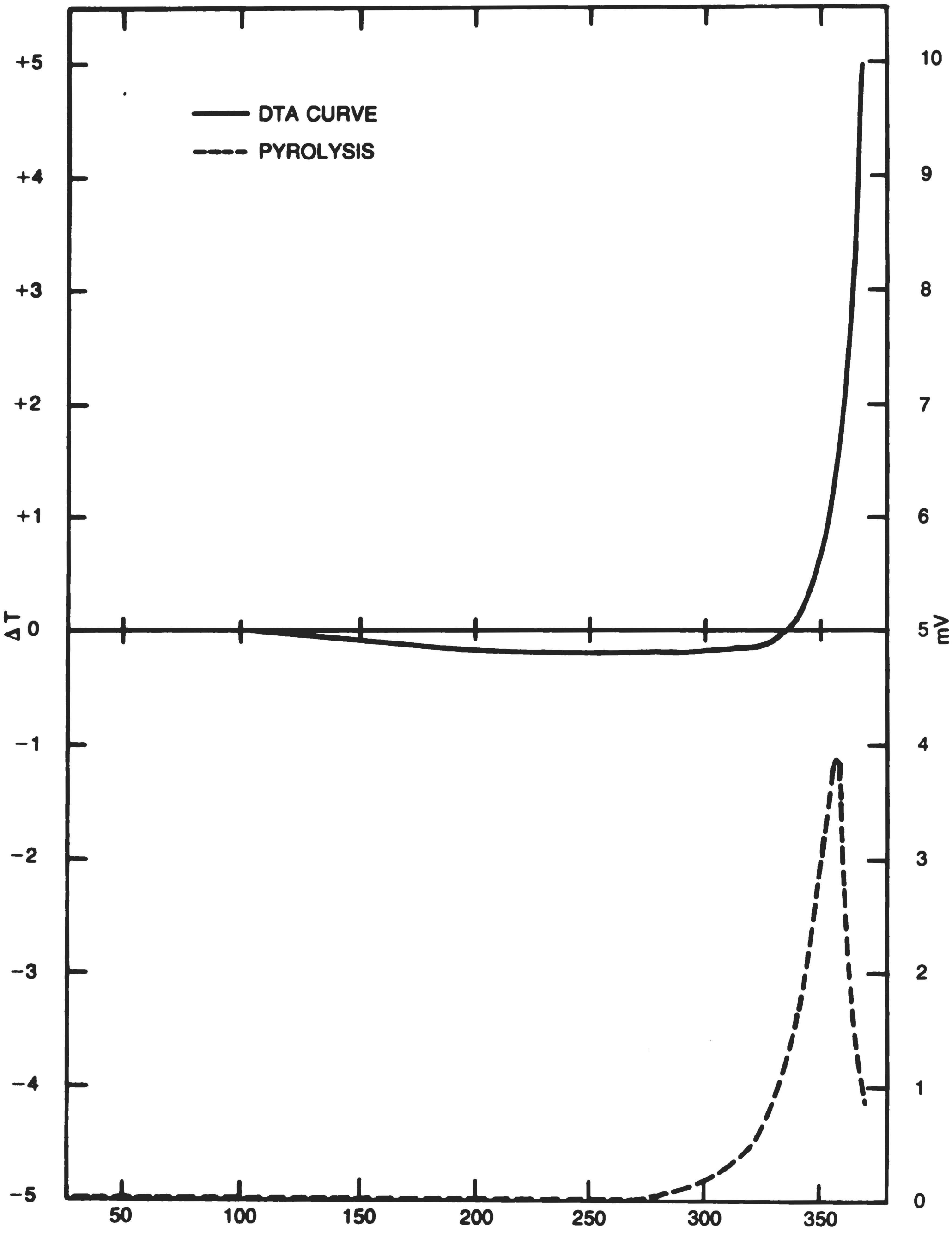


Figure 8-53. DTA curve for TATB.

Table 8-45. Effect of Moisture on the Freezing Point of TNT

Percentage of water	Freezing point in °C
0	80.59
0.1	80.35
0.2	80.20
0.3	79.99
0.5	79.78
1.0	79.09
2.5	77.93

Removal of moisture from a sample of TNT by heating at 100°C is slow as shown in table 8-46. The sample started with a water content of 0.3 percent.

Table 8-46. Removal of Moisture from TNT

Hours of heating at 100°C	Freezing point of sample in °C
0	79.99
2	80.30
3.5	80.46
5	80.55
6	80.59

At ordinary temperatures TNT is essentially nonvolatile. TNT has a crystal density of 1.654 grams per cubic centimeter, a cast density of 1.5 to 1.6 grams per cubic centimeter and a maximum pressed density of 1.63 to 1.64 grams per cubic centimeter. Table 8-47 shows the density of TNT as a function of loading pressure although densities as high as 1.64 grams per cubic centimeter have been reported.

Table 8-47. Density as a Function of Loading Pressure for TNT

Pressure in kilopascals	Pressure in pounds per square inch	Density in grams per cubic centimeter
20,685	3,000	1.34
34,475	5,000	1.40
68,950	10,000	1.47
82,740	12,000	1.49
103,425	15,000	1.52
137,900	20,000	1.55

The density of the liquid in the temperature range of 83°C to 120°C is given as a function of temperature by the equation:

$$D = 1.5446 - 1.016 \times 10^{3} t$$

where D, the density, is in grams per cubic centimeter and t is in degrees centigrade. Several crystalline structures of TNT are known. Samples of TNT obtained by sublimation onto a condensing surface held at a temperature, 78°C, very close to the melting point consist solely of the simple monoclinic form. Freezing the melts at a temperature very close to the melting point also yields a monoclinic form. Crystallization from solvents at room temperature or from strongly supercooled melts yield primarily monoclinic variant forms. Orthorhombic TNT is formed by crystallization from solvents at low temperatures. The unit cell dimensions of the monoclinic form are a=21.275 Angstroms, b=6.093 Angstroms, and c=15.025 Angstroms with eight molecules per unit cell. The unit cell dimensions of the orthorhomic form are a=15.007 Angstroms, b=20.029 Angstroms, and c=6.098 Angstroms. At least seven morphological types of TNT have been identified. Unusual crystal growth has been observed when TNT crystals are held near the melting point. Additives have a great effect on the crystallization process. Picryl chloride induces the formation of the orthorhombic form. Other picryl derivatives, especially 2,4,6-trinitrostilbene, drastically reduce the linear crystallization rate. Two compounds, hexanitrobibenzyl (HNBB) and methylpentanitrodiphenylmethane (MPDM), which are introduced during the purification phase of manufacture, have the same effect. These compounds have adverse effects on melt loading operations. During the melt loading operation cracks and voids tend to form in the cast material. The cracks are caused by an 11 percent shrinkage in the volume of the TNT upon solidification. The voids appear between the grains of the large orthorhombic crystals which are formed. A method to preclude the cracks and voids involves a procedure for overcoming the strong tendency of molten TNT to supercool with subsequent slow initial crystallization at the melt surface resulting from an insufficiency of crystal nuclei. Addition of solid seed TNT crystals to the melt while stirring yields a smooth casting with the desired very fine, randomly-oriented, monoclinic crystals. TNT prepared in this fashion undergoes irreversible crystal growth upon thermal cycling if the maximum temperature is above about 30°C to 35°C. For temperatures above 35°C a linear relationship exists between the growth with a corresponding decrease in density and the maximum temperature attained in the cycle. The growth correlates with the quantity of impurities present. However, the high viscosity of the mixture and the fine temperature control required, make this procedure impractical. Another procedure involves the addition of less than 2 percent HNS. The crystals formed are largely monoclinic and the casts are of sufficient quality. This method is a promising procedure, however TNT surveillance test samples containing 0.5 percent HNS submitted to thermal cycling showed increased exudation, irreversible crystal growth, decreasing density, and, eventually, complete crumbling.

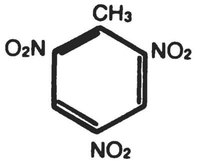


Figure 8-54. Structural formula for TNT.

(2) The viscosity of liquid TNT is 0.139 and 0.095 poise at 85°C and 100°C, respectively. The refractive index values are alpha=1.543, beta=1.674, and gamma=1.717. These values indicate a hardness of 1.4 on the Mohs scale. The observed molecular refraction is 49.6. The surface tension of liquid TNT as a function of temperature is shown in table 8-48.

Table 8-48. Surface Tension of Liquid TNT

Temperature in °C	Surface tension in dynes per centimeter
80	47.07
85	46.63
87.6	46.36
90	46.04
95	45.62

Cast TNT with a density of 1.62 grams per cubic centimeter has a compressive strength of 9,515 to 9,653 kilopascals (1,380 to 1,400 pounds per square inch). The dielectric constant, measured at 35 giga hertz, is shown in table 8-49 for crystal and flaked TNT.

Table 8-49. Dielectric Constant of TNT

Density in grams per cubic centimeter	Dielectric constant, crystals	Dielectric constant, ground flakes
0.9	2.048	2.092
1.2	2.347	2.362
1.5	2.795	2.773
1.7	3.178	3.125

The solubility of TNT in various solvents is shown in table 8-50. Over the range of 82°C to 95°C, molten TNT absorbs 3.22 milliliters of air per 100 grams of TNT. The approximate specific heat of TNT in calories per gram per degree centigrade is given by the equations:

$$0.254+(7.5\times10^{-4})\,T \qquad T<80.5^{\circ}\mathrm{C}$$

$$0.329+(5.5\times10^{-4})\,T \qquad T>80.5^{\circ}\mathrm{C}$$

Additional information concerning the specific heat, entropy, and enthalpy of TNT is available in table 8-51. Please note the difference in units from the above data.

Table 8-50. Solubility of TNT

	Solubility in grams per 100 grams of solvent at °C							
	0	20	25	30	40	50	60	75
Ethanol (95%)	0.65	1.23	1.48	1.80	-	4.61	-	19.5
Ether	1.73	3.29	3.80	4.56	-	-	-	-
Acetone	57	109	132	156	-	346	-	-
Carbon tetrachloride	0.20	0.65	0.82	1.01	-	3.23	-	24.35
Chloroform	6	19	25	32.5	-	150	-	-
Ethylene chloride		18.7	22	29	-	97	-	-
Benzene	13	67	88	113	-	284	-	-
Toluene	28	55	67	84	-	208	-	-
Carbon disulfide	0.14	0.48	0.63	0.85	-	-	-	-
Methyl acetate	-	72.1	80	99	-	260	-	-
Triacetin	-	-	37.7	-	-	-	-	-
Butyl carbitol acetate	-	24	-	-	-	-	-	-
Sulfuric acid	-	4	-	-	-	-	-	-
N,N-dimethylformaide	90	119 at 15°C	142	-	-	-	-	-
Dimethyl sulfoxide	-	-	128	-	-	-	-	-
1-Methyl-2-pyrrolidinone	-	-	118	-	-	-	-	-
Pyridine	-	137	-	-	-	-	-	-

Table 8-50. Solubility of TNT (Cont)

	Solubility in grams per 100 grams of solvent at °C							
	0	20	25	30	40	50	60	75
Chlorobenzene	-	33.9	-	-	-	-	-	-
1,2 Dichloroethane	-	18.7	-	-	-	-	-	-
Diethyl ether	-	3.29	-	-	-	-	-	-
Trichloroethylene	-	3.04	-	-	-	-	-	-
Methanol	-	-	-	-	9.5	-	31.6	-

Table 8-51. Specific Heat, Enthalpy, and Entropy of TNT

Temperature in °K	Specific heat in joules per mole per °K	Enthalpy in joules per mole	Entrophy in joules per mole per °K
10	3.116	10.390	1.732
30	32.71	352.77	17.49
50	60.41	1293.0	40.90
70	82.52	2731.0	64.89
90	101.70	4576.7	87.98
110	118.76	6784.8	110.08
130	133.54	9309.6	131.13
150	148.30	12128	151.28
170	162.84	15240	170.73
190	177.15	18640	189.63
210	191.24	22325	208.05
230	205.09	26288	226.07
250	218.72	30527	243.74
270	232.12	35036	261.08
300	251.80	42296	286.56

Values for the heat of combustion for the crystal range from 809.18 to 817.2 kilocalories per mole. The heat of formation for the liquid or crystal is between 10 and 19.99 kilocalories per mole. The free energy of formation for the crystal is 50.92±0.83. The heat of fusion computed by interpolation of enthalpy curve is 23.53 calories per gram although values from 20.2 to 25.2 have been reported. Values for the heat of sublimation range from 23.2 to 33.7 kilocalories per mole. The Gibbs free energy of sublimation is 69.6±3.0 kilojoules per mole and the standard entropy of sublimation is 146.2±1.3 joules per mole per degree Kelvin. The heat of vaporization is reported in the range of 17 to 22.7 kilocalories per mole. The maximum calculated heat of detonation with liquid water is 1.41 kilocalories per gram; with gaseous water the value is 1.29 kilocalories per gram. For a charge with a density of 1.54 grams per cubic centimeter, the measured values are 1.09 kilocalories per gram with liquid water and 1.02 kilocalories per gram with gaseous water. The enthalpy of TNT relative to the enthalpy at 0°C for the range 25°C to 68°C is expressed by the equation:

$$H-H_0=0.045+0.24625\,T+(4.205\times10^{-4})\,T^2$$

where T, the temperature, is in units of degrees centigrade. For the range 83°C to 117°C the relative enthalpy is expressed by the following equation:

$$H-H_0=12.450+0.45023\,T-(4.0091\times10^{-4})\,T^2$$

In this equation T is also in units of degrees centigrade. The standard enthalpy is 113.2±1.5 kilojoules per mole. The standard entropy for the crystal is 68.12±0.38 calories per degree Kelvin per mole. Thermal diffusivity as a function of temperature is shown in table 8-52.

Table 8-52. Thermal Diffusivity of TNT

Thermal diffusivity in centimeters squared per second × 10^4 at 25°C	Density in grams per cubic centimeter
19.7	0.64
15.0	0.783
12.1	0.980

TNT forms binary and ternary eutectics with various types of nitro compounds and nitrate esters. The dinitrotoluenes and the unsymmetrical TNT isomers form eutectics with 2,4,6-TNT which melt just above room temperature. Removal of these impurities is necessary to prevent exudation from TNT based explosives. TNT is used as a shell filler and as an ingredient in many composition explosives. Dinitrotoluene is also used in the filling of shells.

(3) The following sections of this subparagraph deal with the chemical reactivity of TNT. The sections are divided first by the structure of the TNT molecule involved in the reaction, such as the methyl group, the nitro group, and the aromatic ring. Then the reactions are further subdivided by the type of reaction.

(a) Reactions of the methyl group.

1 The methyl group can be halogenated. Monochlorination can be affected with sodium hypochlorite according to the following equation.

$$PiCH_3 \xrightarrow{NaOCl} PiCH_2Cl$$

(Pi=2,4,6-trinitrophenyl)

The chloride, prepared in situ, is important as the intermediate for preparing 2,2',4,4',6,6'-hexanitrostilbene according to the reaction:

$$2PiCH_2Cl \xrightarrow{Base} \underset{(HNS)}{PiCH{=}CHPi} + 2HCl$$

HNS is a thermally-stable explosive and a nucleant for improving the crystallization habit of TNT in explosive formulations such as composition B. In the presence of excess TNT, the chloride yields 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) which can be oxidized to HNS according to the equation:

$$PiCH_2Cl + PiCH_3 \xrightarrow{Base}$$

$$\underset{(HNBB)}{PiCH_2Cl + PiCH_3} \xrightarrow{Oxidation} HNS$$

Destructive chlorination to chlorpicrin (Cl_3CNO_2) has been noted on warming TNT with Ca hypochlorite. Small amounts of chloropicrin are formed during the preparation of HNS from TNT and sodium hypochlorite. On a production scale, an environmental problem is created since this compound is a toxic lachrymator. Heating TNT under pressure at 150°C to 160°C with phosphorus pentachloride and a trace of iodine is said to give a mixture of products including mainly 2,4,6-trinitrobenzotrichloride and pentachlorobenzyl chloride. Others, however, were unable to prepare the former compound in this way. TNT can be monobrominated with sodium hypobromite, or less conveniently by heating under pressure at 160°C with bromine and magnesium carbonate. Heating TNT with bromine and a trace of iodine under pressure at 200°C gives pentabromobenzyl bromide according to the equation:

$$PiCH_3 \xrightarrow[Trace\ I_2]{Br_2} C_6Br_5CH_2Br$$

2 The methyl group can be oxidized. The oxidation can proceed stepwise through the alcohol and aldehyde to the acid, as follows:

$$PiCH_3 \xrightarrow{O} PiCH_2OH \xrightarrow{O} PiCHO \xrightarrow{O} PiCOOH$$

Trinitrobenzoic acid can be prepared by this procedure. The alcohol and aldehyde are more easily oxidized than the TNT so the oxidization cannot be stopped at either of these stages. Other reactions must be used to prepare these products. Trinitrobenzoic acid is easily and quantitatively converted to 1,3,5-trinitrobenzene (TNB), an explosive superior to TNT in many ways, but more expensive to make. Oxidation of TNT is the preferred procedure for preparing TNB. This can be done in 85 percent yield by heating TNT with 90 percent nitric acid at 150°C under pressure for 18 hours, but the preferred laboratory procedure involves oxidation with potassium or sodium dichromate in concentrated sulfuric acid. Yields in this procedure vary from 43 to 46 percent to 86 to 90 percent, apparently depending on minor variations in technique. The addition of acetic acid as cosolvent is said to give a 98 percent yield of the acid. Oxidation of the methyl group occurs during TNT manufacture with 2 to 4 percent of yield loss occurring in this way. Under certain conditions the alcohol, as a nitrate, and the aldehyde are formed by the oxidation. The two compounds then react to form 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene as shown in figure 8-55. This compound, called white compound, coats the equipment piping and must be cleaned off. By a suitable variation in conditions, this reaction can be minimized, with the alcohol and aldehyde being oxidized preferentially to the acid. Crude TNT contains small amounts of all four of these compounds. About 10 percent of each trinitrobenzyl alcohol and trinitrobenzaldehyde are formed by side reactions during the preparation of HNS from TNT using sodium hypochloride. The two compounds also appear in small amounts during the action of heat or light on TNT. TNT can be oxidized to HNBB, in poor yield, by simply adding base to a solution of TNT in a suitable solvent according to the reaction:

$$2PiCH_3 \xrightarrow{O} \underset{(HNBB)}{PiCH_2CH_2Pi} + H_2O$$

The nitro groups in a portion of the TNT are the oxidizing agent. Small amounts of HNBB are formed by this reaction during the purification of TNT with alkaline sodium sulfite. Air oxidation in the presence of base and copper sulfate is claimed to give yields as high as 82 percent.

$$PiCH_2ONO_2 + PiCHO$$

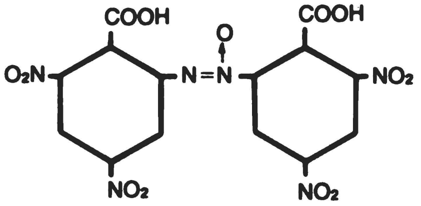


Figure 8-55. White compound.

3 The methyl group can react with aldehydes. Formaldehyde reacts with TNT as follows:

$$PiCH_3 + CH_2O \longrightarrow PiCH_2CH_2OH$$

The reaction can be carried out by heating TNT in a basic solution of aqueous formaldehyde. TNT is only poorly soluble in this solution, however. Better results are obtained when acetone is used as a cosolvent. TNT undergoes the Mannich reaction with formaldehyde and various secondary amines according to the equation:

$$PiCH_3CH_2O + R_2NH \longrightarrow PiCH_2CH_2NR_2$$

In this reaction dioxane was used as solvent and 2 percent sodium hydroxide was added as catalyst; piperazine forms a 1:2 derivative. Benzaldehyde reacts with TNT to form two compounds. The molar ratio between the reactants in one of the compounds is one to one. The reaction proceeds according to the equation:

$$PiCH_3 + C_6H_5CHO \longrightarrow PiCH{=}CHC_6H_5$$

The reaction is catalyzed by piperidine and is run in an aromatic solvent such as benzene or toluene. A series of monosubstituted benzaldehydes react similarly as do also terephthalaldehyde and isophthalaldehyde. One mole of both of the last two reactants combines with two moles of TNT. In the second compound benzaldehyde forms with TNT, one mole of benzaldehyde reacts with two moles of TNT. The reaction proceeds according to the equation:

$$2PiCH_3 + C_6H_5CHO \longrightarrow (PiCH_2)_2CHC_6H_5$$

This reaction is also catalyzed by piperidine but is run in pyridine. Only traces of HNS were obtained from TNT and 2,4,6-trinitrobenzaldehyde.

4 The methyl group reacts with halides and unsymmetrical TNT isomers. In the presence of equivalent potassium hydroxide, TNT reacts as follows with various halides such as 4-nitrobenzyl bromide, picryl chloride, or 2,4-dinitrofluorobenzene:

$$PiCH_3 + RX \xrightarrow{KOH} PiCH_2R + KX$$

Only compounds with highly reactive halogens yield products by this reaction. As the halide reactivity decreases, increasing amounts of HNBB are formed from TNT in the presence of a base. This type of reaction can also occur with compounds containing reactive nitro groups. In the manufacture of TNT, 2,4,6- and 2,4,5-TNT interact in this manner to form MPDM, as shown in figure 8-56. A similar compound can be made from 2,4,6-TNT and 2,3,4-TNT.

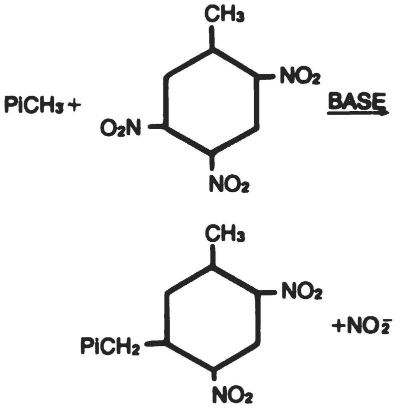


Figure 8-56. TNT and 2,4,5-TNT reaction.

5 The methyl group reacts with various nitroso compounds. The reaction with 4-nitrosodimethylaniline, reaction (A), and subsequent hydrolysis, reaction (B), to yield 2,4,6-trinitrobenzaldehyde, PiCHO, is shown below:

$$PiCH_3 + ONC_6H_4N(CH_3)_2 \xrightarrow{(A)}$$

$$PiCH{=}NC_6H_4N(CH_3)_2 \xrightarrow{(B)}$$

$$PiCHO + H_2NC_6H_4N(CH_3)_2$$

This is the favored procedure for preparing 2,4,6-trinitrobenzaldehyde. Reaction (A) is run at room temperature in pyridine, using iodine as a catalyst, or in a alcohol-acetone mixture with anhydrous sodium carbonate as a catalyst. Reaction (B) proceeds in a strong aqueous hydrochloric acid solution; overall yields are 39 to 52 percent. Reaction (A) can be run in an aqueous medium in the presence of light with a yield of 80 percent and less by-product formation than in the other methods. Other types of aromatic nitroso compounds, for example nitrosobenzene and nitrosotoluene, form nitrones according to the equation:

$$PiCH_3 + 2RNO \longrightarrow PiCH{=}\overset{O\uparrow}{N}R + X$$

where X depends on the specific reaction.

6 The methyl group can undergo nitration and nitrosodation. The reaction with alkaline fluorotrinitromethane proceeds according to the equation:

$$PiCH_3 + FC(NO_2)_3 \xrightarrow{Alk} PiCH_2NO_2$$

Several products are formed with nitrosylchloride, as shown in figure 8-57.

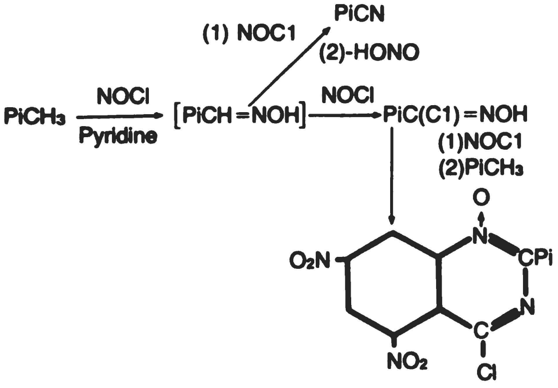


Figure 8-57. Reaction of TNT with nitrosylchloride.

7 Other miscellaneous reactions of the methyl group include the reaction with N,N-dimethylformamide and phosphorus oxychloride in which TNT undergoes the Vilsmeier reaction as shown below:

$$PiCH_3 \xrightarrow[(2)\ KOH]{(1)\ DMF\text{-}POCl_3} PiCH(CHO)_2$$

The resulting dialdehyde was converted to derivatives. The reaction between phthalic anhydride and TNT is reported to form a phthalide derivative as shown in figure 8-58. However the reaction could not be duplicated. When TNT couples with diazonium compounds, the most likely reaction is:

$$PiCH_3 + RN_2Cl \longrightarrow PiCH_2N{=}NR$$

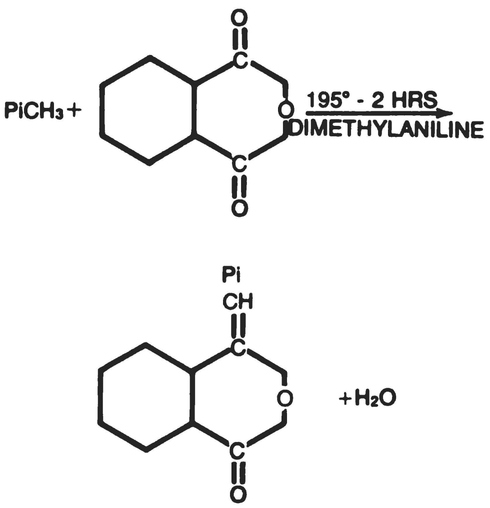


Figure 8-58. Reaction between TNT and phthalic anhydride.

(b) Reactions of the aromatic ring.

1 TNT can be monomethylated to trinitro-m-xylene in 9 to 32 percent yield by heating with lead tetracetate or acetyl peroxide, or by electrolysis with acetic acid-sodium acetate. Attempts to introduce more methyl groups have been unsuccessful.

2 Reduction of TNT with sodium borohydride gives 1-methyl-2,4,6-trinitrocyclohexane in 21 percent yield according to the reaction shown in figure 8-59.

3 One mole of TNT reacts with three moles of diazomethane. The compound obtained from diazomethane and 1,3,5-trinitrobenzene has the seven member ring shown in figure 8-60.

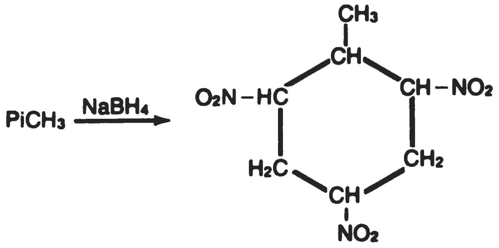


Figure 8-59. Reduction of TNT with sodium borohydride.

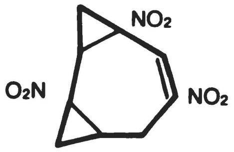


Figure 8-60. Seven member ring structure.

4 TNT undergoes methyl group halogenation as well as ring halogenation with loss of the nitro groups at 150°C to 200°C.

5 Ring cleavage to chloropicrin occurs with alkaline hypochlorites. TNT can also be destroyed by treatment with ozone, in the presence of base, or ultraviolet light. In both cases, the 2,4,6-trinitrobenzyl anion in generated, which is presumably the reactive species.

(c) Reactions of the nitro groups.

1 TNT can be reduced to the triamino compound with tin and hydrochloric acid, or with hydrogen using a Pd-$BaSO_4$ catalyst as shown in figure 8-61.

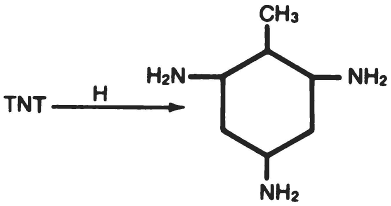


Figure 8-61. Reaction of TNT with hydrogen.

2 4-Amini-2,6-dinitrotoluene can be made by treating TNT in dioxane with ammonium sulfide. A 37 percent yield of material of 99 percent purity was so obtained.

3 Reduction of TNT with ethanolic ammonium sulfide yields 2,4-diamio-6-nitrotoluene. Reaction of TNT with ethyl alcoholic hydrogen sulfide containing a small quantity of ammonia gives a mixture comprising 22 percent unreacted TNT, 22 percent 4-amino-2,6-dinitrotoluene, 4 percent 2-amino-4,6-dinitrotoluene, 44 percent 4-hydroxylamino-2,6-dinitrotoluene, and 8 percent 2-hydroxylamino-4,6-dinitrotoluene. The 4-hydroxylamino compound can be extracted from the reaction mixture. The 4-amino-2,6-dinitrotoluene is an intermediate for one procedure for preparing the thermally-stable, insensitive explosive TATB. The reaction is shown in figure 8-62. Reaction (A) involves an unusual demethylation as well as nitration. The above partial reduction products of TNT, among others, are formed during biodegradation and during the destruction of TNT by reaction with sodium or ammonium sulfide. TNT does not undergo hydrolysis during storage of a saturated solution in sea water over a period of several months at 25°C in active glassware.

(d) Some reactions involve both the nitro and methyl group. An important aspect of TNT reactivity involves redox reactions between the reactive methyl group and the nitro groups, a type of reaction which can be initiated by various energetic stimuli including thermal and photochemical as well as chemical. The following discussion indicates the reactions are both intra- and intermolecular, ultimately leading to diverse monomeric and polymeric products. The intramolecular type involves reaction between the methyl group and an ortho nitro group. This reaction occurs especially easily and is often the first step for other reactions. The reaction also applies to many other derivatives and analogues of 2-nitrotoluene.

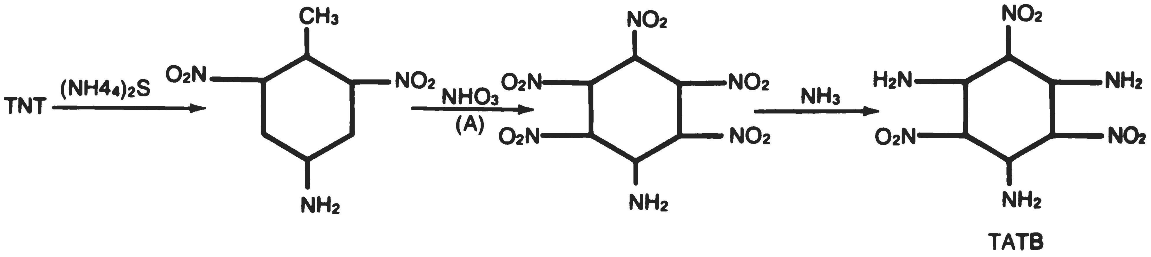


Figure 8-62. Production of TATB from TNT.

1 All types of nitro compounds react easily with bases forming diverse types of products. In the case of TNT, 2,4,6-trinitrobenzyl anion (I) is formed initially and rapidly as shown in figure 8-63. The ion is a highly reactive species thought to be intermediate in the many reactions of TNT conducted under basic conditions. The anion is formed without side reactions by the action of 1,1',3,3'-tetramethylguanidine in dimethylformamide solvent. Based on spectrophotometric evidence, the first dissociation constant of TNT with NaOH is $1.02 \pm 0.2 \times 10^{-12}$. Highly-colored Jackson-Meisenheimer, or sigma, complexes of structure (II) or (III), also shown in figure 8-63, are formed by addition to the ring system. These compounds are formed in both aqueous and anhydrous mediums and with a variety of organic and inorganic nucleophiles. Sulfite ion forms a complex of structure (III) which is a source of yield loss during the purification of TNT if the pH exceeds eight. Cyanide ion also forms a complex of structure (III). TNT as the anion (I) can react with other TNT anion (I)'s and produce adducts of structure (II). A similar reaction takes place with 1,3,5-trinitrobenzene. Primary and secondary aliphatic amines also form sigma complexes. Upon solution in liquid ammonia, a complex of type (III) is initially formed with no evidence of type (I) having been formed. With time, a second NH_2 group becomes attached to the ring carbon with the methyl group; this compound has cis- and trans-isomers. Removal of the ammonia gives a red residue comprising about 50 percent TNT. Acetone carbanion forms a complex of structure (III). Methoxide, ethoxide, and isopropoxide form complexes of structure (II). T-butoxide ion yields structure (I) with TNT.

2 In some cases each mole of TNT can add up to three moles of a base. The compounds formed with potassium hydroxide in a dilute aqueous solution are shown in figure 8-64. The one to one molar ratio compound is the same type compound as structure (II) shown in figure 8-64. Three moles of potassium ethoxide can also react. Addition of two moles of sodium sulfite is also possible.

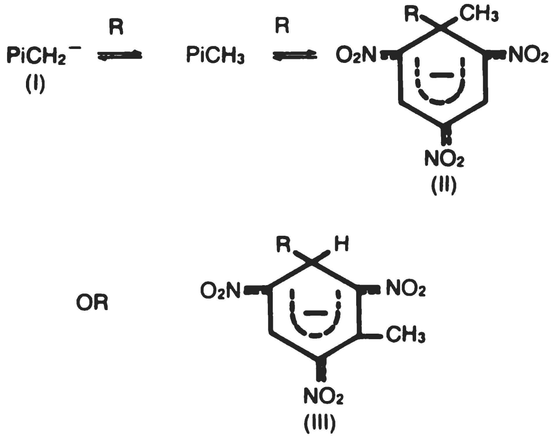
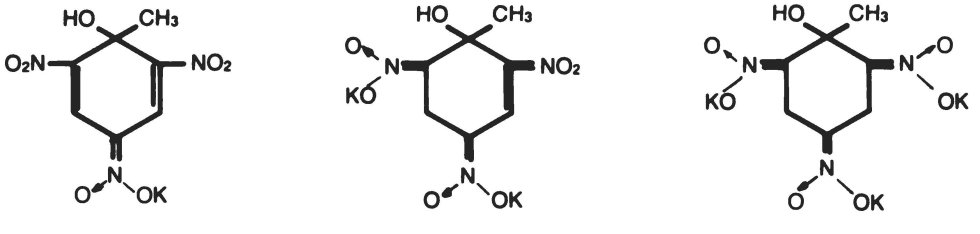


Figure 8-63. Reaction of TNT with bases.



1:1 MOLAR RATIO

1:2 MOLAR RATIO

1:3 MOLAR RATIO

Figure 8-64. Reaction of TNT with potassium hydroxide.

3 Side reactions can occur, especially in the presence of excess base at elevated temperatures and prolonged times of reaction. Potassium hydroxide and anhydrous ammonia can form nitrite ions by cleavage of nitro groups. 2,4,5-Trinitrophenol and 3,5-dinitrophenol have been isolated from the reaction of TNT with NaOH. Redox reactions give polymeric materials via the formation of azo and azoxy groups, as shown in figure 8-65 for the case of phenylhydrazine. Dimerization also occurs by the redox coupling of two molecules of TNT to form $PiCH_2CH_2Pi$. The oxidant in this case is TNT. The complexes of long-chain, primary-secondary aliphatic amines with TNT have low water solubility and may be useful for the removal of TNT from aqueous solutions. The rapid reactions with isopropylamine in acetone has been studied as a possible procedure for the neutralization of TNT in land mines.

(e) The degradation of TNT by electron impact has been studied. The initial step is a methyl-hydrogen transfer to an adjacent nitro-oxygen which is followed by cleavage of the hydroxyl group. The resulting ion then degrades further by several routes which include the loss of small stable molecules such as CO, NO, HC=CH, HCN, etc. All of the TNT isomers undergo similar methyl-hydrogen transfer as the first step except for the 3,4,5-isomer, which lacks the adjacent methyl and nitro groups.

(f) In the manufacturing process, absorption by activated carbon filters is commonly employed to control pollution. The TNT is absorbed at many of the numerous high-energy sites on the surface of the carbon. Basic materials, introduced during activation of the carbon by combustion and oxidation are also present at these sites, then induce oxidation-reduction reactions of the methyl with the nitro groups in the TNT. This is manifested in the simplest form by the formation of small amounts of trinitrobenzoic acid and trinitrobenzene. Coupling and polymerization also occur, via generation of azo and azoxy linkages among others, yielding complex, high molecular-weight materials which are irreversibly bound to the surface and clog the pores of the carbon. This process is, therefore, generally similar to that involved in the thermal and basic decomposition of TNT. When TNT and activated carbon are dry-mixed at room temperature, the TNT rapidly and completely displaces the air absorbed on the carbon. The carbon has a strong catalytic effect on the thermal decomposition of TNT. At 120°C, a 90/10 TNT/carbon mixture decomposes 12.3 times as fast as pure TNT, and a 50/50 mixture 113 times as fast.

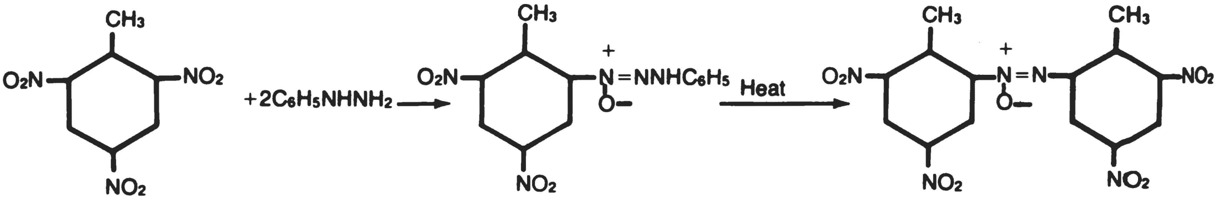


Figure 8-65. Reaction of TNT with phenylhydrazine.

(4) Of the six possible TNT isomers, five are unsymmetrical or meta isomers. Physical properties of the six are summarized in table 8-53.

Table 8-53. Isomers of TNT

Isomer	Melting point in °C	Position of reactive nitro group	Deflagration temperature in °C	
			Pure	With Na_2CO_3
2,4,6 (alpha)	80.9	This is the symmetrical isomer so has none	281-300	
2,3,4 (beta)	110-111	3	301-303	208-215
2,4,5 (gamma)	104-104.5	5	288-293 290-310	191-198
3,4,5 (delta)	133-134	4	305-318	252
2,3,5 (epsilon)	96-97	2	333-337	268-271
2,3,6 (eta)	111.5-112.5	3	327-335	249-250

The unsymmetrical isomers all differ from the 2,4,6-isomer in having notably higher melting points and in having one nitro group which is easily replaced by treatment with various nucleophilic reagents; the position of this group is indicated in table 8-53. Consequently, the reactions of 2,4,6-TNT under basic conditions are entirely different from those of the other five isomers. All of the unsymmetrical isomers have been found in crude TNT, ranging from about 2.5 percent for the 2,4,5-isomer and 1.5 percent for the 2,3,4-isomer down to 0.006 percent for the 3,4,5-isomer. The meta isomers form low melting point eutectics with TNT and so must be removed during the manufacturing process.

(5) TNT is manufactured by the nitration of toluene in successive steps. In the first step toluene is nitrated to mononitrotoluene (MNT). The MNT is then nitrated to dinitrotoluene (DNT). The last step is the nitration of DNT to TNT. The three steps are carried out under different conditions. The trinitration is carried out at a higher temperature than the dinitration, which is carried out at a higher temperature than the mononitration. The trinitration also requires a stronger mixed acid than the dinitration, which requires a stonger mixed acid than the mononitration. In the continuous production system installed at Radford Army Ammunition Plant these requirements are met with a counter flow process. The system consists of eight nitrators. Toluene is introduced into nitrator number one and moves successively through each nitrator to nitrator number eight where nitration to TNT is completed. Mixed acid is introduced into nitrator number eight and moves successively through each nitrator to nitrator number one. The mixed acid consists of nitric acid, 40 percent oleum, and water. Fortification with nitric acid is required between nitrators. The temperature of nitrator number one is maintained at 50°C to 55°C. Each successive nitrator is maintained at a higher temperature than the one immediately proceeding. Nitrator number eight is maintained at about 100°C. Each nitrator is equipped with an agitator. The solubility of toluene and the nitrotoluenes in mixed acid is very low. Therefore, the nitration proceeds in a two phase system and the rate of nitration depends on dispersion. The dispersion depends on keeping the two phases well stirred. Figure 8-66 shows the yield of mononitrotoluene as a function of the rate of stirring with a mixed acid consisting of 11 percent nitric acid, 64 percent sulfuric acid, and 25 percent water for a nitration time of 30 minutes. The results with the use of 40 percent oleum, which consists of 40 percent sulfur trioxide by weight dissolved in sulfuric acid, are analogus. However oleum is more reactive than sulfuric acid. The mononitration is carried out in the first nitrator where the temperature is lowest and the mixed acid has the highest water content. The low temperature reduces the amount of meta and of ring oxidation products formed. Mononitration at –110°C followed by dinitration at 0°C to 25°C yields a product with one tenth the amount of these impurities as when nitration is carried out under normal conditions. This process, however, is much more costly than the one carried out at higher temperatures so is not used. Less degradation occurs because of the higher water content of the mixed acid.

Toluene is much easier to nitrate than benzene because of the presence of a methyl group compared with benzene. The reaction of introducing the first nitro group therefore proceeds very quickly, however the methyl group is readily oxidized. Mononitration also leads to oxidation of the ring and the formation of cresols. If the mixed acid is poor in nitric acid or if an insufficient amount of mixed acid is used, tar formation may take place. To counteract these undesirable effects an excess of mixed acid that is rich in nitric acid could be used. On the other hand, both excess HNO_3 and excess mixed acid favor oxidation processes. Thus a trade-off must be achieved. Other oxidation reactions proceed especially readily under drastic conditions which introduce several nitro groups at a high temperature. This effect is minimized by having multiple nitrators with small temperature differentials between them. A concentration gradient for DNT and TNT exists across the production line. Table 8-54 shows the change in concentration of the nitro body, nitrated material in a six nitrator system. Six nitrators were used in the three Radford production lines before an explosion destroyed one of the lines. The explosion occurred during faulty manual removal of white compound which had coated the nitrator cooling coils. To stop the formation of white compound, an oxidation product, the number of nitrators was increased from six to eight. Each nitrator was also fitted with a centrifugal separator rather than a gravity separator, as the six original nitrators had. This reduced the amount of nitrobody in the system at any given time. Another design of continuous process in current use is the British ROF Process. This procedure also involves multistage countercurrent contacting, with the mono- to-trinitration unit comprising a rectangular box-shaped vessel subdivided into eight stirred nitrator stages with intervening unstirred nitrobody-acid transfer sections. Mononitration is conducted separately in a smaller, similar vessel. This design desirably eliminates all interstage pipework and ductwork connections. This equipment applies to the use of 96 percent sulfuric acid, which requires more staging to affect complete nitration than in the case of the Radford plant, which employs 40 percent oleum. A comparison of the two systems shows that both give an 85 percent yield based on toluene, and that both have the same nitric acid requirement. Radford usage of sulfuric acid is about 79 percent that of the ROF process, calculating both on the basis of a strength of 96 percent. The ROF system employs a lower temperature for mononitration, 35°C to 42°C vs 50°C to 56°C for the Radford process. In West Germany, mononitration is affected by a continuous process, but di- and trinitration are conducted batchwise, because of a high purity requirement. Trinitration is affected with mixed acid comprising 24 percent HNO_3, 70 percent H_2SO_4, and 6 percent SO_3. The reaction requires six hours with slowly rising temperatures. These conditions remove the dinitrotoluene isomers more completely than is possible with the much shorter reaction time used in continuous operation.

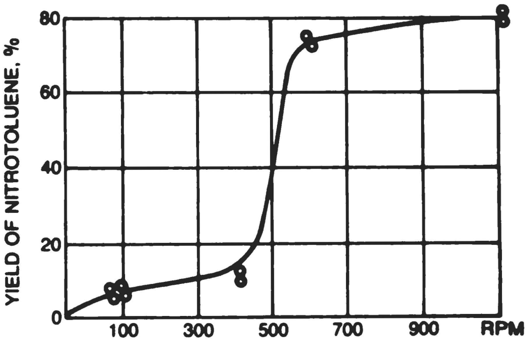


Figure 8-66. Agitation versus MNT yield.

(6) A problem associated with TNT production is the disposal of tetranitromethane (TNM), a toxic, odorous, and explosive material which is obtained in the exit gas from the trinitration step to the extent of about 136 grams to 227 grams per 45.4 grams of TNT. Venting TNM to the atmosphere is now illegal. The TNM can be recovered by scrubbing the gas with aqueous sodium carbonate containing stabilized hydrogen peroxide, which converts the TNM to nitroform. Nitroform is a raw material for making energetic plasticizers. Another objectionable effluent from TNT production is oxides of nitrogen (NOx). These can be removed (>95 percent) by oxidation to nitric acid, followed by scrubbing with sulfuric acid.

Table 8-54. Nitrobody Concentration for a Six Nitrator System

Nitrator Temperature (°C)	1 50-55	2 70	3 80-85	4 90	5 95	6 100
Composition of nitrobody:						
MNT(%)	71.1%	-	-	-	-	-
DNT(%)	18.2	70.9	30.4	10.3	1.6	0.2
TNT(%)	4.2	28.9	69.3	89.5	98.2	99.7

(7) After nitration, the crude TNT requires purification. The ultimate objective of TNT purification is to remove all those products produced during nitration which are more reactive than TNT or which can easily give oily exudation products. Oil exudation from TNT is an undesirable characteristic for the following reasons:

(a) Exudation produces porosity of the TNT charge and the corresponding reduction in density. This reduces the explosive effect. In artillery shells this can produce a dislocation of the charge on firing, compression of the air included in the cavities, and premature explosion.

(b) The oily products can penetrate into the threaded parts of the shell and form "fire channels" through which the ignition of propellent can ignite the charge.

(c) The oily products can penetrate into the detonating fuze if the explosive of the fuze is not protected by a metal envelope, and reduce the detonating power of the fuze.

(8) Table 8-55 lists the impurities that are formed during the manufacture of TNT and the amounts contained in the product after purification. The concentrations listed in the table are maximum values; the actual values are lower.

Table 8-55. Impurities Present in TNT

Compound	Approximate maximum nominal concentration (%) Crude	Finished
2,4,5-Trinitrotoluene	2.50	0.30
2,3,4-Trinitrotoluene	1.75	0.20
2,3,6-Trinitrotoluene	0.50	0.05
2,3,5-Trinitrotoluene	0.05	0.05
3,4,5-Trinitrotoluene	0.006	-
2,6-Dinitrotoluene	0.25	0.25
2,4-Dinitrotoluene	0.50	0.50
2,3-Dinitrotoluene	0.05	0.05
2,5-Dinitrotoluene	0.10	0.10
3,4-Dinitrotoluene	0.10	0.10
3,5-Dinitrotoluene	0.01	0.01
1,3-Dinitrobenzene	0.02	0.02
1,3,5-Trinitrobenzene	0.15	0.10
2,4,6-Trinitrobenzyl alcohol	0.25	0.25
2,4,6-Trinitrobenzaldehyde	0.25	0.25
2,4,6-Trinitrobenzoic acid	0.50	0.50
Alpha-nitrato-2,4,6-trinitrotoluene	0.10	0.10
Tetranitromethane	0.10	none
2,2'-Dicarboxy-3,3',5,5'-tetranitroazoxybenzene (white compound)	0.35	0.05
2,2',4,4',6,6'-Hexanitrobibenzyl (HNBB)	none	0.40
3-Methyl-2',4,4',6,6'-pentanitrodiphenylmethane (MPDM)	none	0.40
3,3',5,5'-Tetranitroazoxybenzene	none	0.01

Of the TNT isomers formed, only the first two listed in the table, the 2,4,5- and 2,3,4-isomers, are present in significant quantities. The dinitrotoluenes result from incomplete nitration. The next eight compounds listed in the table result, directly or indirectly, from oxidation of the methyl group during nitration, while the last three are introduced during purification. The purification process currently in use involves treating TNT with aqueous sodium sulfite called sellite. The meta TNT isomers react with the sodium sulfite to form water-soluble sulfonates by the following reaction:

$$CH_3C_6H_2(NO_2)_3 + Na_2SO_3 \longrightarrow CH_3C_6H_2(NO_2)_2SO_3Na + NaNO_2$$

Current American practice entails continuous treatment of molten TNT, at a temperature greater than 80°C, with an aqueous solution containing about 0.1 part anhydrous sodium sulfite per part TNT. This corresponds to about four times the theoretical requirement according to the equation given above. The liquids are countercurrently contacted in three washers each of which is followed by a centrifugal separator. This purification process is quite sensitive to pH. Yield loss rises sharply above pH 7.5 because of the formation of the water-soluble complex of 2,4,6-TNT with sodium sulfite. In addition, at pH values above about 8 the formation of the two by-products hexanitrobibenzyl (HNBB) and methylpentanitrodiphenylmethane (MPDM) increases strongly. These compounds have an adverse effect on the mode of crystallization of TNT. Table 8-55 shows that meta TNT isomers are not completely removed and that the amounts of all of the DNT isomers and of five of the oxidation products remain unchanged. The ROF TNT Process also employs continuous purification, using a compartmented reactor generally similar to that used by them for nitration. However, the TNT is contacted as a solid at 67.5°C, rather than as a liquid, as in the American process. This is said to result in a higher yield of purer TNT with a requirement of about two-thirds as much sodium sulfite. HNBB and MPDM are not formed. Advantage is taken of the fact that the unsymmetrical isomers form a eutectic which migrates to the crystal surface. This type of process is also employed in West Germany. The process is operated batchwise using 4 to 10 parts Na_2SO_3 per 100 parts TNT with a reaction time of 30 minutes. Use of this purification procedure, taken with a batch trinitration method which removes nearly all of the DNT isomers, yields a TNT of unusually high purity. The solidification point of the product is 80.65°C to 80.80°C. This type of process has also been used in the past in the United States. Disposal of the waste sellite solution, known as red water, is a serious pollution control problem. TNT can be purified by recrystallization from nitric acid. This process has been used for many years in Sweden. The nitric acid, after crystallization and filtration of the 2,4,6-isomer, is recovered by distillation leaving a mixture consisting of about 50 percent 2,4,6-TNT, 25 percent TNT meta isomers, and 25 percent dinitrotoluenes and oxidation products known as isotrioil. The isotrioil is then sold as an ingredient in commercial dynamite. Sweden has had trouble marketing isotrioil, which is the major reason this otherwise attractive process has not been adopted elsewhere. Even after purification, military grade TNT typically shows 0.6 percent to 1.2 percent or more extrudate. A typical analysis of exudate from specification-grade TNT made in 1973 at the Radford Army Ammunition Plant by the continuous process is as follows:

2,4,6-TNT	88.19%
2,3,4-TNT	1.99%
2,4,5-TNT	0.67%
2,4-DNT	7.65%
2,6-DNT	0.98%
2,5-DNT	0.19%

HNBB and MPDM also form eutectics with TNT. Two approaches have been considered for minimizing extrudation. One approach to solving the extrudation problem is to produce TNT with smaller amounts of impurities. This can be done by carrying out nitration under more drastic conditions, which adds to the process cost, and closely controlling the sellite process to minimize production of HNBB and MPDM. Crystallization from nitric acid removes all DNT isomers. Another approach is to add materials to the TNT that absorb the eutectics. Cellulose esters, in the amount of about 0.6 percent, absorb the extrudate and reduce the tendency of the TNT to crack. Polyurethanes remove extrudate and double the compressive strength of the cast.

(10) Two types of TNT are specified for military use:

	Type I	Type II
Form	Flake or crystalline	Crystalline
Color	No darker than number 30257	Light yellow
Solidification point (°C), minimum	80.20	80.40
Moisture (%), maximum	0.10	0.10
Acidity (%), maximum	0.005	0.005
Alkalinity	None	None
Toluene insoluble matter (%), maximum	0.05	0.05
Sodium (%), maximum	0.001	0.001
Granulation		
through a US standard number 14 sieve	95	100
through a US standard number 100 sieve	-	95

For type I flake form the average thickness of the flakes shall not be more than 0.63 millimeters (0.025 inches) and any individual flake shall be no more than 0.1 millimeters (0.004 inches).

Table 8-56. Impact Sensitivity of TNT

Temperature in °C	Inches on Picatinny Arsenal apparatus with 2 kilogram weight
−40	17
Room	14
80	7
90	3
05	2 (five explosions in 20 trials)

Table 8-57. Gap Test Results for TNT

	Density grams per cubic centimeter	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.651	0	3.96
	1.561	5.5	6.25
	1.353	18.0	7.90
LANL small scale gap test	1.633	1.3	0.33
	0.84	49.2	NO GO
	0.77	53.4	4.11
LANL large scale gap test	0.87 (flake)	47.4	37.1
	0.73 (granular)	55.9	60.8

(11) TNT is one of the least sensitive of military explosives; only ammonium picrate, nitroguanidine, and ammonium nitrate are less sensitive. Impact tests yield high values relative to other military explosives, but impact sensitivity increases sharply with increasing temperature, as shown in table 8-56. Diminishing sensitivity has been reported down to −196°C. Gap and projectile test results indicate cast TNT is less sensitive than the pressed materiel. Test results from the modified gap test for cast and pressed TNT are shown in table 8-57. Finely divided TNT, as obtained by fume condensation, is more sensitive to impact than the crystalline material. TNT which has been exposed to light is also more sensitive. The pendulum friction test does not affect TNT. The material is insensitive to rifle bullet impact at room temperature whether unconfined or confined in iron, tin, or cardboard bombs. The same results are obtained at the temperature between 105°C and 110°C with tin or cardboard bombs and in the iron bomb with an airspace. In an iron bomb with no airspace 70 percent of the trials resulted in explosions. The explosion temperature for unconfined TNT is 475°C which is much higher than for other commonly used military explosives. Explosion temperatures for confined samples depend on the purity of the sample and test conditions. Results in the range of 275°C to 295°C are obtained. Heating in a closed glass capillary tube yields a value of 320°C to 325°C. TNT has high minimum detonating charge values for initiation by lead azide or mercury fulminate. The dry material can be detonated by a number six electric blasting cap but the presence of only 7 percent moisture prevents detonation. This is compared to 14 percent and 35 percent moisture required for the desensitization of RDX and PETN respectively. TNT pellets pressed from flake TNT undergo substantial reductions in the rate of detonation and sensitivity to initiation after storage for one week at 65°C. These changes are accompanied by exudation of oily impurities, recrystallization, and sementation of the TNT. TNT is not classified as dangerous with respect to hazard from electric sparks. The sensitivity to electric discharge for 100 mesh TNT is 0.06 joules unconfined and 4.4 joules confined. The fine dust of TNT is sensitive to electric sparks. When ignited in free air, the dust burns completely without detonation; and the temperature of the liquid phase must be 510°C if detonation is to

result from burning. Even when it is under a gas pressure of 100 psi, the liquid phase temperature must be greater than 285°C if TNT is to burn with subsequent explosion. Figure 8-67 shows the results of trials of the Susan test for TNT.

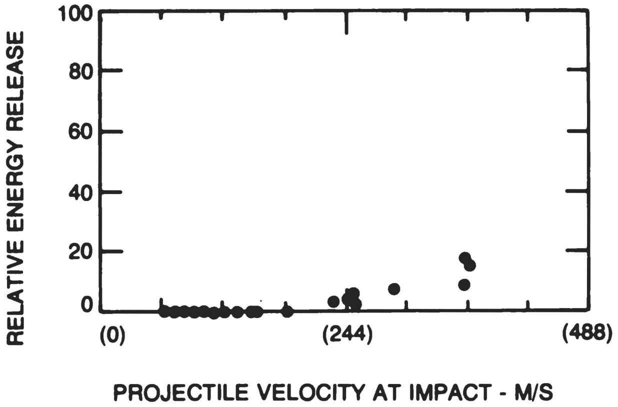


Figure 8-67. Susan test results for TNT.

(12) TNT is the standard explosive to which all the other explosives are compared. In the sand test, 48 grams of sand are crushed. The detonation velocity may be computed by the following equations:

$$D=1.873+3.187p \qquad \text{for } 0.9 < p < 1.534$$

$$D=6.762+3.187(p-1.534)-25.1(p-1.534)^2 \qquad \text{for } 1.534 < p < 1.636$$

where D is in kilometers per second and p, the density, is in grams per cubic centimeter. Detonation velocities of stick charges can be substantially increased by the presence of an axial channel. The detonation temperature also increases with density. At densities of 1.0 and 1.59 grams per cubic centimeter the detonation temperature is 3,000°K and 3,450°K, respectively. The detonation pressure as a function of density is shown in table 8-58.

Table 8-58. Detonation Pressure of TNT

Density in grams per cubic centimeter	Detonation pressure in kilobars
1.59	202
1.63	190
1.64	190
1.65	222

In the copper and lead cylinder compression tests the cylinders are compressed 3.5 and 16 millimeters, respectively. The depth of the dent in the plate dent test is about 0.205 millimeters. The energy of detonation at 1.65 grams per cubic centimeter is 1,265 calories per gram or 4.10 joules per gram. At 1.62 and 1.64 grams per cubic centimeter 684 and 690 liters of gas are evolved, respectively. Fragmentation effects of pressed and cast TNT charges are shown in table 8-59.

Table 8-59. Fragmentation Effects of TNT

Density in grams per cubic centimeter	Pressed/cast	Average number of fragments produced	Average velocity of fragments in meters per second
1.54	pressed	1,070	3,620
1.58	cast	1,850	3,570

The Chapman-Jouguet particle velocity at 1.59 grams per cubic centimeter is 1.83 kilometers per second. The Von Neumann peak pressure at 1.614 grams per cubic centimeter is 237 kilobars. The critical charge diameter of stick charges of TNT is influenced by several factors including initial density, grain size, initial temperature, and degree of crystallivity. TNT cast with many crystallization centers, as is obtained by adding TNT seed crystals to the melt just before solidification, has a smaller critical diameter than that made by conventional crystallization from a clear melt. Cast and pressed charges of the same density have very different critical diameters. The reaction time of pressed TNT is less than half that of the cast material. Axially oriented TNT crystals show unstable detonation while radially oriented crystals detonate smoothly. TNT detonation products vary with the degree of confinement as shown in table 8-60. Increasing confinement shifts the formation of carbon monoxide to that of solid carbon, and the formation of hydrogen gas to that of water. The degree of conversion of the nitrogen atoms to elemental nitrogen remains consistent regardless of confinement.

Table 8-60. Effects of Confinement on TNT Detonation Products

Confinement	Product modes per mole of TNT						
	CO_2	CO	C(s)	N_2	H_2O	H_2	NH_3
Heavily confined	1.25	1.98	3.65	1.32	1.60	0.46	0.16
Both ends of cylinder open	1.07	2.56	3.28	1.34	1.40	0.74	-
Unconfined	0.06	5.89	1.01	1.36	0.17	2.31	0.02

Trace amounts of methane, hydrogen cyanide, and ethane were also detected. In the Trauzl test, 10 grams of TNT expand the cavity by 285 to 305 cubic centimeters.

(13) TNT shows no deterioration after 20 years storage in a magazine or after two years storage as a liquid at 85°C. Only a small amount of decomposition occurs after storage at 150°C for 40 hours. Above that temperature slow decomposition occurs. Autoignition occurs after about 38 hours at 200°C. The thermal decomposition of liquid TNT is characterized by the sigmodial curve typical of an autocatalytic reaction. Explosions occur after an induction period that varies with temperature. However, heating at the boiling point causes distillation but not explosion in small samples. TNT vapor was found to undergo no decomposition over the range 250°C to 301°C at 35 to 500 torr. Even at 357°C the vapor does not explode although decomposition is quite extensive. As shown in figure 8-68, differential thermal analysis indicates an endotherm at 75°C to 100°C and an exotherm at 260°C to 310°C. The TGA curve is shown in figure 8-69. Although at least 25 products are formed, the major products obtained by heating a sample of TNT for 26 hours at 200°C are:

Unreacted TNT	75-90%
Explosive coke	0-13%
4,6-Dinitroanthranil	2-4%
2,4,6-Trinitrobenzaldehyde	1-2%
Azo and azoxy compounds	0.4%
2,4,6-Trinitrobenzyl alcohol	0.2%

The structure of 4,6-dinitroanthranil is shown in figure 8-70. The explosive coke is a brown, intractable powder, apparently polymeric, melting about 360°C, and containing nitro groups. The infrared spectrum indicates the presence of the nitro groups. Since similar results were obtained from heating TNT in a inert atmosphere and exposed TNT to air, oxidation must have occurred at the expense of nitro groups which would correspondingly be converted to azo or azoxy compounds or to an anthranil by inter- and intramolecular reaction, respectively, with the methyl groups. The most likely type of azoxy compound formed is shown in figure 8-71. Polymerization and crosslinking by reactions of this type can explain the formation of the explosive coke. The compound of the gases evolved was found to vary with the extent of reaction and with the temperature. The complicated nature of the process is shown by the fact that the evolved gases contain not only water, corresponding to the formation of the products cited above, but also CO, N_2, NO, N_2O, and even acetylene. Rupture of the C-H bond in the methyl group is the rate determining step in thermal decomposition of TNT. The activation energy of thermal decomposition is 40.9 ± 1.6 kilocalories per mole during the induction period and 30.2 ± 0.6 kilocalories per mole for the post induction period. Added nitroaromatic compounds have no effect on the rate of thermal decomposition of TNT. Nitramine and aliphatic nitrated esters have only a slight effect. Strong promoters of decomposition include potassium nitrate, potassium chloride, certain iron and cobalt compounds, and ammonia. Other active compounds include: hydroquinone, benzoic acid, activated carbon, various plastic materials used to seal or line ordnance, trinitrobenzaldehyde, 4,6-dinitroauthranil and explosive coke. The last three compounds are thermal decomposition products of TNT. Aluminum oxide has a pronounced effect, while PbO, Fe, Al, and Fe_2O_3 are less effective in that order, and Sn and CuO have little or no effect. Previous exposure to ultraviolet light for several hours also accelerates thermal decomposition. Moisture has no effect on the stability of TNT, which is unaffected by immersion in sea water. However, at 50°C ethanol reacts with alpha or gamma but not beta TNT. In case of alpha TNT the products are ethyl nitrite and an unidentified nitrocompound that melts at 77.5° to 77.9°C and is soluble in exudate oil.

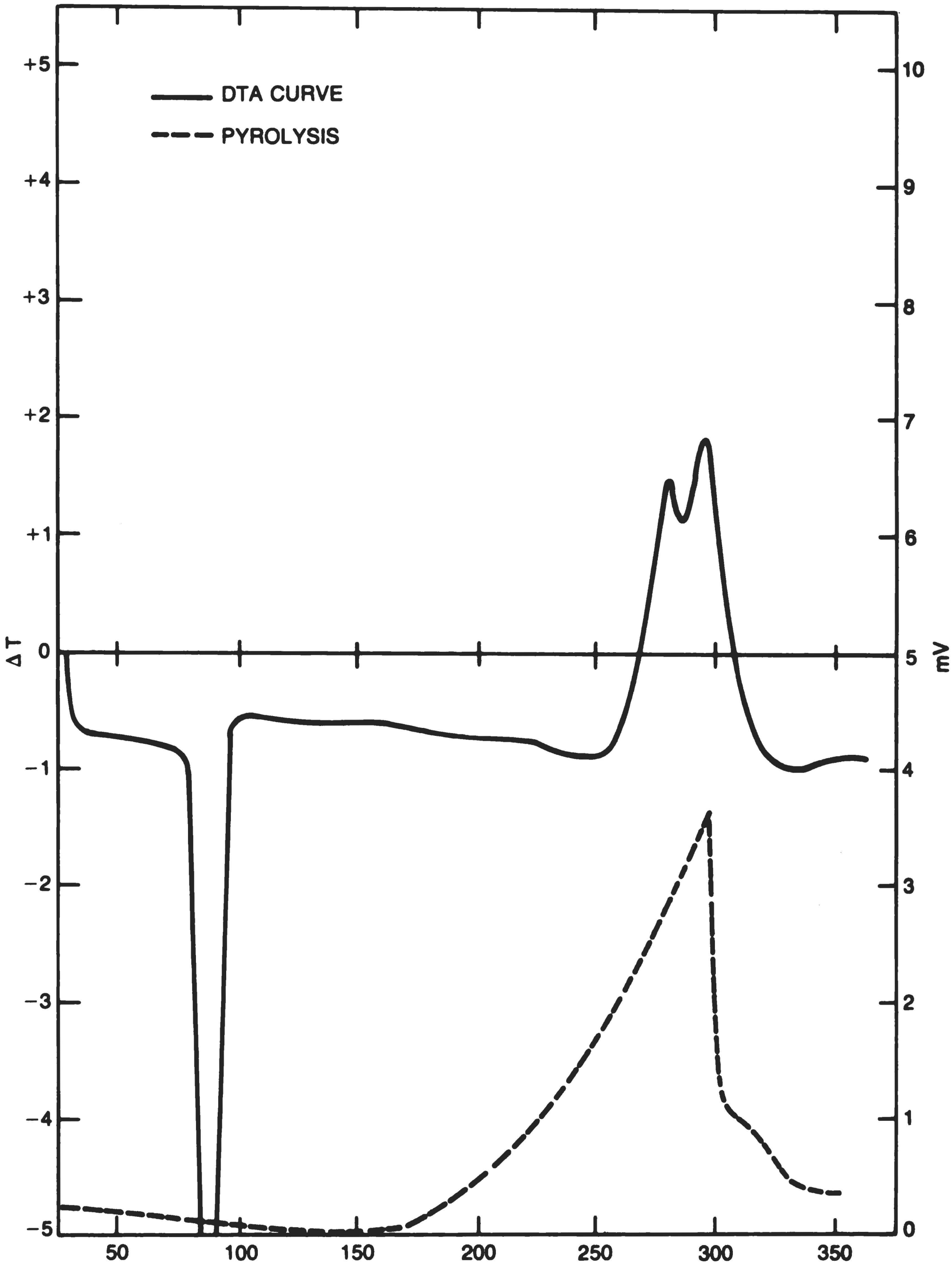


Figure 8-68. DTA curve for TNT.

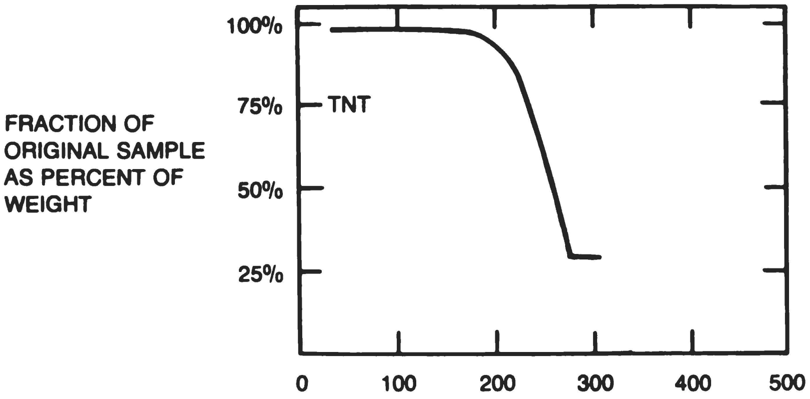


Figure 8-69. TGA curve for TNT.

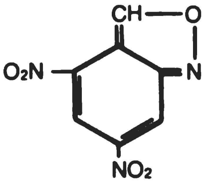


Figure 8-70. 4,6-Dinitroanthranil.

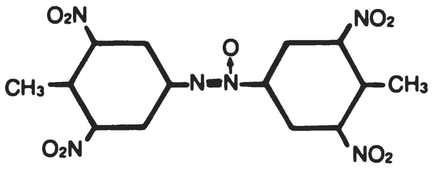


Figure 8-71. Explosive coke azoxy compound.

(14) Photolysis of aqueous solutions of TNT, such as the wastes obtained from munition plants, leads to the formation of pink water. Ultraviolet light excites the nitro group to a triplet state according to the equation:

$$ArNO_2 + \text{optical energy} \longrightarrow {}^3ArNO_2$$

Where Ar represents the aryl radical, which is the aromatic benzene ring with one hydrogen atom removed. The high energy triplet state extracts the hydrogen from the hydroxyl group of certain phenols according to the equation:

$${}^3ArNO_2 + ROH \longrightarrow {}^3ArNO_2H + RO$$

This reaction is reversible and occurs with certain other nitro compounds. Flash photolysis of TNT entails intramolecular hydrogen abstraction from the methyl group by the ortho nitro group according to the reaction shown in figure 8-72. Reaction sequence (1) has been identified in nonpolar solvents. Reaction sequence (2) has been identified in solar or basic solvents. Photoexcitations of TNT at 215°C in the gas phase or at room temperature in certain solvents, especially dioxane, leads to the formation of 2,4,6-trinitrobenzyl free radicals. Ultraviolet irradiation of aqueous solutions of TNT has yielded a mixture of products, 15 of which have been identified. The methyl group has undergone reaction in all cases yielding one of the following compounds: an alcohol, an aldehyde, a carboxyl, or a derivative of one of these compounds. A nitro group has reacted in some cases, but this is always the ortho and never the para group to the methyl group. Solid TNT produces trinitrobenzoic acid upon exposure to light.

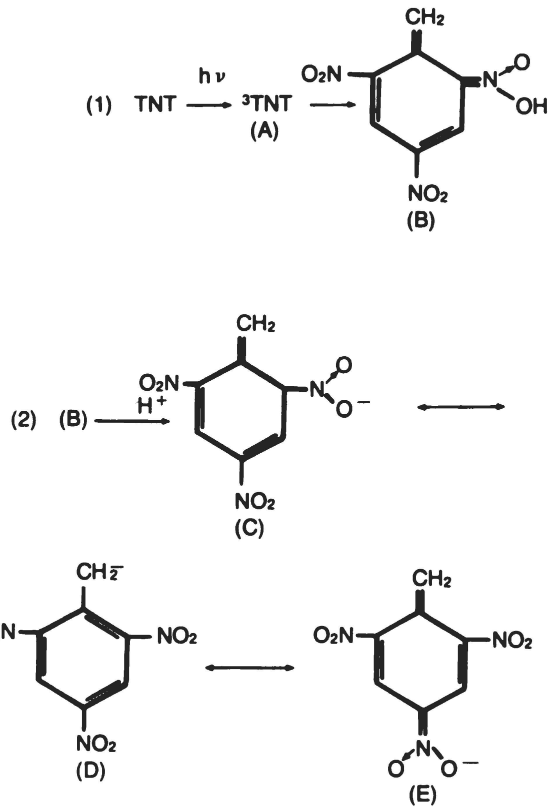


Figure 8-72. Photoexcitation of TNT.

8-5. Ammonium Nitrate.

a. Ammonium nitrate (figure 8-73) has a nitrogen content of 35 percent, an oxygen balance to H_2O and N_2 of 20 percent, and a molecular weight of 80.05. The crystal modifications of ammonium nitrate are shown in table 8-61.

Table 8-61. Crystal Modifications of Ammonium Nitrate

Form	Crystal system	Density in grams per cubic centimeter	Range °C
Liquid			Above 169.6
I Epsilon	Regular (cubic) (isometric)	1.58 to 1.61	125.0 to 169.6
II Delta	Rhombohedral or tetragonal	1.64 to 1.67	84.1 to 125
III Gamma	Orthorhombic	1.64 to 1.66	32.3 to 84.1
IV Beta	Orthorhombic	1.71 to 1.75	−18 to 31.2
V Alpha	Tetragonal	1.70 to 1.72	−18 to −150

The density of the molten material in grams per cubic centimeter is 1.402 and 1.36 at 175°C and 200°C, respectively. When heated at atmospheric pressure, decomposition occurs at 230°C and deflagration occurs at 325°C. There may even be decomposition at temperatures as low as 100°C since constant weight cannot be obtained at this temperature and decomposition is quite perceptible above the melting point. The boiling point of the pure material is 210°C. Distillation without decomposition can be carried out at 11 torr. On the Mohs scale a scratch hardness of 1.1 is reported. Specific heat values as a function of temperature are listed in table 8-62.

Table 8-62. Specific Heat of Ammonium Nitrate

Temperature in °C	Specific heat in calories per gram per degree centigrade
−200	0.07
−150	0.19
−100	0.30
− 80	0.35
− 50	0.37
0	0.40
50	0.414
100	0.428

The heat of fusion is 18.23 calories per gram. The heat of formation is 88.6 kilocalories per mole. Under constant pressure, the heat of combustion is 49.4 kilocalories per mole and at constant volume, the heat is 50.3 kilocalories per mole. At 25°C the latent heat of sublimation is 41.8 kilocalories per mole.

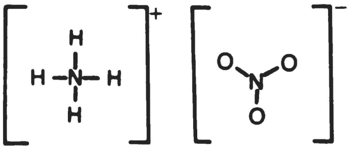


Figure 8-73. Structural formula for ammonium nitrate.

b. Ammonium nitrate can decompose according to any of the nine equations listed below. Unless otherwise stated, the heats of decomposition are based on solid phase ammonium nitrate. For molten ammonium nitrate add about 4,000 calories per mole to the values. The values for the heat liberated are at constant pressure and 18°C for solid ammonium nitrate with all decomposition products in gaseous form. None of these reactions occur as a single reaction, but are always accompanied by other reactions. The predominate reactions are the ones listed in (2) and the two listed in (7):

(1) $NH_4NO_3 \longrightarrow HNO_3 + NH_3 + 38.30$ kilocalories. This reaction takes place at a temperature somewhat above the melting point of ammonium nitrate. The corresponding value for the solid salt is -41.70 kilocalories.

(2) $NH_4NO_3 \longrightarrow N_2O + 2H_2O + 13.20$ kilocalories with H_2O gas and 33.10 kilocalories for H_2O liquid. For the same reaction the value of -10.7 kilocalories has been reported. This reaction takes place in the temperature range of 180°C to 200°C when the ammonium nitrate is unconfined. Oxides other than N_2O form at 203°C to 285°C. Decomposition at 260°C is accompanied by puffs of white smoke.

(3) $NH_4NO_3 \longrightarrow H_2 + 0.5O_2 + 2H_2O + 30.50$ kilocalories for H_2O gas or 50.40 for H_2O liquid. For the same reaction, values from 27.72 to 30.50 kilocalories are reported for H_2O gas. This reaction takes place when ammonium nitrate is heated under strong confinement or when initiated by a powerful detonator. This is the principal reaction of complete detonation of ammonium nitrate. According to calculations, this reaction develops an approximate temperature of 1,500°C and pressure of 11,200 kilograms per square centimeter. The gas evolved is calculated to be 980 liters per kilogram at standard temperature and pressure.

(4) $NH_4NO_3 \longrightarrow NO + 0.5N_2 + 2H_2O + 9.0$ kilocalories for H_2O gas or 28.90 kilocalories for H_2O liquid. A value of 6.87 kilocalories has also been reported for the reaction with the H_2O gas. This may be one of the side reactions taking place during incomplete detonation. A pressure of 4,860 kilograms per square centimeter and a temperature of approximately 518°C are developed.

(5) $NH_4NO_3 \longrightarrow 0.5HN_3 + 0.75NO_2 + 0.25NO + 0.25N_2 + 1.25H_2O - 21.20$ kilocalories. This is a reaction of decomposition that occurs when ammonium nitrate is under confinement at 200°C to 260°C. This endothermic reaction is followed, at 260°C to 300°C, by explosion of the gaseous products of reaction. This explosion is an exothermic reaction liberating 48.49 kilocalories of heat which is more than 1.5 times as great as the heat liberated by reaction (3) above.

(6) $3NH_4NO_3 \longrightarrow 2N_2 + N_2O_3 + 6H_2O + 20.80$ kilocalories for H_2O gas or 40.60 for H_2O liquid. A value of 21.80 has also been reported for the reaction with the H_2O gas. This reaction cannot take place alone because N_2O_3 exists only in the dissociated state as $NO + NO_2$.

(7) $4NH_4NO_3 \longrightarrow 2NO_2+3N_2+8H_2O+29.80$ kilocalories for H_2O gas or 49.80 kilocalories for H_2O liquid. A value of 24.46 has been reported for the reaction with the H_2O gas. This is another possible side reaction occurring during incomplete detonation. For this reaction, a similar endothermic reaction can take place:

$$4NH_4NO_3 \longrightarrow 3NO_2+5H_2O+N_2+NH_3+NO \quad -84.88 \text{ kilocalories}$$

If the gaseous products are heated, an explosive exothermic reaction takes place.

(8) $5NH_4NO_3 \longrightarrow 2HNO_3+4N_2+9H_2O +35.10$ kilocalories for H_2O gas or about 55 kilocalories for H_2O liquid with HNO_3 dissolved. This reaction takes place under certain conditions such as in the presence of spongy platinum and gaseous HNO_3.

(9) $8NH_4NO_3 \longrightarrow 16H_2O+2NO_2+5N_2 +16.58$ kilocalories. This reaction takes place during incomplete detonation and is accompanied by a yellow flame. The calculated value for the total gas developed by this reaction is 945 liters per kilogram.

c. Ammonium nitrate decomposed by strong alkalies liberates ammonia and decomposed by sulfuric acid forms ammonium sulfate and nitric acid. In the presence of moisture, ammonium nitrate reacts with copper to form tetraminocupric nitrate, $Cu\,(NO_3)_2 \cdot 4NH_3$, which has the same sensitivity to impact and brisance as lead azide. For this reason tools of brass and bronze are not used in operations with explosives containing ammonium nitrate.

d. Ammonium nitrate can be manufactured by several methods. The most common method is by passing ammonia gas into 40 percent to 60 percent nitric acid. Both the ammonia and nitric acid are produced by a catalytic process from atmospheric nitrogen, so the ammonium nitrate obtained is of very high purity. The solution is then concentrated in evaporating pans provided with air agitation and heating coils. To form ammonium nitrate crystals, one of three methods is used. One method involves transferring the material that has fudged in the evaporating pan to a flat grainer that is equipped with slowly rotating stainless steel paddles.Stirring in the open cools the syrup, drives off the remainder of the water and produces small, rounded crystals of ammonium nitrate. Another method involves transferring the solution, which has been concentrated to about 95 percent, from the evaporating pan to the top of a spraying tower. In the tower the solution is sprayed and allowed to fall where the remainder of the moisture evaporates and spherical grains, about the size of buck shot, of ammonium nitrate are formed. The grains are called prills. In the third method crystals are formed by vacuum evaporation at two torr, centrifuging, and drying to remove the remaining one to two percent moisture.

e. Ammonium nitrate used for military purposes must meet the following requirements:

Moisture:
  Maximum, 0.15 percent.
Ether-soluble material:
  Maximum, 0.05 percent.
Water-insoluble material of ether-extract:
  Maximum, 0.10 percent.
Water-insoluble material:
  Retained on a 250 micron (No. 60) sieve, none.
  Retained on a 125 micron (No. 120) sieve.
    Maximum, 0.01 percent.
Acidity, as nitric acid:
  Maximum, 0.02 percent.
Nitrites:
  None.
Chlorides, as ammonium chloride:
  Maximum, 0.02 percent.
Phosphates, as diammonium phosphate:
  0.21 ±0.04 percent.
Sulfates, as diammonium sulfate:
  0.007 to 0.014 percent.
Boric acid:
  0.14 ±0.03 percent.
Ammonium nitrate:
  Minimum, 98.5 percent.
Density:
  Particle, g/ml.
    Minimum, 1.50.
  Bulk, g/ml.
    Minimum, 0.80.
  Bulk, lbs/cu ft.
    Minimum, 50.0.
pH:
  5.9 ±0.2.

Granulation (percent by weight):
  Through a 3360 micron (No. 6) sieve.
    Minimum, 99.0.
  Retained on a 1680 micron (No. 12) sieve.
    50.0 - 85.0.
  Retained on a 840 micron (No. 20) sieve.
    Minimum, 97.0.
  Through a 500 micron (No. 35) sieve.
    Minimum, 0.5

The material must be free of nitrite and alkali. The granulation of ammonium nitrate is closely controlled so that satisfactory fluidity and density can be obtained in composition explosives.

f. Ammonium nitrate is the least sensitive to impact of any of the military explosives. Impact sensitivity varies with temperature as shown by the following data:

Temperature in °C	Impact height in inches (Picatinny apparatus)
25	31
100	27
150	27
175	12

The material is unaffected by the steel shoe in the pendulum friction test and does not explode in the five second explosion temperature test. Heating pure, unconfined ammonium nitrate produces a more or less rapid decomposition accompanied by a flash and a hissing sound but no explosions. If a crystal or a piece of cast ammonium nitrate is thrown upon a hot plate at a temperature of about 500°C, the material immediately catches fire and burns rapidly with a yellowish flame and a crackling or hissing sound, but leaves no residue. If a large piece of cast ammonium nitrate is thrown upon a red hot plate, the decomposition proceeds quickly enough to resemble an explosion. The minimum temperature at which a confined charge will explode is around 260°C to 300°C under a pressure of about 17,237 kilopascals (2,500 pounds per square inch). The sensitivity may be increased by the addition of powdered copper, iron, aluminum, zinc, chromium oxide, or chromium nitrate. Powdered limestone, kieselguhr, and clay reduce the sensitivity to heat. No explosions occur in the rifle bullet impact test. In the sand test, only partial explosion of ammonium nitrate results even if boosted with a charge of tetryl or RDX. Larger charges, when properly combined, can be detonated by means of a booster charge of tetryl but not by means of a lead azide or mercury fulminate blasting cap. If ammonium nitrate is unconfined, a number eight blasting cap will not cause complete detonation. The molten material is easier to initiate than the solid and the dry material easier to initiate than the moist. The sensitivity of ammonium nitrate to initiation decreases with increases in loading density. If the density exceeds 0.9, charges of one to three pounds cannot be detonated completely by large booster charges. Larger quantities cannot be detonated completely at densities greater than 1.1. The admixture of up to eight percent of nonexplosive carbonaceous material somewhat sensitizes ammonium nitrate to initiation.

g. The brisance of ammonium nitrate cannot be measured in the sand test because of a failure to completely detonate. The lead cylinder compression test indicates a brisance of 54 percent of TNT for a sample with a density of 1.3 grams per cubic centimeter. Ammonium nitrate has a very low ability to propagate a detonating wave. In unconfined charges that are long and small in diameter, the detonating wave dies out before reaching the opposite end of the cartridge. Ammonium nitrate has a very low velocity of detonation. Factors affecting the velocity of detonation are density, degree of confinement, charge diameter, particle size, strength of the initiating impulse, temperature of the sample, and the presence of certain impurities such as organic materials or oxidizable metals. The rate of detonation increases with decreasing particle size. A decrease in the apparent density of the charge and an increase in confinement causes an increase in the velocity of detonation. An increase in the temperature of the charge from 15°C to 140°C results in an increase of 400 meters per second in the rate of detonation. Within certain limits an increase in the strength of the initiating agent, the diameter of the charge, and presence of organic compounds or oxidizable metals can increase the rate of detonation. The velocity of detonation varies from 1,100 meters per second to 3,000 meters per second. The Trauzl test indicates ammonium nitrate is 75 percent as powerful as TNT and the ballistic mortar test indicates a power of 79 percent of TNT at a density of 1.0 grams per cubic centimeter.

h. The vacuum stability test at 150°C indicates ammonium nitrate is a very stable material even at that temperature. Heating for 100 days at 100°C causes no appreciable decomposition. Decomposition does not appear to begin until the compound melts. At 220°C nitrous oxide, water, and nitrogen are formed. High temperature decomposition is used to manufacture nitrous oxide. If an organic material such as cellulose is present, decomposition of the mixture begins at 100°C and is pronounced at 120°C. The DTA curve for ammonium nitrate is shown in figure 8-74 and the TGA curve is shown in figure 8-75. Admixture with TNT has little if any effect on the stability of ammonium nitrate at temperatures less than 120°C.

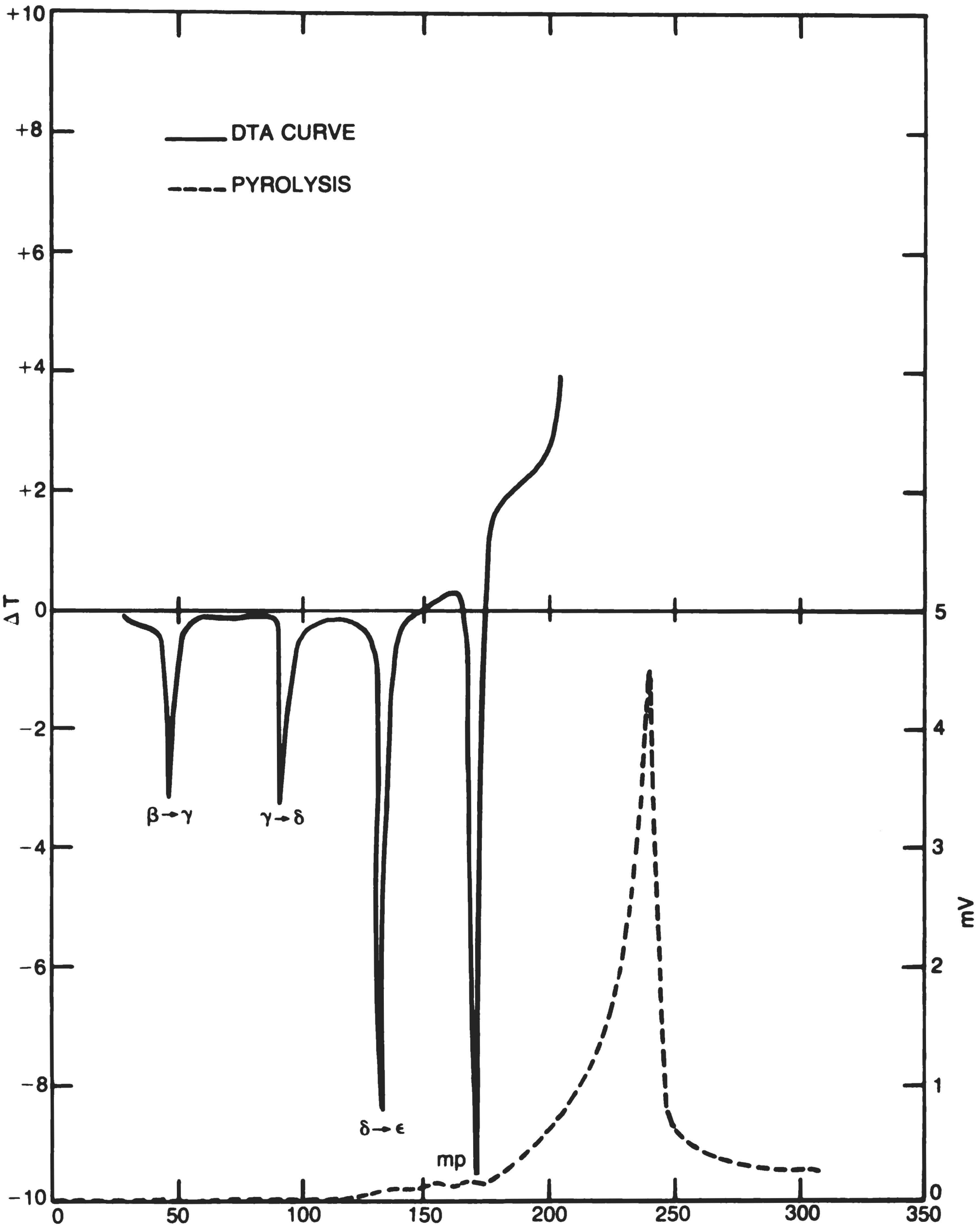


Figure 8-74. DTA curve for ammonium nitrate.

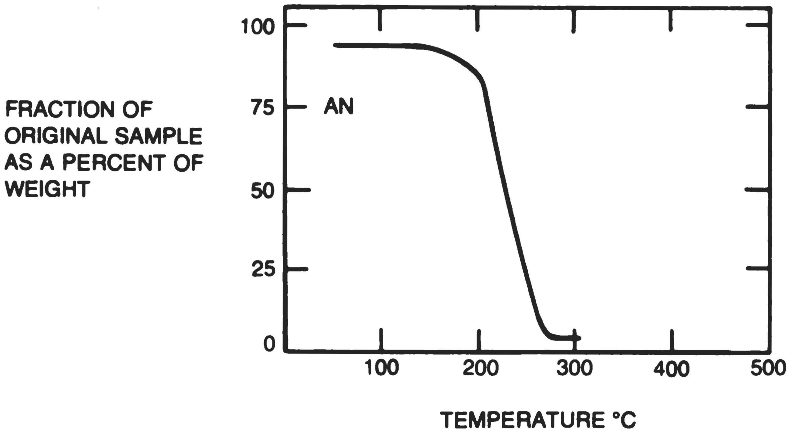


Figure 8-75. TGA curve for ammonium nitrate.

8-6. Compositions. Compositions are explosives in which two or more explosive compounds are mixed to produce an explosive with more suitable characteristics for a particular application. Generally, the characteristics of the composition are intermediate between the characteristics of the individual explosive ingredients. For example, the addition of TNT to RDX reduces brisance somewhat but considerably improves sensitivity. The composition explosives are categorized by the number of ingredients contained in the mixture.

a. *Binary Mixtures.*

(1) Amatols.

(a) Amatols are binary mixtures of ammonium nitrate and TNT. The percentages of ammonium nitrate and TNT are reflected in the nomenclature for each mixture, for example, 80/20 amatol consists of 80 percent ammonium nitrate and 20 percent TNT. Ammonium nitrate is insoluble in TNT. The chemical and physical properties of the constituents determine the properties of the amatol. The mixture begins to melt at TNT's melting point but the ammonium nitrate, which has a higher melting point, remains solid. The two ingredients may be dissolved separately. Table 8-63 compares the properties of some of the common amatol compositions. Amatols can be used for shell and bomb filling.

Table 8-63. Properties of Amatols

Properties	Amatol composition				
	80/20	60/40	50/50	45/55	40/60
Nitrogen content	31.7%	28.4%	26.8%	25.9%	25.1%
Oxygen balance to CO_2	+1.20%	−17.6%	−27.0%	−31.7%	−36.4%
Oxygen balance to CO	+11.06%	+2.13%	−2.32%	−4.55%	−6.78%
Color	Lt buff	Lt buff	Buff	Buff	Buff
Melting point, °C	-	-	81	-	-
Heat of combustion at constant volume	1,254	-	2,073	-	2,402
Specific heat 20° to 80°C	-	-	0.383	-	-
Heat of detonation with liquid water at constant volume in kilocalories per gram	1,04-1,200	-	950	-	920

(b) 80/20 amatol is manufactured by heating ground and screened ammonium nitrate to 90° - 95°C in a mixing kettle with a steam jacket. The ammonium nitrate cannot contain more than 0.25 percent water and must be finely granulated. The proper amount of molten TNT at 95°C is gradually added with mechanical agitation. The mixture is thoroughly blended by continuing the agitation at 95°C for at least 15 minutes after the TNT has been added. The mixture is then suitable for press loading or extrusion. The explosive is a plastic mass resembling wet brown sugar. Improper granulation of the ammonium nitrate can, on loading, cause separation of the molten TNT. To manufacture amatols with a 60 percent or less ammonium nitrate content, molten TNT is placed in the steam jacketed kettle. The screened and dried ammonium nitrate, which has been heated to 90° to 95°C, is added with agitation at a rate that prevents lumping. Agitation at 90° to 95°C is maintained until thorough blending and uniform fluidity are obtained. The temperature of the mixture is then reduced to 85°C for cast loading. The explosive resembles cast TNT.

(c) Impact tests indicate 80/20, 60/40, 50/50, and 40/60 amatols are 90 to 95, 95 to 100, 93 to 100, and 93 to 100 percent as sensitive as TNT, respectively. Amatols are unaffected by the rifle bullet impact test and the pendulum friction test. Explosion temperature test values for all the amatols are lower than that of TNT: 280°C to 300°C for 80/20 amatol, 270°C for 60/40 amatol, and 254°C to 265°C for 50/50 amatol. In the sand test 50/50 amatol is less sensitive to initiation than TNT, requiring a minimum charge of 0.05 gram of tetryl. However, 50/50 amatol can be detonated by diazodinitrophenol, and special tests have shown that less of this initiating agent is required to detonate cast or pressed 50/50 amatol than is required for cast or pressed TNT.

(d) Detonation characteristics for the amatols are listed in table 8-64. In the table, percentages are relative to TNT and density is given in grams per cubic centimeter.

Table 8-64. Detonation Characteristics of Amatols

	80/20 Amatol	60/40 Amatol	50/50 Amatol	40/60 Amatol
Brisance by sand test	74%	90%	90%	94%
Brisance by fragmentation test	-	81% at density of 1.53	82% at density of 1.55	-
Brisance by copper cylinder compression test	-	-	-	81% at density of 1.56
Power by Trauzl test	126%	-	116%	120%
Power by ballistic mortar test	130%	128%	123%	-
Detonation velocity in meters per second at 1.59 to 1.6 grams per cubic centimeter	5,300	6,200	6,400	6,550

Other experimental determinations of the velocity of detonation yields divergent results from those shown in the table, at least partially due to the variations caused by the granulation of the ammonium nitrate. Amatols have better oxygen balance than TNT producing larger amounts of gaseous explosion products. This accounts for the greater power of the amatols.

(e) The stability of 50/50 amatol is a little less than that of TNT at temperatures of 100° and 120°C as indicated by vacuum stability tests. There evidently is very slight reaction between TNT and ammonium nitrate at those temperatures. At temperatures below the melting point of TNT, there is no evidence of reaction. After storage at 50°C for three months, there is no change in the sensitivity, brisance, or stability of 50/50 amatol; and many additional months of such storage without effect might be anticipated. The DTA curve for 80/20 amatol is shown in figure 8-76. Amatols are hygroscopic due to the presence of the ammonium nitrate.

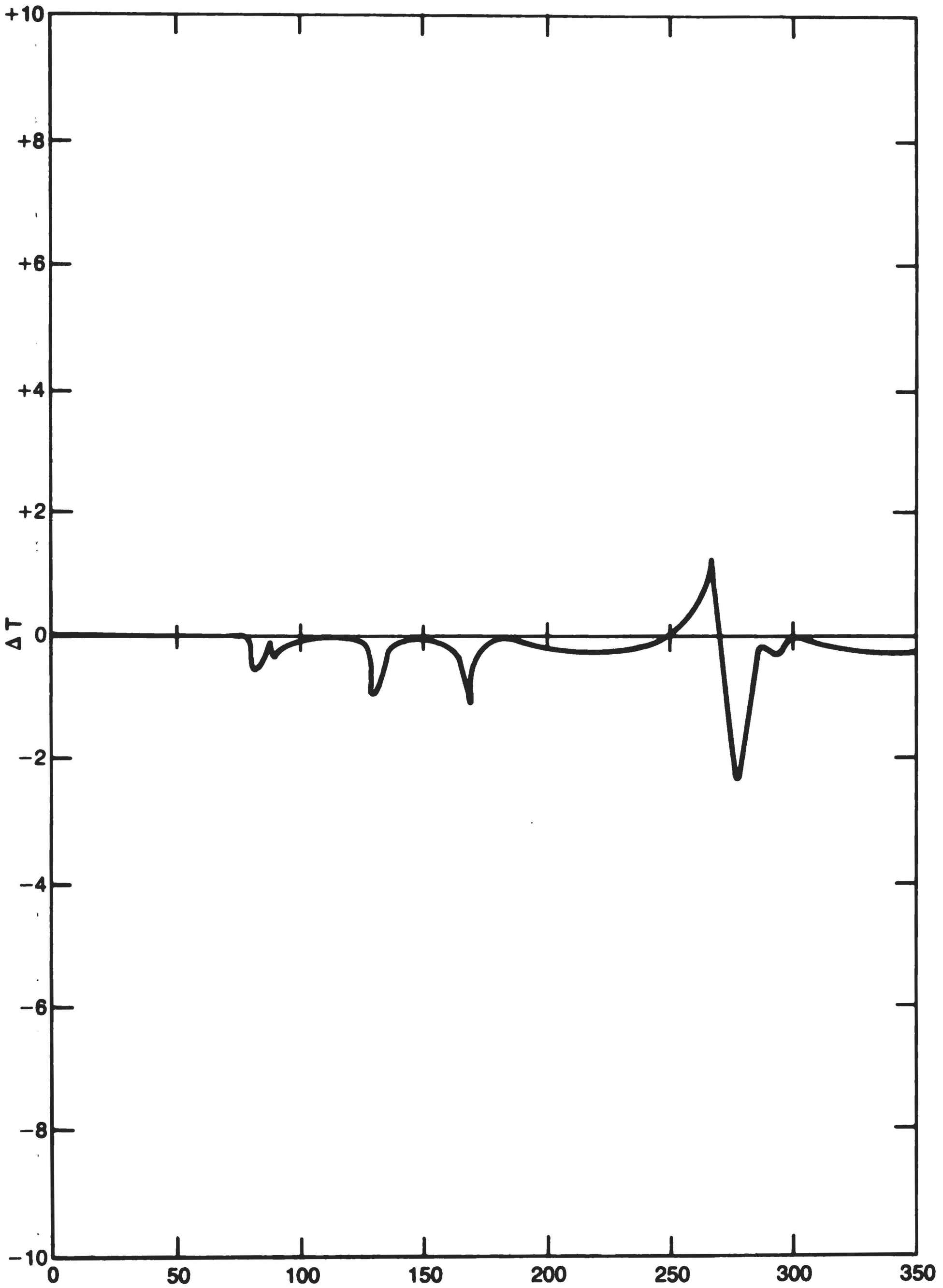


Figure 8-76. DTA curve for 80/20 amatol.

(f) 50/50 Amatol has an air blast energy of 84 percent of TNT, a water shock energy of 94 percent of TNT, and a shaped charge efficiency of 54 percent of TNT.

(g) Determination of the composition of amatol can be made by extracting a weighted sample with benzene, drying the residue, and weighing this. The weight of the residue is calculated to percentage of ammonium nitrate and the difference between this and 100 percent represents the percentage of TNT.

(2) Composition A.

(a) Composition A explosives consist of a series of formulations of RDX and a desensitizer. Table 8-65 lists the composition of the explosives. Compositions A and A2 contain the same percentages of materials as composition A3 but the type of wax used and the granulation requirements for the RDX are different. Composition A contains beeswax, while composition A2 contains a synthetic wax. Compositions A and A2 are no longer used. All of the composition A explosives are press loaded. The density of composition A3 is 1.47 and 1.65 grams per cubic centimeter when pressed to 20,685 kilopascals (3,000 pounds per square inch) and 82,740 kilopascals (12,000 pounds per square inch), respectively. Composition A3 may be completely dissolved in benzene and acetone, when these solvents are used successively. The color of the composition depends on the color of the particular desensitizer used. For composition A3 the heat of formation is −24.8 to −28.4 kilocalories per gram and the heat of detonation is 1,210 kilocalories per gram.

Table 8-65. Composition A Explosives

	Ingredients in percent				
Composition	RDX	Desensitizing wax	Stearic acid	Polyethylene	Comments
A3	91.0±0.7	9.0±0.7	-	-	High explosive, projectile filler
A3 type II	90.8±0.9	-	-	9.2±0.9	High explosive, projectile filler
A4	97.0±0.5	3.0±0.5	-	-	Boosters
A5 type I	98.5±0.5	-	1.5±0.5	-	Shaped charges, grenades
A5 type II	98.0 minimum	-	1.6 minimum	-	Also contains 0.4 percent lubricant
A6	86	14	-	-	Projectile filler

(b) The manufacture of composition A3 is carried out by heating a water slurry of RDX nearly 100°C and agitating. The wax, which contains a wetting agent, is added during agitation and agitation is continued while the mixture is allowed to cool to a temperature less than the melting point of the wax. After being caught on a filter, the composition is air-dried at 77°C.

(c) The relative impact sensitivity of composition A3 is 125 percent of TNT. There are no initiations in the rifle bullet impact test or pendulum friction test with either the steel or fiber shoe. The five second explosion temperature test result is 250°C to 280°C. In the booster sensitivity test, with material pressed to a density of 1.62 grams per cubic centimeter, detonations in 50 percent of the trials are caused by 100 gram tetryl pellets separated from the composition A3 by acrawax B pellets 4.318 centimeters (1.7 inches) thick. The minimum detonating charge of lead azide is 0.25 grams. The flamability index is 195 percent of TNT.

(d) The sand test indicates composition A3 is 107 to 115 percent as brisant as TNT and the plate dent test indicates 126 percent. In the fragmentation test a three inch shell containing 0.861 grams of composition A3 at a density of 1.64 grams per cubic centimeter produced 710 fragments versus 514 for the same weight of TNT. The fragment velocity at a distance of 2.75 meters (9 feet) is 853.44 meters per second (2,800 feet per second) and at a distance of 7.77 meters (25.5 feet) the fragment velocity is 771.14 meters per second (2,530 feet per second). The detonation velocity for a sample of composition A3 at a density of 1.62 grams per cubic centimeter is 8,100 to 8,200 meters per second. The Trauzl test and ballistic mortar indicate composition A3 is 144 percent and 135 percent of TNT, respectively.

(e) When subjected to the vacuum stability test for 48 hours at 100°C and 120°C composition A3 evolves 0.3 cubic centimeters of gas and 0.6 cubic centimeters of gas, respectively. These values are less for RDX, but slightly more for TNT. The 100°C heat test indicates that composition A3 undergoes volatilization. Composition A3 is nonhygroscopic, so is not affected by moisture during storage. Storage above 75°C is not recommended because of the softening effect on the wax coating. Figures 8-77 and 8-78 show the DTA curves for composition A and A3, respectively.

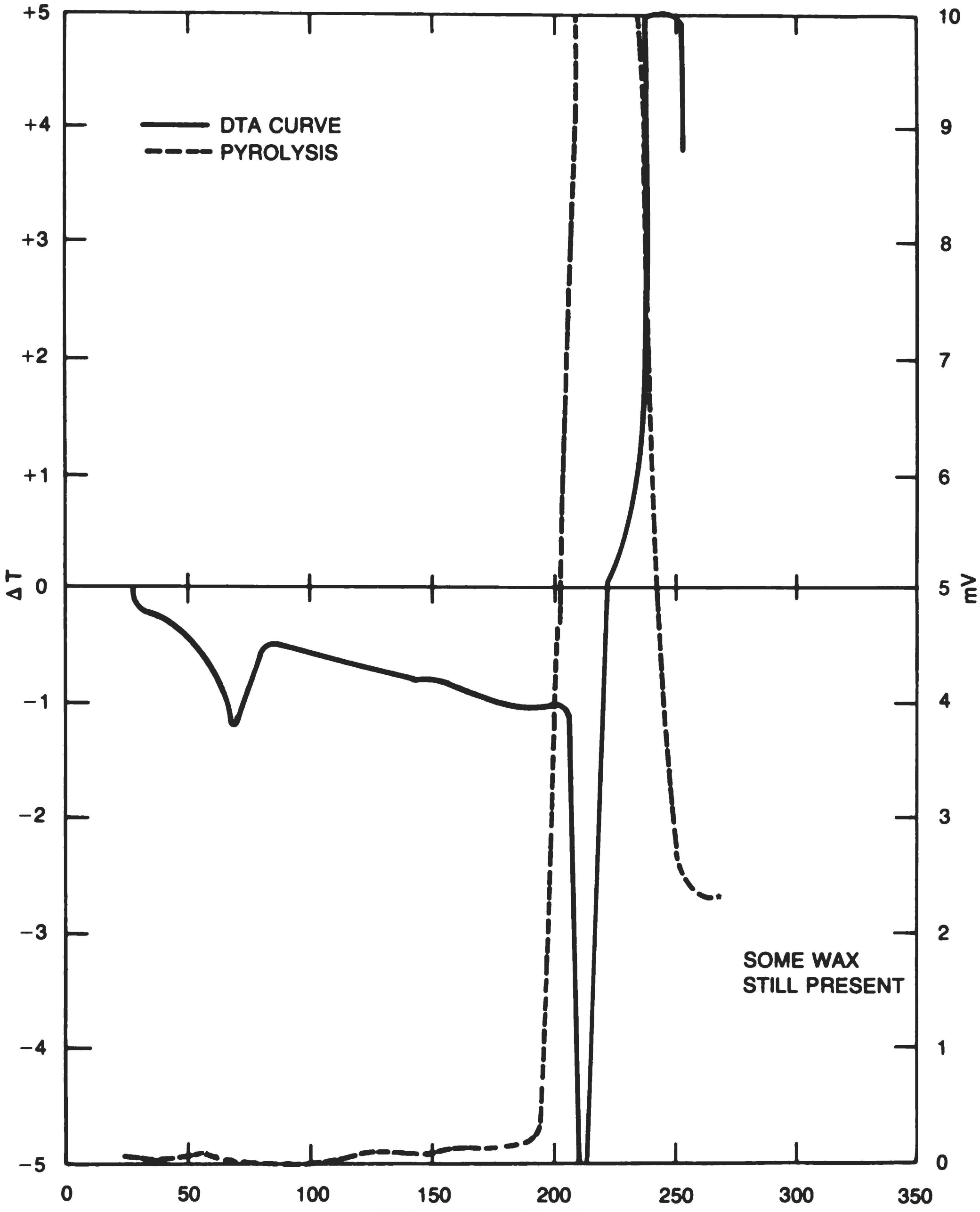


Figure 8-77. DTA curve for composition A.

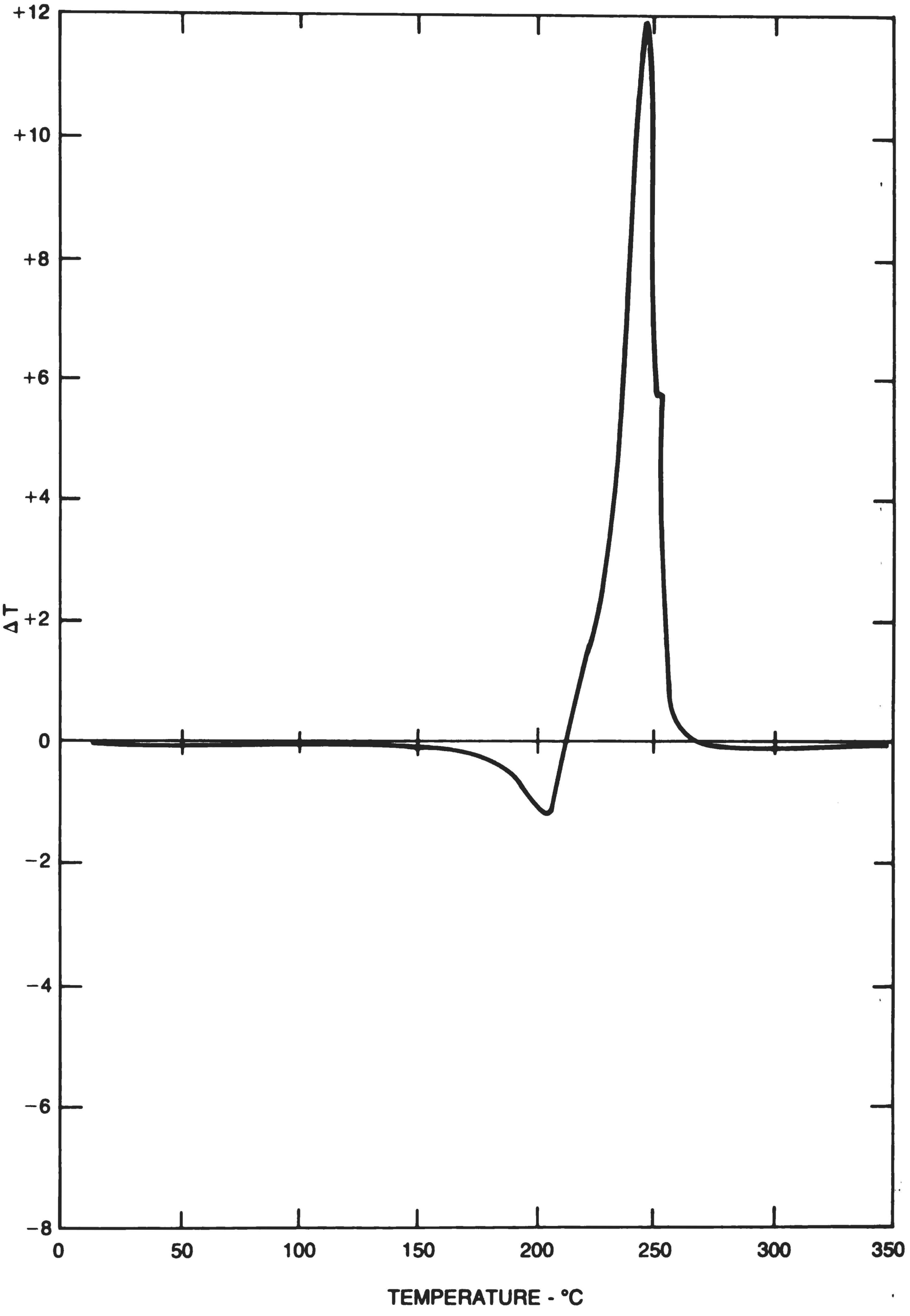


Figure 8-78. DTA curve for composition A3.

(3) Composition B.

(a) Composition B type explosives are mixtures of RDX and TNT. Composition B refers to mixtures of approximately 60 percent RDX and 40 percent TNT. Other portions of RDX and TNT are called cyclotols. Table 8-66 compares the properties of some composition B type explosives.

Table 8-66. Cyclotol Properties

Composition and properties	Cyclotol Type I	Cyclotol Type II A	Cyclotol Type II B	Composition B	Composition B2	Composition B3
Percent RDX	75±2	70±2	69.6±2.0	59.5±2.0	60	59.9±1.0
Percent TNT	25±2	30±2	29.9±2.0	39.5±2.0	40	40.5±1.0
Percent wax	-	-	-	1±.03	-	-
Calcium silicate	-	-	0.5±0.15	-	-	-
Oxygen balance to CO_2, %	−35	−37	-	−43	−43	-
Color of material	Yel-buff	Yel-buff	-	Yel-brown	Yel-brown	-
Castability at 90°C	Difficulty poured	Difficulty poured	-	Easily poured	Easily poured	-
Thermal characteristics (in units of calories per gram):						
Heat of combustion	2,625	2,685	-	-	2,820	-
Heat of explosion	1,225	1,213	-	-	1,195	1,200
Heat of fusion	5.0	-	-	-	-	-
Impact sensitivity properties with 2 kilogram weight:						
Bureau of Mines apparatus	-	60	-	75	75	-
Picatinny Arsenal apparatus	-	14	-	14	14	-
Weight of sample in milligrams	-	20	-	19	19	-
Rifle bullet impact test:						
Percent explosions	30	30	-	3	5	-
Percent partials (smokes)	40	30	-	13	55	-
Percent burned	0	0	-	4	25	-
Percent unaffected	30	40	-	80	15	-
Sensitivity to initiation	-	LA 0.20	-	LA 0.20	LA 0.20	-
(minimum detonating charge in grams)	-	MF 0.21	-	MF 0.22	MF 0.22	-
Detonation characteristics:						
Brisance by plate dent test (percent TNT)	-	136	-	129 - 132	132	-
Brisance by sand test (percent TNT)	-	118	-	113	114	-
Fragmentation test:						
Number of fragments from 90mm HE, M71 shell	1,514	1,165	-	998	998	-
Weight of bursting charge in grams	1,008	1,005	-	993	993	-
Number of fragments from shell containing TNT	703	703	-	703	703	-
Fragment velocity in meters per second (feet per second)						
at distance 2.74 meters (9 feet)	-	-	-	896	903.7	-
				(2,940)	(2,965)	-
at distance 7.77 meters (25 feet)	-	-	-	816.8	853.4	-

Table 8-66. Cyclotol Properties (Cont)

Composition and properties	Cyclotol Type I	Cyclotol Type II A	Cyclotol Type II B	Composition B	Composition B2	Composition B3
The value for TNT at 2.24 meters is 792 meters per second and at 7.77 meters is 719 meters per second.	-	-	-	(2,680)	(2,800)	-
Detonation rate in meters per second at room temperature for 2.54 centimeter diameter charge (d in grams per cubic centimeter)	8,252 at d 1.743	8,060 at d 1.73	- -	7,840 at d 1.68	7,900 at d 1.72	- -
Gas volume in cubic centimeters per gram	862	854	-	-	845	-
Stability tests:						
Heat test at 100°C:						
Percent loss in 1st 48 hours	0.07	-	0.2	-	-	-
Percent loss in 2nd 48 hours	-	0.08	-	0.2	-	-
Explosion in 100 hours	-	None	-	None	-	-
Hygroscopicity in percent at 30°C and 90% relative humidity	-	Nil	-	0.02	Nil	-
Vacuum stability test results in cubic centimeters evolved in 48 hours:	0.23	-	-	0.7	-	-
at 100°C	0.41	0.86	-	0.9	0.29	-
at 120°C	-	-	-	11+	-	-
at 150°C						
Blast effect in air as a percent of TNT:						
Peak pressure	111	110	-	110	104	-
Impulse	126	120	-	110	116	-
Energy	-	-	-	116	-	-
Shaped charge effectiveness as a percent of TNT:						
Hole volume with glass cones	-	-	-	178	178	-
Hole volume with steel cones	-	-	-	162	162	-
Hole depth with glass cones	-	-	-	125	125	-
Hole depth with steel cones	-	130	-	148	148	-

(b) Composition B grade A is formulated as a 60/40 RDX/TNT mixture, but high quality castings usually are higher in RDX content because a TNT rich section is removed from the top of the casting. The casting has a nominal formulation of 36 percent TNT, 63 percent RDX, and 1 percent wax. The grade A composition B is also made from grade A RDX. The theoretical maximum density of both grades A and B composition B is 1.737 grams per cubic centimeter, the open melt density is 1.68 to 1.70 grams per cubic centimeter, and the vacuum melt density is 1.715 to 1.720 grams per cubic centimeter. The theoretical maximum density of composition B3 is 1.750 grams per cubic centimeter and the vacuum melt density is 1.725 to 1.730 grams per cubic centimeter. 75/25 Cyclotol has a theoretical maximum density of 1.776 grams per cubic centimeter and a vacuum melt density of 1.74 to 1.75 grams per cubic centimeter. 70/30 Cyclotol has a theoretical maximum density of 1.765 grams per cubic centimeter and an open melt density of 1.71 to 1.73 grams per cubic centimeter.

(c) RDX is slightly soluble in molten TNT and the two compounds form an eutectic mixture that freezes at 79.0°C and contains 95.84 percent TNT and 4.16 percent RDX. When heated, RDX undergoes some softening at a relatively low temperature because of the melting of the wax present and further melting at the eutectic temperature. As the temperature is increased, some of the RDX is dissolved and at 100°C there are in equilibrium 42.8 parts of molten solution and 57.2 parts of solid RDX. The viscosity of composition B as cast is an important characteristic that is affected markedly by the granulation of the RDX and the nature of the wax used, the wax causing an increase in the viscosity. Representative viscosity values for composition B at 83° and 95°C are 3.1 and 2.7 poises, respectively.

(d) Composition B is manufactured from TNT and water wet RDX. The TNT is melted at approximately 100°C in a steam jacketed melting kettle equipped with a stirrer. The damp RDX is added slowly with stirring, and after addition of the RDX is completed, most of the water is poured off and heating and agitation are continued until all moisture has been driven off. The wax is then added and mixed thoroughly with the other ingredients by stirring. The nature of the wax is important since only certain waxes mix with the RDX and TNT and do not tend to segregate during cooling. The thoroughly mixed composition B then is cooled with continued agitation until the fluidity is satisfactory for casting. The composition B is either cast directly into bombs or solidified into chips approximately 4.8 square centimeters by .6 centimeters. The chips are produced when the composition B is to be stored or shipped for use elsewhere.

(e) Impact sensitivity for solid composition B is between that of TNT and RDX. Cast composition B is more sensitive than the powdered material. As judged by the pendulum friction test, powdered composition B is no more sensitive than TNT, and at 100°C the two explosives show no increase in sensitivity to friction. Like TNT, cast composition B can be drilled without undue hazard. The explosion temperature test value of composition B (270°) is only slightly greater than that of RDX, but the sensitivity of composition B to electrical sparks is more nearly that of TNT than that of RDX. Composition B is intermediate between TNT and RDX in sensitivity to initiation. Cast composition B is somewhat less sensitive to initiation than the pressed material. Table 8-67 lists the gap test results for composition B.

(f) Composition B3 behaves reasonably well in the Susan test. Ignition occurs at the beginning of the pinch stage only after extensive splitting and deformation of the nose cap. The threshold velocity is about 55 meters per second. The reaction level as a function of projectile velocity is shown in figure 8-79. Even at 457 meters per second the full potential of the reaction is not released. These results indicate composition B3 is difficult to ignite by mechanical means and has a low probability for violent reactions once ignited, provided confinement is light. Composition B3 has been observed to detonate in impact geometries where there was good inertial confinement at the time of ignition and where the impact subjected the charge to mechanical work.

Table 8-67. Gap Test Results for Composition B

	Density	Percent voids	Sensitivity in millimeters
LANL small scale gap test:			
Composition B, grade A	1.710 (cast)	1.1	0.41 - 0.66
Composition B3	1.721 (cast)	1.8	1.1 - 1.4
75/25	1.753 (cast)	1.1	0.25 - 0.41
LANL large scale gap test:			
Composition B, grade A	1.712 (cast)	2.2	44.58
Composition B3	1.727 (cast)	1.4	50.34
75/25 Cyclotol	1.757 (cast)	0.6	43.15
	1.734 (cast)	2.2	45.74
PX gap test:			
Composition B	1.714 (cast)	2.2	2

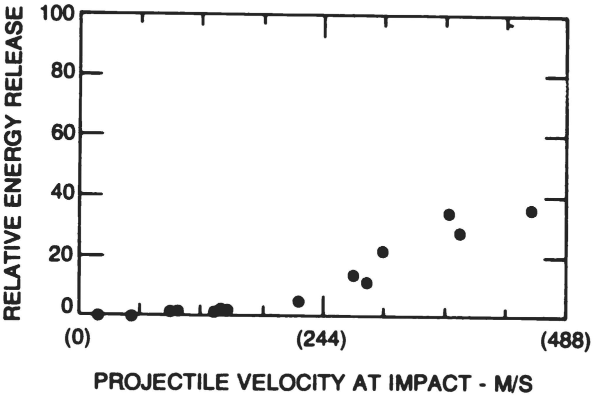


Figure 8-79. Susan test results for composition B3.

(g) 75/25 Cyclotol has both good and bad properties, as measured by the Susan test. The reaction level as a function of projectile velocity is shown in figure 8-80. The threshold velocity for a reaction is about 55 meters per second. This value is typical of TNT bonded cast explosives and higher than most plastic bound explosives. On the other hand, reaction levels are moderately high at relatively low velocities and on occasion are considerably higher. 75/25 Cyclotol is considered relatively difficult to ignite by mechanical means but capable of a large reaction once ignited.

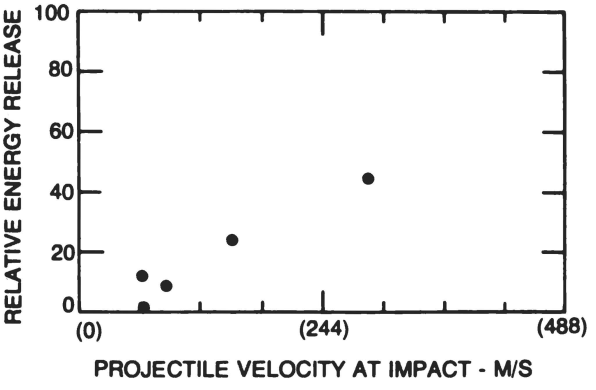


Figure 8-80. Susan test results for 75/25 cyclotol.

(h) Grade A composition B with a density of 1.713 grams per cubic centimeter and 64 percent RDX by weight has a detonation velocity of 8,018 meters per second and a detonation pressure of 292.2 kilobars. Cyclotol with 77 percent RDX by weight with a density of 1.743 grams per cubic centimeter has a detonation pressure of 312.5 kilobars.

(i) Storage of composition B at 75°C for one month causes no decrease in stability. Storage at 65°C for over one year causes no change in acidity, sensitivity to impact, or brisance. However, five months of such storage causes slight exudation. If the composition B is made from TNT which has a freezing point of 80.71°C, slight exudation occurs at a storage temperature of 71°C. Composition B, therefore, is of a high order of chemical stability but should not be stored at too elevated a temperature because of physical instability at such temperatures. Composition B reacts slightly with rust at 100°C. At ordinary temperature, dry composition B causes very slight corrosion of copper and brass but does not affect aluminum, mild steel, stainless steel, nickel, cadmium, or zinc. In the presence of 0.5 percent moisture, composition B causes some corrosion of cadmium and zinc also.

(j) The RDX content of composition B can be determined by extracting a weighed sample with benzene saturated with RDX, drying the residue, and calculating the weight of this to percentage of RDX. The desensitizer content is determined by extracting another weighed sample with acetone cooled to 5°C, drying the residue, and calculating the weight of this to percentage of desensitizer. The percentage of TNT in the composition is obtained by subtracting from 100 the sum of the percentages of RDX, desensitizer, and moisture found present.

(k) Composition B2 is not a standard explosive. Differing from composition B only in the absence of wax, composition B2 has a greater density when cast and is slightly more brisant. The detonation velocity is also slightly higher. Composition B2 is distinctly more sensitive than composition B, as judged by large scale impact and rifle bullet impact tests, and is slightly more sensitive to initiation. The two compositions are of the same stability and hygroscopicity. Greater impact sensitivity makes composition B2 less suitable than composition B for use in bombs.

(1) The DTA curves for composition B and 75/25 cyclotol are shown in figures 8-81 and 8-82, respectively. The TGA curve for composition B is shown in figure 8-83.

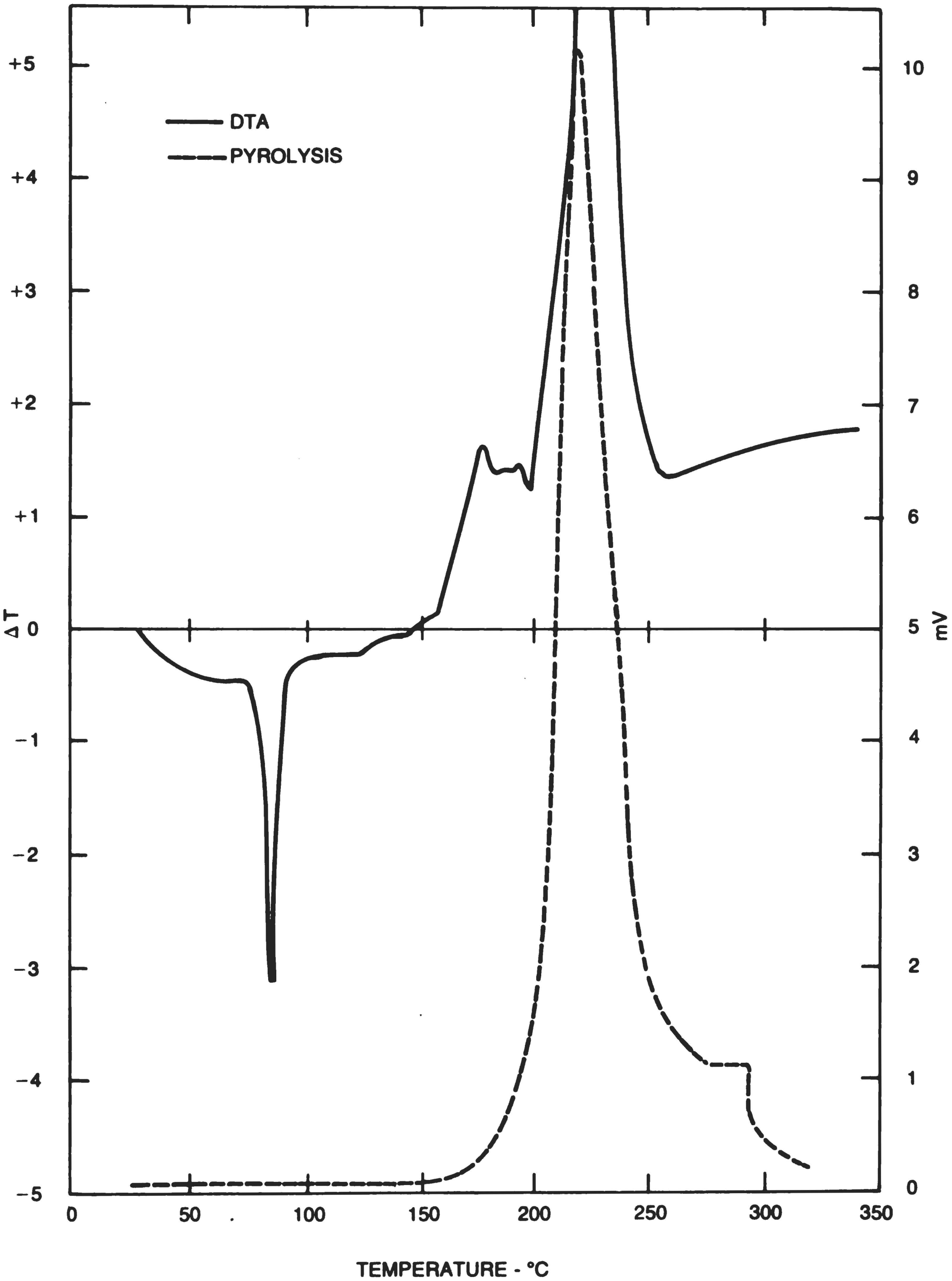


Figure 8-81. DTA curve for composition B.

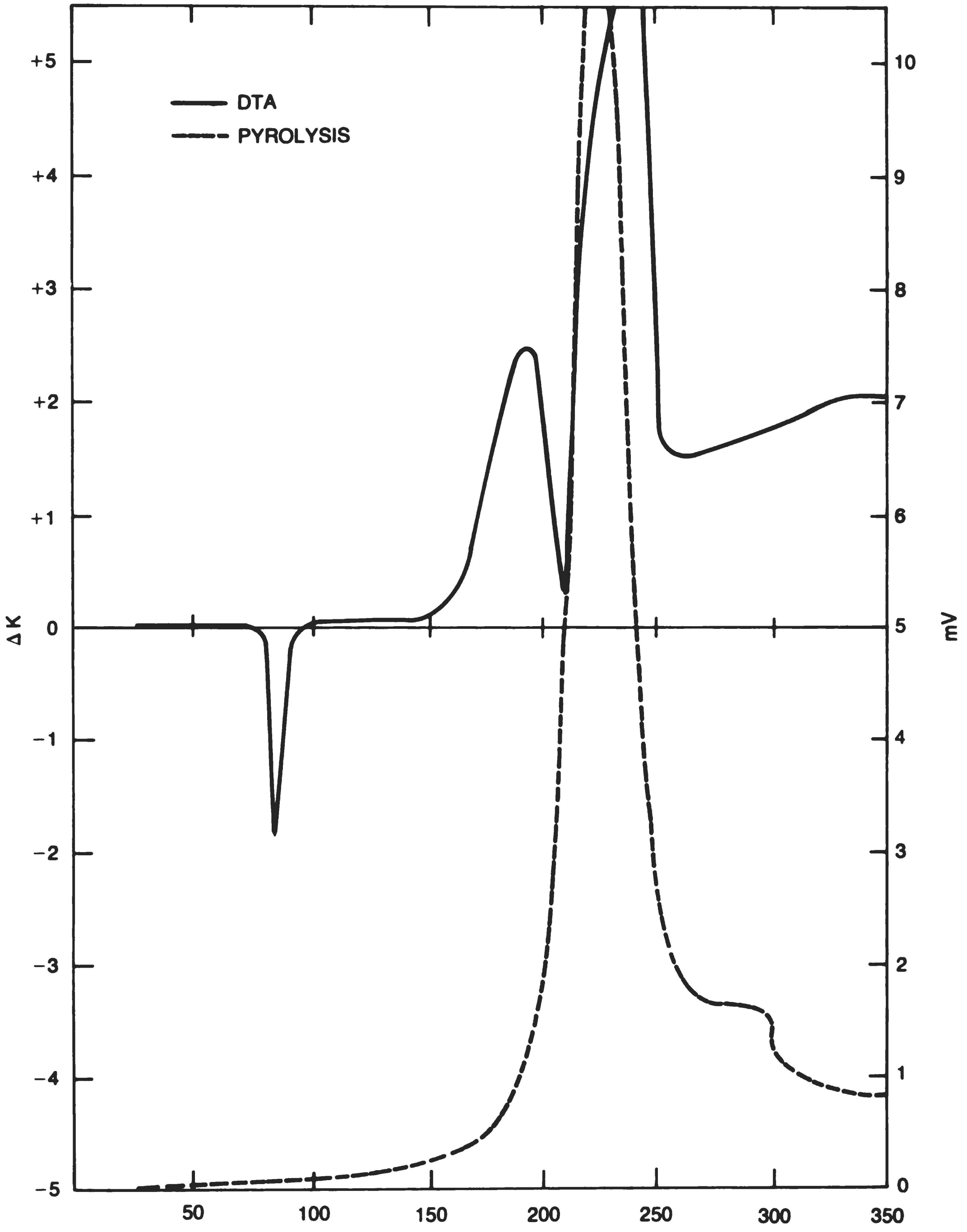


Figure 8-82. DTA curve for 75/25 cyclotol.

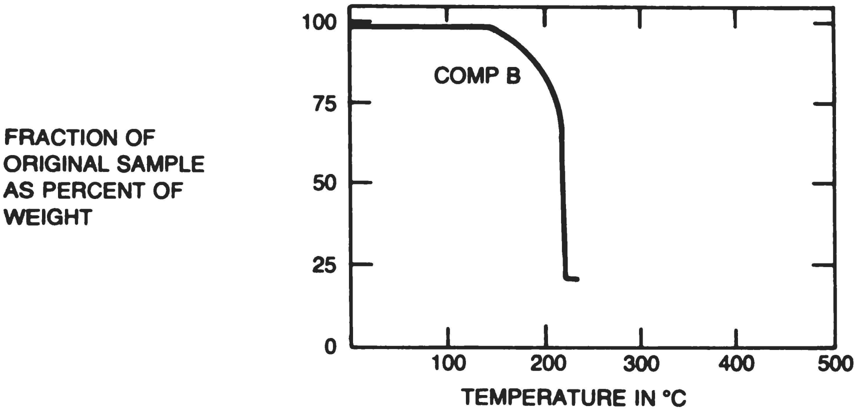


Figure 8-83. TGA curve for composition B.

(4) Composition C.

(a) During World War II, the British used a plastic demolition explosive that could be shaped by hand and had great shattering power. As standardized by the United States, this explosive was designated as composition C and contained 88.3 percent RDX and 11.7 percent of a nonexplosive oily plasticizer. Included in the plasticizer was 0.6 percent lecithin, which helped to prevent the formation of large crystals of RDX which would increase the sensitivity of the composition. Composition C was plastic from 0° to 40°C, but became brittle and less sensitive below 0°C and tended to become gummy and exude oil at temperatures above 40°C. Composition C was replaced by composition C2 which contained 80 percent RDX and 20 percent explosive plasticizer. This explosive plasticizer was composed of mononitrotoluene, a liquid mixture of dinitrotoluenes, TNT, nitrocellulose, and dimethylformamide. Composition C2 remained plastic from −30° to 52°C, but became less plastic in hot storage because of evaporation of volatile matter. Composition C2 has been replaced by composition C3, which contains 77±2 percent RDX and 23±2 percent explosive plasticizer. The plasticizer contains mononitrotoluene, a liquid mixture of dinitrotoluenes, TNT, tetryl, and nitrocellulose. It is a yellowish, puttylike solid that has a density of 1.60 and is soluble in acetone.

(b) In the manufacture of composition C3, the mixed plasticizing agent is placed in a steam jacketed, melting kettle equipped with a stirrer and heated to nearly 100°C. Water wet RDX is added slowly, and heating and stirring are continued until a uniform mixture has been obtained and all the water has been driven off. The mixture then is cooled while being agitated.

(c) One grade of composition C3 is manufactured. This grade includes two classes that differ only in acidity. Both class A and B material is used for the manufacture of demolition blocks, and class B explosive is also used in the loading of ammunition in which lower acidity is desirable. The requirements applicable to composition C3 are as follows:

Composition:
  RDX plus nitrocellulose, 78.0±2.0 percent.
  Plasticizer minus nitrocellulose, 22.0±2.0 percent.
Moisture:
  Maximum, 0.25 percent.
Acetone insoluble material:
  Maximum, 0.15 percent.
Inorganic acetone insoluble material:
  Maximum, 0.05 percent.
Grit:
  Maximum particles per 50 gram sample
    Retained on No. 40 sieve, none.
    Retained on No. 60 sieve, 5.
Plasticity:
  Minimum extension in length at 25° to 30°C, 90 percent.
Acidity:
  Class A maximum, 0.064 percent
  Class B maximum, 0.05 percent

(d) Composition C3 is of the same sensitivity to impact as TNT and is not exploded in the pendulum friction test. The rifle bullet impact test produces partial explosions in 40 percent of the trials, which indicates greater sensitivity than that of TNT but much less sensitivity than that of RDX. The five second explosion temperature test value, 280°C, is only slightly greater than that of TNT. Composition C3 is less sensitive to initiation than TNT, requiring a minimum detonating charge of 0.08 gram of tetryl or 0.20 gram of lead azide in the sand test. Storage for four months at 65°C in an atmosphere of 95 percent relative humidity does not impair the sensitivity to initiation. In the booster sensitivity test 50 percent detonations are produced by 100 grams of tetryl separated from pressed composition C3 with a density of 1.62 grams per cubic centimeter by acrawax B pellets 3.45 centimeters thick.

(e) The chemical stability of composition C3 is acceptable, but the physical stability is not entirely satisfactory. The results of the 120°C heat test are: 3.20 percent loss in the first 48 hours, 1.63 percent in the second 48 hours, and no explosions in 100 hours. Composition C3 is volatile to the extent of a 1.15 percent weight loss when exposed to air at 25°C for five days, and hygroscopic to the extent of 2.4 percent when exposed to air with 90 percent relative humidity at 30°C. Tests have shown composition C3 to be of unimpaired brisance after immersion in water for 24 hours. Storage at 77°C causes considerable exudation. In vacuum stability tests at 100°C and 120°C for 48 hours, 1.21 and 11 + cubic centimeters of gas are evolved, respectively. Figure 8-84 shows the DTA curve for composition C3.

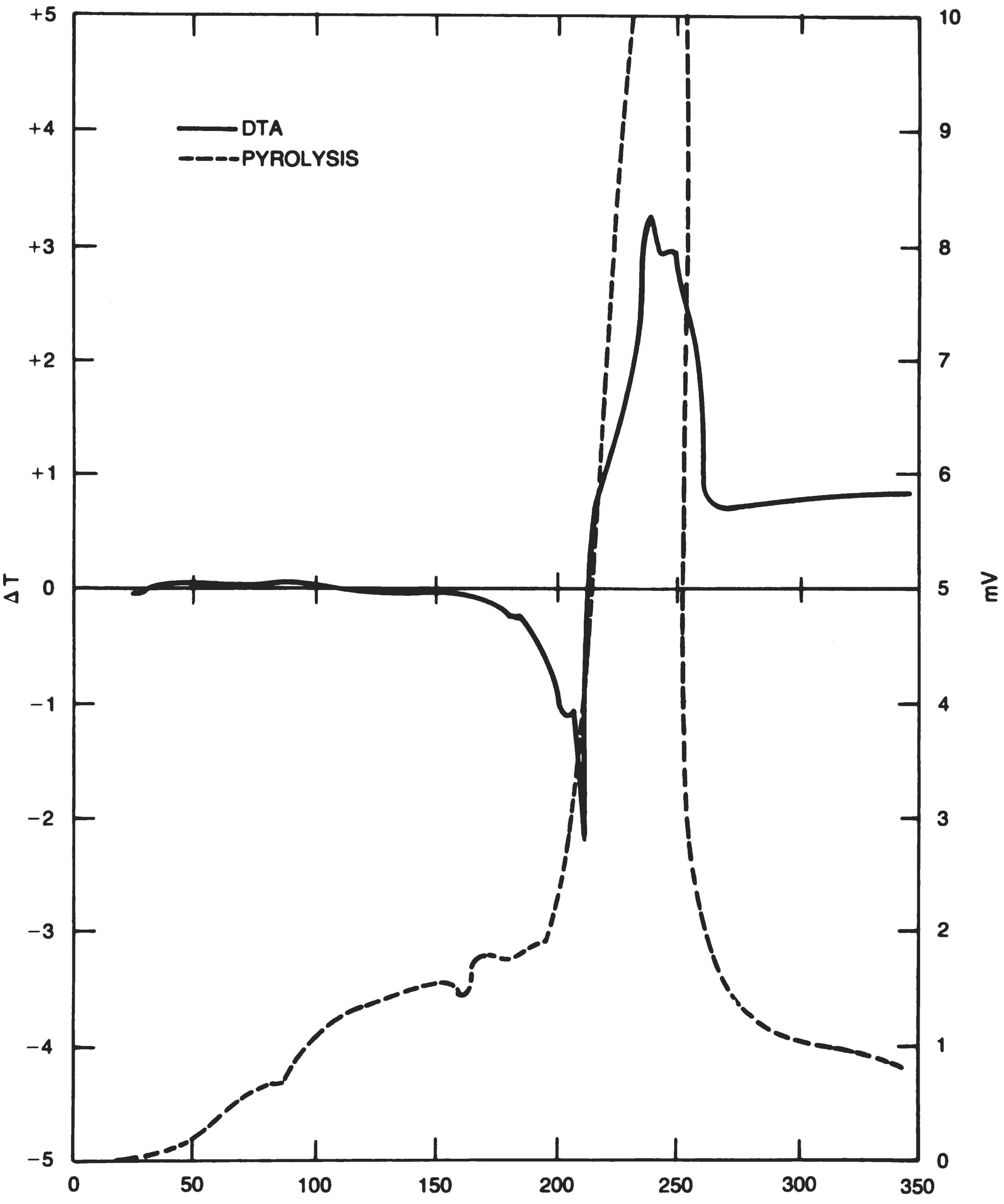


Figure 8-84. DTA curve for composition C3.

(f) In an air blast the peak pressure is 105 percent of TNT and the impulse is 109 percent of TNT.

(g) Composition C3 hardens at −29°C and has undesirable volatility and hygoscopicity characteristics, so composition C4 has been developed. The ingredients of the three classes of composition C4 are:

Class I:	61 percent RDX class A or B, type A or B 30 percent RDX class E, type A or B 9 percent polyisobutylene
Class II:	92 percent RDX class H, type A or B 9 percent polyisobutylene
Class IV:	89.9±1 percent RDX 10±1 percent polyisobutylene 0.2±0.02 percent dye composition which consists of: 90 percent lead chromate 10 percent lamp black

Composition C4 is a pufflike material of dirty white to light brown color. The theoretical maximum density of the mixture is 1.75 grams per cubic centimeter with a nominal density of 1.72 grams per cubic centimeter. The heat of formation is −32.9 to −33.3 calories per gram. The maximum heat of detonation with liquid water is 1.59 kilocalories per gram and with gaseous water 1.40 kilocalories per gram. Composition C4 remains plastic between −57°C and +77°C with no exudation in this temperature range. This explosive is considered a very satisfactory demolition explosive and has almost entirely replaced all the other composition C explosives.

(h) Composition C4 is manufactured by placing the water wet RDX in a stainless steel mixing kettle and adding the plastic binder. The mass is blended by tumbling the kettle until a homogeneous mixture is obtained. The resulting dough is then dried in trays by forced air at 50°C to 60°C. About 16 hours of drying are required to reduce the moisture content to below 0.25 percent.

(i) The detonation characteristics of the composition C explosives are listed in table 8-68. The detonation pressure is 257 kilobars for composition C4 with a density of 1.58 grams per cubic centimeter.

Table 8-68. Detonation Characteristics of Composition C Explosives

Test	Characteristics as a percentage of TNT			
	C	C2	C3	C4
Sand test	108	99	112	116
Plate dent test	112	111	114-118	115-130
Fragmentation test	-	-	113	-
Detonation velocity in meters per second	7,400	7,800	7,625	8,040
Trauzl test	126	-	117	-
Ballistic mortar test	125	126-143	126	130

(j) Impact tests indicate composition C4 is less sensitive than composition C3. The rifle bullet test results, with only 20 percent of the vials burning, also indicate less sensitivity. Composition C4 is unaffected in the pendulum friction test and has a five second explosion temperature of 263°C to 290°C. The minimum initiating charge required is 0.20 grams of lead azide or 0.10 grams of tetryl.

(k) Composition C4 is more stable than composition C3. The results of 100°C heat test are: 0.13 percent loss in the first 48 hours, no loss in the second 48 hours, and no explosions in 100 hours. The vacuum stability test at 100°C yields 0.20 cubic centimeters of gas in 40 hours. Composition C4 is essentially nonhygroscopic.

(5) Composition CH6.

(a) CH6 is an explosive mixture containing:

97.50±0.50 percent RDX
1.50±0.15 percent calcium stearate
0.50±0.10 percent graphite
0.50±0.10 percent polyisobutylene

The primary use of CH6 is in boosters and leads. When compared with tetryl, the material withstands higher temperature before cook off and has higher output yield, yet matches the sensitivity of tetryl. CH6 is pellitized at a density of 1.61 grams per cubic centimeter but the normal loading density is approximately 1.55 grams per cubic centimeter.

(b) In the sand test, CH6 crushes 61.3 grams of sand which indicates a brisance of 128 percent of TNT. The velocity of detonation is 8,223 meters per second.

(6) Ednatols.

(a) Ednatols are mixtures of haleite (ethylene dinitramine) and TNT. The most used haleite/TNT portions are 60/40, 55/45, and 50/50. Ednatols are yellowish, uniform blends with a melting point of 80°C. The eutectic temperature is about 80°C. In an extrudation test at 65°C there was no extrudate. Ednatols are considered satisfactory for bursting charges in ammunition. All of the following data in the discussion of the properties of ednatol refer to the 55/45 mixture. 55/45 Ednatol has an oxygen balance to carbon dioxide of −51 percent and to carbon monoxide of −17 percent. The density of the cast explosive is 1.62 grams per cubic centimeter, which is four percent greater than that of cast TNT or haleite pressed under 206,850 kilopascals (30,000 pounds per square inch).

(b) Ednatol is manufactured by heating TNT to about 105° in a steam jacketed melting kettle equipped with a stirrer. Wet haleite is added slowly with agitation to the molten TNT. After the haleite has been added, heating and stirring are continued until all the moisture has been driven off. The mixture is then cooled to about 85°C while being agitated, and loaded by pouring. Like TNT, ednatol undergoes some contraction in volume upon solidification.

(c) The sensitivity of ednatol, 95 centimeters with a two kilogram weight, is between the sensitivity of haleite and TNT. Ednatol is unaffected by either the steel or fiber shoe in the pendulum friction test. The rifle bullet impact test produces ignitions in seven percent of the trials with no detonations. The explosion temperature test value, 190°C, is the same as for haleite. This value is lower than the values for all of the other noninitiating high explosives. As might be expected, ednatol is more sensitive than TNT but less sensitive than haleite to initiation. The minimum detonating charge of mercury fulminate is 0.22 grams to 0.23 grams. In the booster sensitivity test using a 100 gram tetryl pellet, the 50 percent detonation point with acrawax B was 325 centimeters (1.28 inches).

(d) The sand test indicates ednatol is 112 percent as brisant as TNT. The plate dent test also indicates a brisance of 112 percent of TNT. The fragmentation test indicates a brisance of 118 percent of TNT, with fragment velocities of 832 kilometers per second at 2.74 meters and 741 kilometers per second at 7.77 meters. The velocity of detonation for a one inch diameter, unconfined, cast charge is 7,340 meters per second, 106 percent of TNT. As measured by the ballistic pendulum test and the Trauzl test, ednatol is 119 percent and 120 percent as powerful as TNT.

(e) In the 100°C heat test, a loss of 0.2 percent is reported in the first 48 hours and 0.1 percent in the second 48 hours with no explosions in 100 hours. In the vacuum stability test at 100°C one cubic centimeter of gas is evolved and at 120°C more than 11 cubic centimeters of gas are evolved. Dry ednatol has no effect on brass, aluminum, steels, cadmium, and nickel but causes very slight corrosion of copper, magnesium, and aluminum-magnesium alloys. Wet ednatol has no effect on stainless steel, but causes slight corrosion of aluminum and considerable corrosion of copper, brass, magnesium, magnesium-aluminum alloys, and mild steels. Ednatols are essentially nonhygroscopic when exposed to humid air.

(f) In an air blast the peak pressure is 108 percent of TNT, the impulse is 110 percent of TNT, and the energy is 108 percent of TNT. In an underwater blast, the energy is 113 percent of TNT. The shaped charge effectiveness is about 120 percent of TNT.

(g) The composition of ednatols can be determined by extracting a weighed sample with cold ether saturated with haleite and drying and weighing the residue. The weight of residue and loss in weight are calculated to percent of haleite and TNT, respectively.

(7) LX-14.

(a) LX-14 is an explosive which consists of 95.5 percent HMX and 4.5 percent estane 5702-F1. The mixture is a white solid with violet spots. LX-14 has a theoretical maximum density of 1.849 grams per cubic centimeter, a nominal density of 1.83 grams per cubic centimeter, and a melting point of greater than 270°C, with decomposition. The heat of formation is 1.50 kilocalories per mole. The calculated heats of detonation are 1.58 kilocalories per gram with liquid water and 1.43 kilocalories per gram with gaseous water. At a density of 1.835 grams per cubic centimeter the detonation velocity is 8,830 meters per second.

(b) As shown in figure 8-85, LX-14 is moderately easy to ignite in the Susan test, requiring an impact velocity of about 48 meters per second. Nosecap deformation is generally greater than 25 millimeters before ignition is observed. Reaction levels are large and somewhat erratic once the threshold velocity is exceeded. This data indicates that accidental, mechanical ignition of LX-14 has a moderately low probability of building into a violent reaction or detonation where there is little or no confinement. Figure 8-86 shows the DTA curve for LX-14.

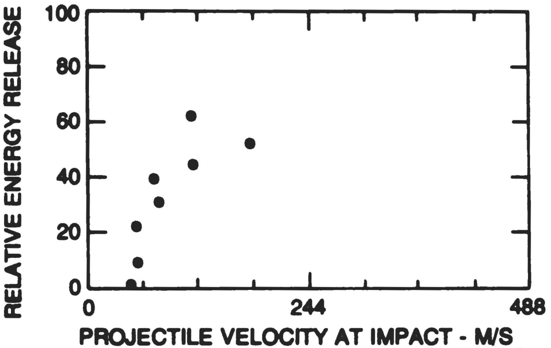


Figure 8-85. Susan test results for LX-14.

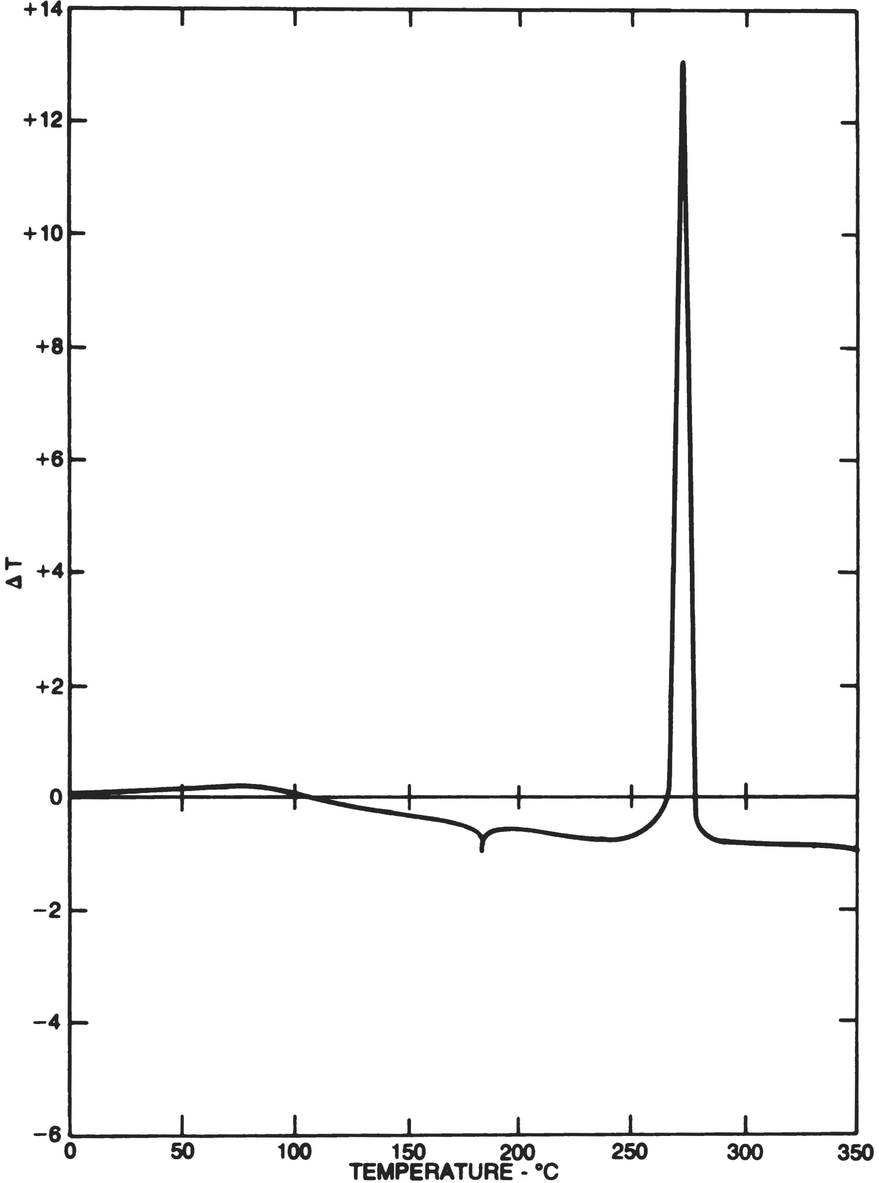


Figure 8-86. DTA curve for LX-14.

(8) Octols.

(a) Octols are mixtures of HMX and TNT. The properties of the two most commonly used octols are summarized in table 8-69.

Table 8-69. Properties of Octols

	Type I	Type II
Percent HMX	75±2.0	70±2.0
Percent TNT	25±2.0	30±2.0
Density in grams per cubic centimeter:		
Theoretical maximum	1.832-1.843	1.819-1.822
Open melt cast	1.800	1.790
Vacuum melt cast	1.801-1.825	1.805-1.810
Calculated heat of detonation in calories per gram:		
With liquid water	1,570	-
With gaseous water	1,430	-
Heat of combustion in calories per gram	2,676	2,722
Heat of fusion in kilocalories per mole	2.57	-
Specific heat in calories per gram per degree centigrade (76,9/23.1 HMX/TNT):		
at $-79^\circ C$	0.200	-
$-80^\circ C < t < 80^\circ C$	0.240	-
$33^\circ C < t < 74^\circ C$	0.245	-
$90^\circ C < t < 150^\circ C$	0.323	-
Temperature of solid slurry phase change °C	79	79
Latent heat of solid to slurry phase change in calories per gram	5.87	7.05
Vapor pressure at 100°C in torr	0.1	-
Impact sensitivity (Picatinny Arsenal Apparatus):		
inches	17	18
Sample weight in milligrams	25	26
inches	15	19
Sample weight in milligrams	19	20
Friction pendulum:		
Steel shoe	Unaffected	Unaffected
Fiber shoe	Unaffected	Unaffected
Autoignition temperature, °C	100	108
Explosion temperature, °C:	288	289
Seconds 0.1 (no cap used)	-	-
Seconds 1	-	-
Seconds 5 (flames erratically)	350	335
Sensitivity to initiation: (minimum detonating charge lead azide in grams)	0.3	0.3

Table 8-69. Properties of Octols (Cont)

	Type I	Type II
Sensitivity to setback pressure in kilopascals at 71°C		
Probability of reaction:		
0.1 percent	655,025	551,600
50 percent	820,505	820,505
99.9 percent	1,027,355	1,213,520
0 percent	524,020	634,340
Pit fragmentation (105mm MI HE projectile)	Number of fragments	Number of fragments
1/2-2 grains	1,611	1,297
2-5 grains	777	665
5-10 grains	535	497
10-25 grains	719	661
25-50 grains	480	471
50-75 grains	246	247
75-150 grains	339	322
150-750 grains	293	295
750-2,500 grains	8	12
Detonation rate (no confinement-cast) in meters per second		
Charge density in grams per cubic centimeter	1.81	1.80
Charge dimensions in centimeters:		
1.27×1.27×15.24	8,643	8,377
2.54×2.54×15.24	8,328	8,241
3.81×5.08×15.24	8,396	8,305
	8,364	8,310
Vacuum stability (milliliters of gas per five grams of sample per 40 hours)		
at 120°C	0.39, 0.65	0.37, 0.76
at 130°C	1.13	0.97
at 140°C	2.66	1.50
at 150°C	11	5.10
at 160°C	-	11
Air blast		
Weight of charge, 3,022 grams		
Distance from charge, 3,048 centimeters		
Overpressure, kilopascals	258.6	261.3
Impulse, kilopascal milliseconds	124.8	146.2
Distance from charge, 457.2 centimeters		
Overpressure kilopascals	90.3	100.6
Impulse, kilopascal milliseconds	86.2	106.9
Distance from charge, 609.6 centimeters		
Overpressure, kilopascals	48.9	46.2
Impulse, kilopascal milliseconds	62.7	77.2

(b) Octol is used as an oil well formation agent and in fragmentation and shaped charges. In fragmentation tests using a 105 millimeter M1 shell, 15 percent more fragments are produced and the average velocity of the fragments is 100 meters per second faster than with a similar shell loaded with composition B. This improvement is attributed to both the higher rate of detonation of octol and the greater density of octol which permits a greater weight of explosive in the same volume. Table 8-70 compares the performance of TNT, composition B, and octol in producing craters in a 105 millimeter shaped charge shell.

Table 8-70. Crater Volume in Mild Steel Targets

Depth of penetration in centimeters	Volume in cubic centimeters		
	TNT	Composition B	Octol
4	23.8	33.1	37.0
8	36.2	49.7	57.4
12	43.2	61.4	68.9
16	49.1	69.2	78.7
20	53.0	75.1	85.0
24	56.2	79.4	89.9
28	58.6	83.0	94.0
32	61.8	86.2	98.1
36	64.3	89.3	101.8
40	-	92.3	105.3
44	-	-	110.4

(c) The gap test results for 75/25 octol are given in table 8-71.

(d) As shown in figure 8-87, 75/25 octol has both good and bad properties. The threshold velocity for reaction is about 55 meters per second which is typical of TNT bonded cast explosives. On the other hand reaction levels become moderately high at relatively low velocity. The variability of results is less than that observed with 75/25 cyclotol. This data indicates 75/25 octol is rather difficult to ignite accidentially by mechanical means but capable of a large reaction once ignited under some conditions.

(e) In the manufacture of octols, TNT is melted in a steam jacketed kettle equipped with an agitator. The temperature of the TNT is maintained at about 100°C and water wet HMX is added slowly. Stirring is continued until the water is driven off. The kettle temperature is then reduced until a viscosity suitable for casting is obtained. The viscosity of the slurry has a strong dependence on the particle size distribution and polymorphic variety of HMX used. In order for the slurry to have an efflux time of less than 15 seconds the solid HMX must consist of the beta polymorph having particle diameters in the range of 500 to 800 microns. Even when octol is cast at a temperature of less than 90°C, there is a large amount of settling of HMX crystals while the charge is still molten. This can lead to erratic performance of the ammunition loaded. Several methods to prevent the settling are being considered. Casting temperature is kept as low as possible to prevent air entrapment in the cast. Figure 8-88 shows the DTA curve for 75/25 octol.

Table 8-71. Gap Test for 75/25 Octol

	Density	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.829	0	4.88
	1.541	15.8	10.90
LANL small scale gap test	1.810	1.1	0.56 - 0.71
LANL large scale gap test			
regular HMX	1.822 (cast)	0.7	49.45
large crystal HMX	1.815 (cast)	1.4	47.32
vacuum cast	1.795	2.0	43.56

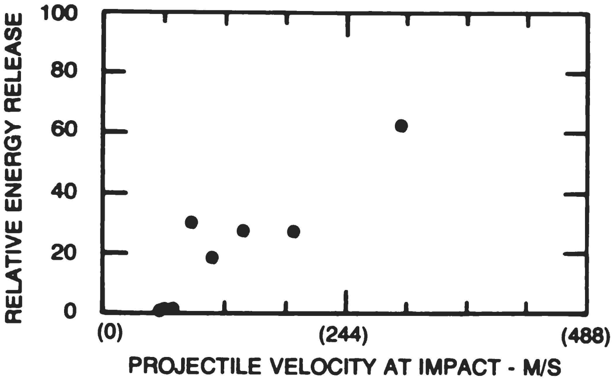


Figure 8-87. Susan test results for 75/25 octol.

(9) Pentolite.

(a) Pentolites are castable explosive mixtures containing PETN and TNT. The most commonly used blend consists of 50/50 PETN/TNT. Other blends such as 75/25, 40/60, 30/70, and 10/90 have been occassionally employed but the 50/50 blend is superior in the characteristics of sensitivity to initiation, brisance, and suitability for melt loading. 87 percent TNT and 13 percent PETN form a eutectic with a freezing point of 76.7°C. Cast 50/50 pentolite, therefore, consists of 42.2 percent PETN, and 57.8 percent of the eutectic mixture. 50/50 Pentolite has an oxygen balance to CO_2 of -42 percent, a heat of combustion of 1.549 kilocalories per gram, and a heat of formation of -23.4 to -24.3 kilocalories per gram. The heat of detonation with liquid water has been experimentally determined as 1.23 kilocalories per gram and the maximum calculated value is 1.53 kilocalories per gram. The heat of detonation with gaseous water has been experimentally determined as 1.16 kilocalories per gram and the maximum calculated value is 1.40 kilocalories per gram. The cast density of pentolites does not vary appreciably with blend composition. 50/50 Pentolite has a cast density of 1.63 to 1.67 grams per cubic centimeter while 10/90 pentolite has a cast density of 1.60 grams per cubic centimeter. The density of pressed pentolite is between 1.60 and 1.65 grams per cubic centimeter. Since pentolites are blends they are soluble in the same solvents as their constituent ingredients.

(b) Pentolite is manufactured by either of two methods. In the more modern, slurry method, the PETN is suspended by agitation in water heated above 80°C. TNT is then added. The temperature of the water causes the TNT to melt and coat the particles of PETN. The slurry is then cooled with rapid agitation, causing the TNT to solidify. The granules then are separated on a filter or in a centrifugal wringer and dried at a temperature below 75°C. In the coprecipitation method, the PETN and TNT are dissolved separately in acetone, the solutions are mixed and filtered, and the two explosives are precipitated simultaneously by pouring the solution into water with vigorous agitation. The precipitated solid is then separated and dried. The slurry method permits better particle size control than the coprecipitation method. Acetone is used in the slurry method for obtaining PETN of the desired particle size, but less acetone is used than in the coprecipitation method. The slurry method also takes less time per production cycle. Casting is usually accomplished at about 90°C. Constant stirring is required to keep the PETN suspended as only about 20 percent of the PETN dissolves at that temperature. Small elongated crystals are desirable for this operation to minimize settling of the PETN and prevent the production of nonuniform charges. At 90°C to 94°C PETN crystals retain their original shape characteristics since very little solution occurs. These crystals are enclosed by crystalline TNT. Added wax causes no obvious change in microstructure.

(c) Two grades of pentolite are used for military purposes. These differ only in that grade II material complies with a bulk density requirement. Grade I is used for melt loading, while grade II is used in the manufacture of pellets and the press loading of ammunition. The requirements are:

Volatile matter	Maximum, 0.5 percent	
Composition	PETN, 50±2 percent TNT, 50±2 percent	
Total acetone insoluble	Maximum, 0.04 percent	
Inorganic acetone insoluble	Maximum, 0.02 percent	
Grit	None	
Acidity or alkalinity	Maximum, 0.005 percent	
PETN granulation applicable to pentolite manufactured by the coprecipitation method		
Through sieve number	30	200
Percent, minimum	95	0
Percent, maximum	-	30
100°C vacuum stability test	Maximum 5 milliliters of gas	
Bulk density	Grade 11, 0.70-0.10 gram per milliliter	

(d) The Picatinny Arsenal impact apparatus and the Bureau of Mines apparatus yield conflicting results; 12 inches and 34 centimeters, respectively.The rifle bullet impact test confirms the more sensitive test result. The five second explosion temperature test result is essentially that of PETN. In the pendulum friction test pentolite is unaffected. The minimum detonating charges of lead azide and mercury fulminate required for pentolite are intermediate between those for PETN and TNT and are very close to that of tetryl. The gap test results are given in table 8-72.

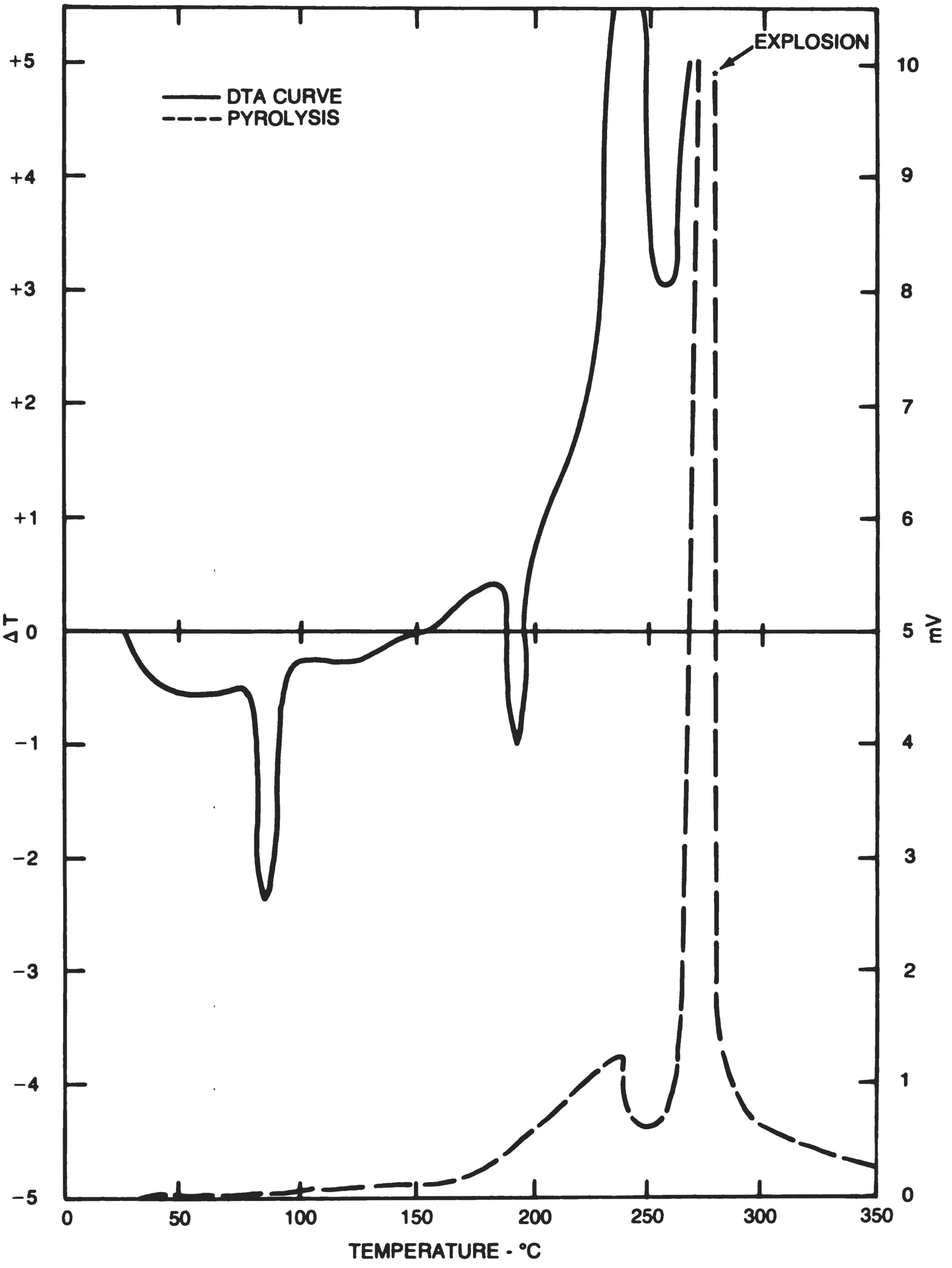


Figure 8-88. DTA curve for 75/25 octol.

Table 8-72. Gap Test Results for 50/50 Pentolite

	Density	Percent voids	Sensitivity in millimeters
NSWC small scale gap test	1.671	2.3	10.03
	1.363	30.3	12.45
LANL small scale gap test	1.700 (cast)	0.6	0.76-0.97
	1.676 (hot pressed)	2.0	3.12
	0.75	56.1	4.80
LANL large scale gap test	1.702	0.8	64.74
	1.635	4.4	68.66

The presence of rust or grit increases the sensitivity of pentolite. A mixture of equal weights of pentolite and dry rust has an impact test value of 21 centimeters compared with 32 centimeters for the pentolite used to make the mixture.

(e) Sand test shows 50/50 pentolite to be as brisant as tetryl and 114 percent as brisant as TNT. Fragmentation tests of shell charges, however, show pentolite to be 13 percent as brisant as TNT and plate dent tests indicate the ratio to be 126 percent. The approximate velocity of detonation as a function of packing density is given by the equation:

$$D = 5480 + 3100(p - l)$$

where D is in meters per second and p, the density, is in grams per cubic centimeter. This ideal velocity of detonation is applicable to charges with a diameter of one inch. The variation in detonation velocity as a function of temperature is given by the equation:

$$D - D_0 = (-0.4 \times 10^{-3})(T - T_0)$$

where T is in degrees centigrade and D is in millimeters per microsecond. D_0 is the initial detonation velocity at temperature T_0, and D is the detonation velocity at temperature T. The Chapman-Jouquet detonation pressure is 232 to 255 kilobars. In deflagration to detonation transfer studies with pentolite that is heavily confined and ignited by a hot wire, a low velocity detonation regime precedes steady state detonation for 30 to 80 microseconds. Compression waves precede the burning front in this predetonation region and appear to coalesce into a shock front. The Trauzl test indicates 50/50 pentolite is 122 percent as powerful as TNT while the ballistic mortar test indicates a power of 126 percent of TNT.

(f) Vacuum stability tests indicate 50/50 pentolite is slightly less stable than PETN although storage for two years at 65°C produces no excessive acidity or great deterioration of stability. 50/50 Pentolite withstands 10 remelting operations at approximately 98°C without becoming unduly instable or unduly acid, but subsequent storage at 65°C for six months renders the sample unduly acid. Slow decomposition starts at 110°C and is followed by the main pyrolysis reactions which generate NO_2 rapidly. The rate of the pyrolysis of the mixture is faster than that of either TNT or PETN. While storage at 65°C has only a limited effect on the chemical stability of pentolite, some exudation occurs for storage temperatures above 50°C. This may be due to the formation of a eutectic mixture of TNT and impurities in PETN. One of the impurities present in PETN is dipentaerythritol hexanitrate, which melts at 73.6°C and forms a eutectic mixture with TNT that freezes at only 57.9°C.

(g) Because of the somewhat lower stability and greater sensitivity of PETN as compared with RDX, the corresponding relationship of pentolite to composition B, and the tendency of pentolite to undergo some exudation above 50°C, pentolite has generally been replaced by composition B. Figure 8-89 shows the DTA curve for pentolite.

(h) The composition of pentolite is determined by extracting a weighed sample with chloroform saturated with PETN, drying the residue, and weighing. The weight of the residue and the loss in weight are calculated to percentage of PETN and TNT, respectively.

(i) Underwater blast for pentolite with a density of 1.6 grams per cubic centimeter are given by the equations:

$$\text{Peak pressure} = 2.25 \times 10^4 (W^{1/3}/R)^{1.3} \text{ psi}$$

$$\text{Impulse} = 2.18 W^{1/3} (W^{1/3}/R)^{1.05} \text{ psi-sec}$$

$$\text{Energy} = 3.27 \times 10^3 W^{1/3} (W^{1/3}/R)^{2.12} \text{ inch lb/inch}^2$$

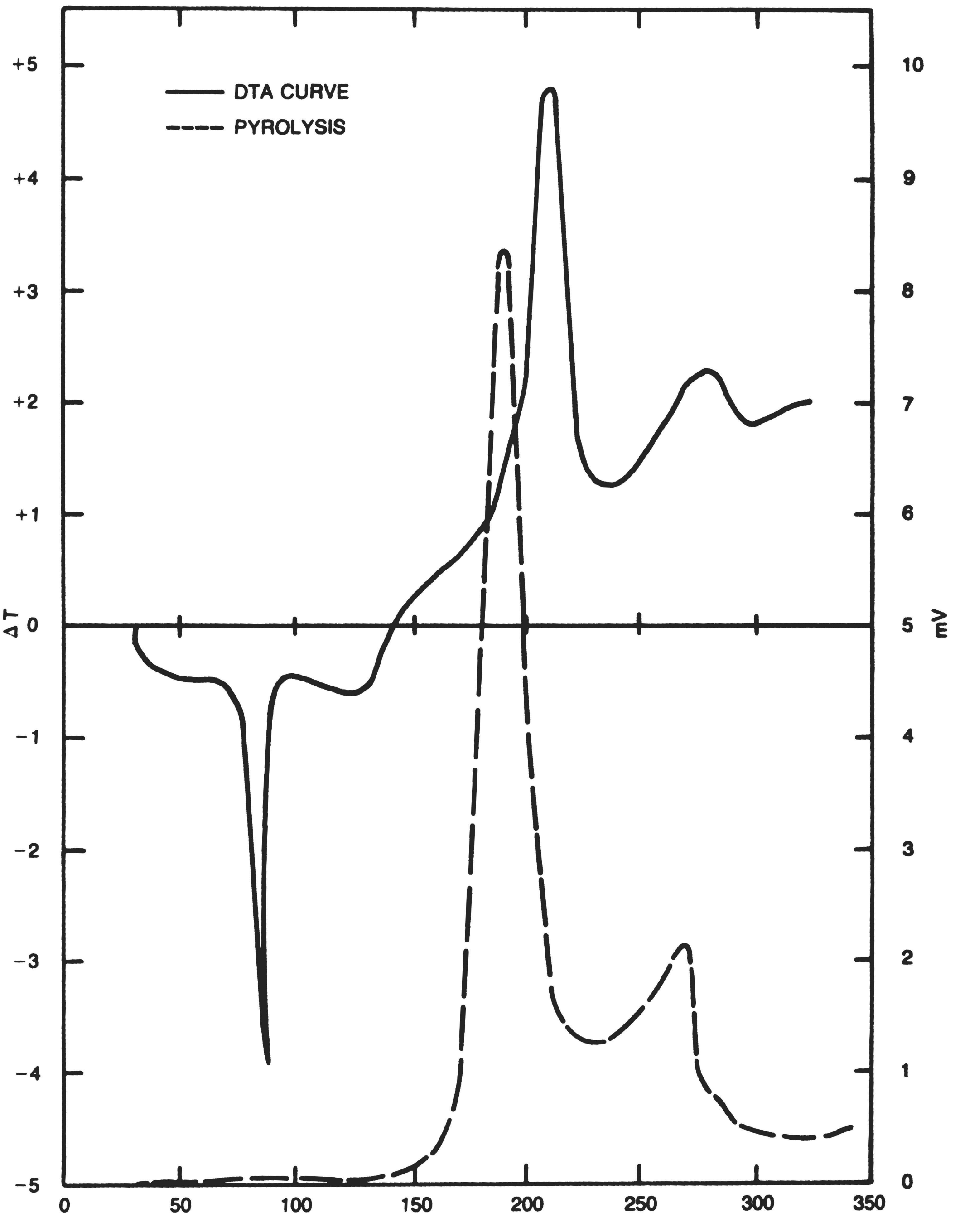


Figure 8-89. DTA curve for pentolite.

where *W* is the charge weight in pounds and *R* is the distance in feet from the center of a spherical charge. The ratio of underwater shock energy of pentolite to the total chemical energy is 0.57 to 0.59.

(10) Picratol.

(a) Picratol is a mixture of 52 percent ammonium picrate and 48 percent TNT. Molten TNT has little or no solvent action on ammonium picrate, and consequently, cast picratol consists essentially of a physical mixture of crystals of the two explosives. The density of cast picratol is 1.61 to 1.63. This permits a weight of charge almost equal to that of ammonium picrate pressed under 68,950 to 82,740 kilopascals (10,000 to 12,000 pounds per square inch). The solubility and reactivity characteristics of picratol are essentially that of the two ingredients.

(b) Picratol is manufactured by heating TNT to above 90°C in a steam jacketed melting kettle equipped with a stirrer. The ammonium picrate is added slowly, without preheating, with continuous agitation and this is continued for a short time after all the ammonium picrate has been added. The thick slurry is allowed to cool to about 85°C before being loaded into ammunition components. Like molten TNT, picratol undergoes marked contraction in volume upon solidification. The contraction is much less than in the case of TNT.

(c) The standard small scale impact tests indicate picratol to be as sensitive to impact as TNT, rather than ammonium picrate and large scale impact tests of cast charges confirm this. Pendulum friction tests show no difference between picratol, TNT, and ammonium picrate with respect to sensitivity to friction. When subjected to the rifle bullet impact test, picratol burns in about 40 percent of the trials but undergoes no detonation. Ammonium picrate burns in about 30 percent of the trials. The explosive temperature test value of picratol, 285°C, is less than that of ammonium picrate, 318°C, and much less than that of TNT, 475°C. Picratol is as insensitive to initiation as ammonium picrate, having a minimum detonating charge value of 0.06 gram of tetryl. The overall sensitivity of picratol, therefore, is not greater than that of TNT.

(d) 52/48 picratol is only 94 percent as brisant as TNT, as judged by the sand test, but the plate dent test indicates the two to be equally brisant, and the fragmentation of shell charges show picratol to be 102 percent as brisant as TNT. The rate of detonation of cast picratol is 101 percent that of cast TNT. Picratol and TNT are of equal power, as measured by the ballistic pendulum test, and have equal blast effects.

(e) The stability of picratol is very slightly less than that of either TNT or ammonium picrate as measured by vacuum stability tests at 100°, 120°, and 150°C. These test results may indicate slight reaction between the ammonium picrate and the molten TNT ingredients at the elevated temperatures of the tests. At ordinary temperatures, there is no evidence of such reaction and picratol appears to be of the same high order of stability as its ingredients.

(f) The composition of picratol can be determined by extracting a weighed sample with cold ether that has been saturated with ammonium picrate. The residue is dried and weighed and this and the loss in weight are calculated to percentage of ammonium picrate and TNT, respectively.

(11) Tetrytols.

(a) Tetrytols are light yellow to buff mixtures of TNT and tetryl. As is the case for tetryl, tetrytols are no longer used by the United States but are still being used by other nations including various NATO allies. Tetrytols resemble tetryl more closely than they resemble TNT. They are more powerful but less sensitive than TNT. Tetrytols can be cast into munitions, which is an advantage over press loading. Table 8-73 compares the physical characteristics of various tetrytol compositions. The pressed density listed is for material that passed through a number 100 US standard sieve and was subjected to a pressure of 20,685 kilopascals (3,000 pounds per square inch). 70/30 Tetrytol is the most commonly used form and has a voidless density of 1.71 grams per cubic centimeter. All of the tetrytols are subject to exudation above 65°C. TNT and tetryl form a eutectic mixture that has a freezing point of 67.5°C. The solubility characteristics and chemical reactivity of the tetrytols are essentially those of the individual ingredients.

(b) Tetrytol is manufactured by heating TNT in a melting kettle equipped with an agitator until all the TNT is melted and the temperature of the liquid slightly exceeds 100°C. The proper amount of tetryl is then added with continued stirring. Part of the tetryl dissolves in the TNT. The temperature is then allowed to decrease until the mixture has thickened somewhat and is considered to be of the maximum viscosity suitable for pouring in the melt loading operation. The tetrytol is then poured into the ammunition component or a mold. As cast, tetrytol is a mixture of tetryl and the TNT-tetryl eutectic. The eutectic contains approximately 55 percent tetryl.

Table 8-73. General Characteristics of Tetrytols

Percentage composition by weight	Cast density in grams per cubic centimeter	Pressed density in grams per cubic centimeter	Molecular weight	Oxygen balance to CO_2	Melting point °C	Former United States usage
80/20 Tetrytol	1.51	-	274	−52	68	not used
75/25 Tetrytol	1.59	1.34	270	−54	68	bursting charge, demolition explosive
70/30 Tetrytol	1.60	1.36	266	.55	68	bursting charge, burster charge in chemical shells
65/35 Tetrytol	1.60	1.38	264	−56	68	burster charge in land mines

(c) There is no difference in the impact sensitivity of 65/35, 70/30, or 75/25 tetrytol. All are less sensitive than tetryl and more sensitive than TNT. All tetrytols are unaffected by the steel and fiber shoes in the pendulum friction test. The rifle bullet impact test, in which a 30 caliber bullet is fired into the open end of a pipe confined charge, yields the following results:

	Unaffected percentage	Partially affected percentage
80/20 Tetrytol	80	20
75/25 Tetrytol	70	30
70/30 Tetrytol	45	55
65/35 Tetrytol	90	10

In a wax gap test 75/25 tetrytol is somewhat more sensitive than composition B, but appreciably less sensitive than pentolite. The following shows the minimum priming charge required for the tetrytols.

	Grams lead azide	Grams mercury fulminate
80/20 Tetrytol	0.17	0.22
75/25 Tetrytol	0.19	0.23
70/30 Tetrytol	0.22	0.23
65/35 Tetrytol	0.23	0.23

For a priming charge of diazodinitrophenol (DDNP) the minimum charge required is 0.19 grams for pressed 75/25 tetrytol at a density of 1.4 grams per cubic centimeter and 0.31 grams for cast 75/25 tetrytol.

(d) In the plate dent test the brisance of 75/25 tetrytol at densities of 1.66 grams per cubic centimeter and 1.62 grams per cubic centimeter is 118 percent and 114 percent of TNT, respectively. 70/30 Tetrytol at 1.60 grams per cubic centimeter has a brisance of 117 percent of TNT. The sand test indicates 70/30 tetrytol is 97.5 percent and 111 percent as brisant as tetryl and TNT, respectively. The following detonation velocities were measured in one inch diameter charges without confinement. For cast 75/25 tetrytol with a density range of 1.55 to 1.60 grams per cubic centimeter and an average of 1.57 grams per cubic centimeter, the measured detonation velocities ranged from 7,290 to 7,410 meters per second with an average of 7,350 meters per second. For cast 65/35 tetrytol with a density range of 1.56 to 1.61 grams per cubic centimeter and an average of 1.58 grams per cubic centimeter, the measured detonation velocities ranged from 7,310 meters per second to 7,370 meters per second with an average of 7,340 meters per second. The ballistic mortar test indicates 75/25 and 70/30 tetrytols are 122 percent and 120 percent of TNT, respectively.

(e) 70/30 Tetrytol is slightly less stable than tetryl at 100°C and higher temperatures, as shown by vacuum stability tests. However, at 65°C and lower temperatures, samples have been stored for two years with no change in stability, acid content, sensitivity, or brisance. Although tetryl undergoes partial decomposition on melting, the melting of tetrytol does not have the same effect. Tetrytol that has been melted and solidified 12 times shows no change in freezing point, sensitivity to impact, or 100°C vacuum stability test value although the temperature was each time raised to 107°C and maintained at that value for half an hour prior to solidification by cooling. Storage at 65°C causes some separation of an oily extrudate and distortion of blocks of tetrytol, so the maximum storage temperature is less than 65°C. This low storage temperature has caused the United States to discontinue the use of tetrytol. Tetrytol is incompatible with 3M adhesives EC8708 and EC1099. Dry tetrytol is compatible with copper, brass, aluminum, magnesium, stainless steel, mild steel coated with acid proof paint, and mild steel plated with copper, cadmium, zinc or nickel. Magnesium-aluminum alloys are slightly affected by dry tetrytol. Wet tetrytol is compatible with stainless steel and mild steel coated with acid proof black paint. Copper, brass, aluminum, magnesium, magnesium-aluminum alloy, mild steel, and mild steel plated with cadmium, copper, zinc, or nickel are slightly affected by wet tetrytol.

(f) The shaped charge effectiveness of 70/30 tetrytol at a density of 1.64 grams per cubic centimeter, as gauged in a constant volume test, is appreciably lower than composition B, cyclotol, and composition A, when all are at roughly equivalent packing densities. 60/40 Tetrytol is as efficient a shaped charge filler as 50/50 pentolite and somewhat better than TNT. Both 75/25 and 65/35 tetrytols are approximately 1.2 to 1.25 times more effective shaped charge fillers than TNT.

(g) Determination of the composition of a sample of tetrytol can be made by treating a weighed sample with sufficient boiling carbon tetrachloride to dissolve the TNT present, cooling to 0°C, evaporating a weighed portion of the solution to dryness, and correcting for the amount of tetryl dissolved by the carbon tetrachloride at 0°C.

(12) Tritonal.

(a) Tritonal is a silvery solid that contains:

TNT	80 percent
Flaked aluminum	20 percent

Metallic aluminum is insoluble in TNT so tritonal begins to melt at the melting point of TNT. Tritonal has a heat of combustion of 4,315 calories per gram per degree centigrade at constant pressure and a thermal conductivity of 0.0011 calories per gram per degree centigrade at 0°C. These values are 120 percent and 200 percent of those for TNT. At 20°C the calculated specific heat is 0.305 calorie per gram per degree centigrade. Like TNT, tritonal undergoes considerable expansion on melting and contraction on freezing. The solubility characteristics of tritonal are essentialy those of TNT. Tritonal is used as a filler in bombs and shells. The density of the cast material is 1.73 grams per cubic centimeter.

(b) The chemical reactivity of tritonal is that of TNT and aluminum. In addition in the presence of moisture, the TNT and aluminum undergo slight reaction with the evolution of gas. This is not of practical importance because of the very slight hygroscopicity of TNT and the fact that any moisture present is driven off by heat during the manufacture of tritonal.

(c) 80/20 Tritonal is manufactured from TNT and grained aluminum. The TNT and aluminum are run slowly through separate chutes into a steam heated melting kettle equipped with a stirrer which is kept in motion while the ingredients are being added. Heating and mixing are continued until all the TNT is melted, the temperature is greater than 81°C, and the fluidity of the mixture is considered satisfactory. The tritonal is then loaded by pouring into bombs, using at least the same precautions and techniques used in the melt loading of TNT.

(d) Although the pendulum friction test shows no measurable difference in sensitivity between tritonal and TNT, impact tests indicate tritonal to be somewhat more sensitive to impact that TNT and less so than tetryl. The rifle bullet impact test value for tritonal is more similar to that of tetryl than that of TNT. The explosion temperature test value of tritonal, 470°C, is almost identical with that of TNT. Liquid tritonal at 90°C is slightly more sensitive than the solid, as judged by rifle bullet impact tests. As indicated by the sand test, the minimum detonating charge of lead azide, 0.30 gram, is slightly greater than that required for TNT. Nonstandard initiation sensitivity tests with diazodinitrophenol as the initiator show tritonal and TNT to be of essentially the same sensitivity to initiation.

(e) The sand test indicates 80/20 tritonal is 108 to 114 percent as brisant as TNT. The plate dent test and the fragmentation test indicate a brisance of 93 percent and 91 percent of TNT respectively. The rate of detonation of cast tritonal is approximately 97 percent that of cast TNT. The heat of explosion of tritonal is 59 percent greater than that of TNT, but tritonal is only 124 percent as powerful as TNT, as measured by the ballistic pendulum test. The Trauzl test indicates tritonal is 153 percent as powerful as TNT.

(f) As tritonal has the same 150°C vacuum stability test value as TNT, aluminum and TNT do not react at that or lower temperatures. Tritonal, therefore, has the same stability as TNT, if free from moisture. Deterioration in the presence of moisture is not serious, probably because the formation of a layer of oxide on the surface of the particles of aluminum prevents or retards further reaction. Tritonal, like TNT, can undergo exudation if stored at elevated temperatures, but this tendency is less than that of TNT because of the presence of 20 percent by weight of metallic particles that tend to hold oily exudate by surface tension. This prevents the oily exudate from coalescing and exuding.

(g) When tested for blast effect, tritonal has a peak pressure of 113 percent of TNT and an impulse value of 118 percent of TNT.

(h) The composition of a sample of tritonal is determined by extracting a weighed sample with benzene, drying the residue, and weighing the sample. The loss in weight represents TNT and the weight of residue represents aluminum. Each is calculated to a percentage basis.

b. *Ternary Mixtures.*

(1) Amatex 20.

(a) Amatex 20 consists of:

RDX	40 percent
TNT	40 percent
Ammonium nitrate	20 percent

The mixture has a nominal density of 1.61 grams per cubic centimeter and is used as a filler in ammunition items.

(b) Amatex 20 is slightly less sensitive than TNT, with impact test results of 15 to 18 inches on the Picatinny Arsenal apparatus. In the rifle bullet impact test of 100 trials, six detonated low order, three burned, and the rest are unaffected. The relative gap test value is 105 percent of TNT. The five second explosion temperature is 240°C.

(c) The detonation velocity at 1.61 grams per cubic centimeter is 6,944 meters per second, although values of 6,830 meters per second at a density of 1.68 grams per cubic centimeter have been reported. A detonation pressure of 240 kilobars has been reported for a charge with a density of 1.68 grams per cubic centimeter. The ballistic mortar test indicates amatex 20 is 110 percent as powerful as TNT. Vacuum stability tests indicate amatex 20 is a highly stable explosive.

(2) Ammonal.

(a) Ammonals are mixtures containing, as principle ingredients, ammonium nitrate and powdered aluminum incorporated with high explosives such as TNT, DNT, and RDX. Powdered carbon was also used in earlier ammonals. In the ammonals that do not contain carbon, the mixture of ammonium nitrate and high explosive detonates developing a very high temperature which causes volatilization of the aluminum powder. Secondary reactions which follow involve the oxidation of the vaporized aluminum, either by the air, if oxygen is present, or by the products formed on detonation of TNT and ammonium nitrate according to the following equations:

$$3CO_2 + 2Al \longrightarrow Al_2O_3 + 3CO$$
$$3H_2O + 2Al \longrightarrow Al_2O_3 + 3H_2$$

Both these reactions are highly exothermic and develop much additional heat which causes greater expansion of the gases and consequently greater blast effect. Many different combinations of ingredients have been used, both militarily and commercially. The most recent United States military ammonal consists of 22 percent ammonium nitrate, 67 percent TNT, and 11 percent flaked aluminum. The oxygen balance of the compound is -55 percent to CO_2 and -22 percent to CO. The major use of this composition is as a projectile filler.

(b) As in the case of ammonium nitrate in amotols, the ammonium nitrate of ammonals might be hydrolyzed in the presence of moisture with the formation of ammonia but, due to the presence of aluminum, the amount of ammonia will be much greater. This amount might be as much as three times greater with ammonals than with 80/20 amatol. The ammonia reacts with TNT to form a complex addition compound which ignites at 67°C. In addition, the reaction between aluminum and moisture produces hydrogen, which is highly inflammable in oxygen or compounds containing oxygen.

(c) The general effect of incorporating aluminum in ammonium nitrate/TNT mixtures is as follows:

1 Increase in sensitivity to impact, friction, and rifle bullet impact.

2 Increase of temperatures of detonation from about 1,700°C to about 3,914°C to 4,000°C.

3 A 20 percent increase in power.

4 An increase in some cases of the total volume of gas evolved on detonation.

5 A decrease in velocity of detonation and brisance.

(d) Ammonals are manufactured by a method similar to that used for the preparation of amatols. The calculated amount of TNT is placed in a kettle that is equipped with an agitator and steam jacket. The temperature of the kettle is raised to between 85°C and 100°C. The calculated amount of ammonium nitrate, which was previously heated to the same temperature as the contents of the kettle, is then added. Finally aluminum powder is added and the mass cooled while continuing the agitation. If the ammonal mixture contains less than 40 percent TNT, press loading is necessary. For compositions with more than 40 percent TNT, the mixture can be cast loaded.

(e) In general, ammonals are fairly insensitive and stable mixtures but are hygroscopic due to the presence of ammonium nitrate. In the presence of moisture, ammonals react with the same metals as amatols: copper, bronze, lead, and copper plated steel.

(3) High Blast Explosives.

(a) Three compositions of high blast explosives are used as shown in table 8-74.

Table 8-74. High Blast Explosives

	HBX-1	HBX-3	H-6
RDX (including nitrocellulose, calcium chloride, and calcium silicate	40.4±3.0%	31.3±3.0%	45.1±3.0%
TNT	37.8±3.0%	29.0±3.0%	-
Aluminum	17.1±3.0%	34.8±3.0%	29.2±3.0%
Wax and lecithin	4.7±1.0%	4.9±1.0%	21.0±3.0%
Oxygen balance			
to CO_2	−68	−75	-
to CO	−35	−49	-
Density in grams per cubic centimeter:			
Theoretical maximum	1.76	1.882	-
Nominal	1.69 - 1.74	1.81 - 1.86	1.75
Heat of combustion in calories per gram	3,882	4,495	-
Heat of detonation in calories per gram:			
with liquid water	1,840	2,110	-
with gaseous water	1,800	2,110	-
Impact sensitivity as a percentage of TNT	75	70	-
Rifle bullet impact sensitivity as a percentage of TNT	75	80	-
Gap test sensitivity as a percentage of TNT	80	90	-
Fragmentation test in 90-mm, HE, M71 shell, number of fragments (TNT-703)	910	476	-
Brisance by sand test as a percent of TNT	102	93.5	-
Detonation velocity in meters per second	7,222	6,920	7,190
at density (in grams per cubic centimeter)	1.75	1.86	1.71
Detonation pressure in kilobar	-	-	23.7
Ballistic mortar:	133% TNT	111% TNT	-
% TNT in air (shock)	121	116	-
% TNT in air (impulse)	121	125	-
Heat test at 100°C:			
% Loss in 1st 48 hrs	0.058	0.70	-
% Loss in 2nd 48 hrs	0	0	-
Explosions in 100 hrs	None	None	-
Hygroscopicity, % loss (in 7 days at 30° and 95% relative humidity)	2.98	2.01	-

Table 8-74. *High Blast Explosives (Cont)*

	HBX-1	HBX-3	H-6
Blast effects:			
% TNT under water (shock)	111	101	-
% TNT under water (bubble)	145	191	-

(b) HBX explosives are prepared by melting TNT in a steam jacketed kettle equipped with a mechanical stirrer. Water wet RDX is added slowly with stirring and heating until all the water is evaporated. Powdered aluminum is added and the mixture is stirred until uniform. D2 wax and calcium chloride are then added and the mixture is cooled to a temperature suitable for casting. HBX can also be prepared by adding the calculated amount of molten TNT to molten composition B to obtain the desired proportion of RDX and TNT. Then the appropriate weights of other ingredients are added to complete the composition. D2 wax, also referred to as composition D2, consists of 84 percent paraffin wax, 14 percent nitrocellulose, and 2 percent lecithin. Figure 8-90 shows the DTA curve for H6.

(4) HMX, TNT, and aluminum mixture 3 (HTA-3).

(a) There are two types of HTA-3 as shown in table 8-75:

Table 8-75. HTA-3 Composition

	Type I	Type II
Percent HMX	49	49
Percent TNT	29	28.65
Percent aluminum	22	22
Percent calcium silicate	-	0.35

The mixture has an oxygen balance to CO_2 of −21 percent and a specific gravity of 1.90 when cast. The heat of combustion is 3,687 calories per gram and the heat of explosion is 1,190 calories per gram. The specific heat is 0.245 calories per gram per degree centigrade.

(b) To manufacture HTA-3, TNT is heated to about 100°C in a steam jacketed kettle equipped with an agitator. Water wet HMX is added slowly to the molten TNT. Stirring and heating are continued until all the water is evaporated. Aluminum powder is then added and the mixture is cooled with continued stirring. When a satisfactory viscosity is obtained the HTA-3 is cast.

(c) The impact test result on the Picatinny Arsenal apparatus is 17 inches for a 25 milligram sample. In the pendulum friction test HTA-3 is unaffected by either the steel or fiber shoe. The rifle bullet impact test indicates a relatively high sensitivity. 90 percent of the trials explode and the other 10 percent burn. HTA-3 requires a minimum detonating charge of 0.30 grams of lead azide. The five second explosion temperature is about 370°C.

(d) In the sand test, HTA-3 crushes 61.3 grams of sand indicating a brisance of 128 percent of TNT for an unconfined cast charge 2.54 centimeters in diameter. The detonation rate is 7,866 meters per second. In the 120°C vacuum stability test, 0.37 cubic centimeters of gas are evolved in 40 hours from a one gram sample.

(5) Minol-2.

(a) Minols are mixtures of TNT, ammonium nitrate, and aluminum. Minol-2 which is the type currently used, has the following composition:

TNT	40±3 percent
Ammonium nitrate	40±3 percent
Aluminum	20±3 percent

The explosive is a grey solid with a cast density of 1.62 to 1.74 grams per cubic centimeter. The heat of formation is 46.33 kilocalories per mole. The heat of detonation is 2.01 kilocalories per gram with liquid water and 1.86 kilocalories per gram with gaseous water. The heat of combustion is 3,160 calories per gram. At a density of 1.74 grams per cubic centimeter and a temperature of −5°C, minol-2 has a specific heat of 0.30 calories per gram per degree centigrade. Minols are used in four types of ordnance: underwater depth bombs, block buster bombs, concrete fragmentation bombs, and general purpose bombs. In underwater ordnance the confinement effects of the water somewhat offset the effects of the relatively low detonation velocity. In block buster bombs a sustained and powerful impulse is more destructive than a high peak pressure. In concrete fragmentation bombs, the high impulse will impart a satisfactory velocity to the fragments but will not pulverize the concrete.

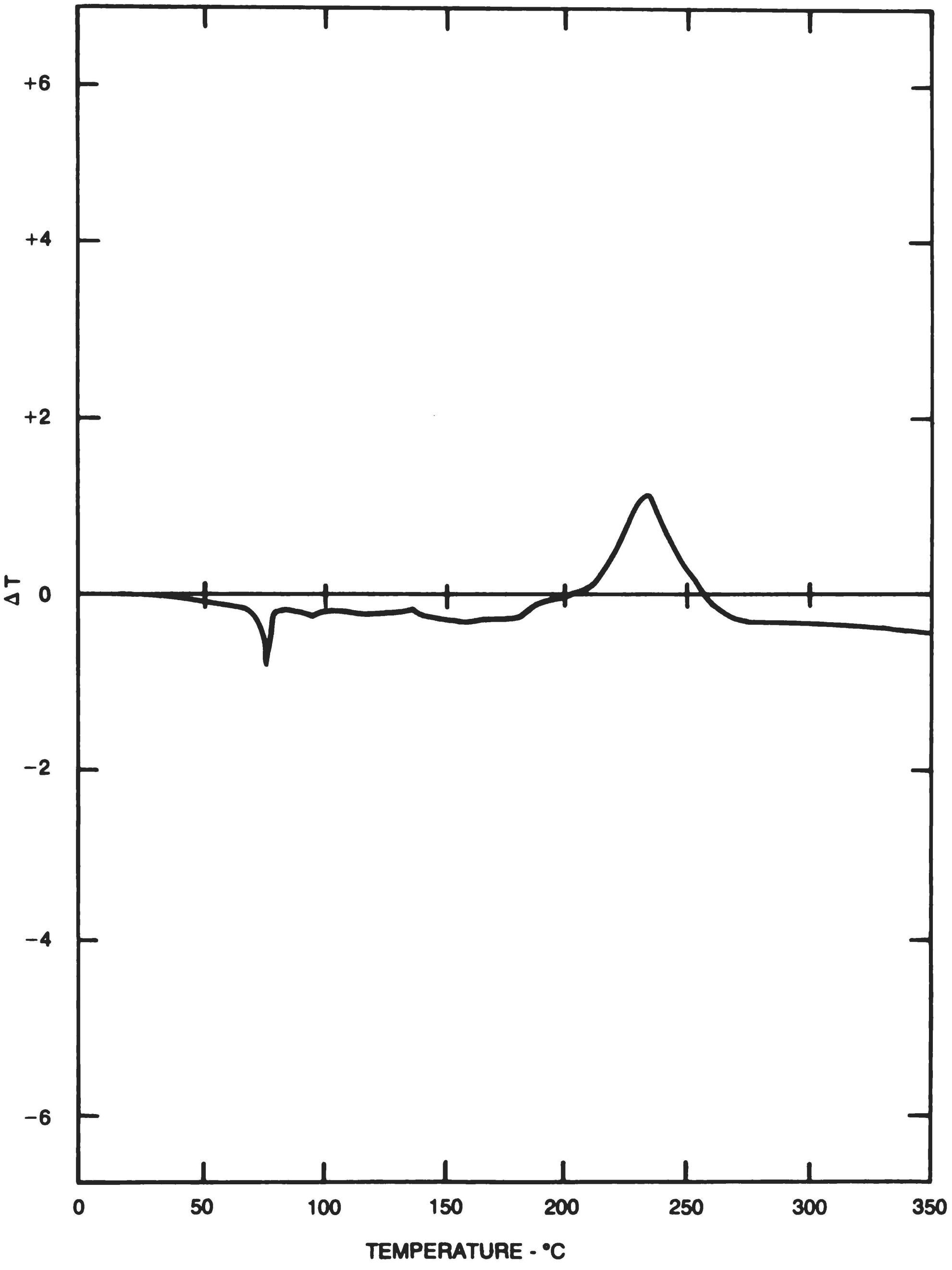


Figure 8-90. DTA curve for H6.

(b) Minols are manufactured by adding appropriate quantities of dry ammonium nitrate and aluminum powder to molten TNT at about 90°C under agitation. Originally the aluminum was in the form of a fine powder, however, such a fine degree of subdivision is not necessary. The larger aluminum particles do not cause any loss of performance and have a smaller surface area per unit volume and so reduce the reactivity of the aluminum in the mixture and increase the stability.

(c) The impact sensitivity, as measured by the Picatinny Arsenal apparatus with a 17 milligram sample, is 13 inches. Using the Bureau of Mines apparatus, with a 20 milligram sample, the drop height is 35 centimeters. In the rifle bullet test 62 percent of the trials were affected. The five second explosion temperature is 224°C to 260°C. The flammability index is 100. The 50 percent level in the booster sensitivity test is 3.71 centimeters using a 100 gram tetryl pellet and minol-2 with a density of 1.74 grams per cubic centimeter. The relative gap test value is 120 percent of TNT.

(d) In the sand test minol-2 crushes 40.5 grams of sand indicating a brisance of 86 percent of TNT. The plate dent test indicates a brisance of 66 percent of TNT. In the fragmentation test the fragment velocity is about the same as for TNT. The detonation velocity at a density of 1.62 to 1.68 grams per cubic centimeter is 5,900 meters per second and at 1.77 grams per cubic centimeter is 6,200 meters per second. The ballistic pendulum test and the Trauzl test indicate that minol-2 is 143 percent and 165 percent as powerful as TNT, respectively.

(e) In the 100°C vacuum stability test minol-2 does not evolve any gas in 48 hours, but in the 120°C test a 5.0 gram sample evolves 2.1 cubic centimeters of gas in 40 hours. When stored in munitions, minols tend to spew or ooze. The cause of this problem has not been determined at the present time. Minol-2 expands more but extrudes less than TNT or tritonal under similar temperature cycling conditions. Dry minol-2 is stable and unreactive when cycled between ambient temperature and 100°C. If the minol-2 is prepared with dry ammonium nitrate there is no phase change under 50°C. However, when ammonium nitrate that is not thoroughly dry is used, the minol-2 will exhibit a reversible phase transition beginning at 32°C, producing volume changes of about 3.8 percent. These volume changes could cause microcrystalline cracks and pores which could reduce detonation velocity and mechanical strength.

(6) Torpex.

(a) Torpex is a silvery white solid when cast. The composition of torpex is 41.6 percent RDX, 39.7 percent TNT, 18.0 percent aluminum powder, and 0.7 percent wax. The density of cast torpex is 1.82 grams per cubic centimeter. At 15°C the specific heat is 0.24 calories per gram per degree centigrade. When the explosive undergoes solidification, there is a decrease in volume of six percent. Torpex is nonhygroscopic where exposed to air of 90 percent relative humidity at 30°C. When heated, torpex undergoes partial melting near the melting point of TNT. The partially liquid explosive has viscosity values of 4.5 and 2.3 poises at 83°C and 95°C, respectively. This is approximately the viscosity of glycerin at room temperature.

(b) Torpex is manufactured by melting TNT in a steam jacketed kettle equipped with a stirrer and heating the molten TNT to approximately 100°C. RDX that is slightly wetted with water is added slowly and mixing and heating are continued until all water has been driven off. Grained aluminum is added and the mixture is stirred until uniformity is obtained. The mixture is then cooled, with continued stirring, until the viscosity is suitable for pouring. The aluminum tends to settle out of the torpex in large castings if the liquid is allowed to set too long. To prevent this, a portion of the casting is poured and allowed to cool to the point of crusting over before another layer of torpex is poured. Torpex of slightly different composition can be manufactured by melting 12.5 parts of TNT, adding 69.5 parts of composition B and, after heating and stirring, adding 18 parts of aluminum. This illustrates the fact that torpex is essentially aluminized 50/50 cyclotol.

(c) Torpex is considerably more sensitive to impact than composition B and undergoes partial or complete explosions in all trials in the rifle bullet impact test. Torpex is more impact sensitive at higher temperatures as is indicated by the following data.

Temperature in degrees centigrade	Impact sensitivity
25	15
32	7
104	8

The five second explosion temperature test value, 260°C, is the same as that of RDX. Cast torpex is much more sensitive to initiation than cast TNT and pressed torpex is as sensitive as RDX to initiation by mercury fulminate.

(d) Sand tests indicate torpex to be 98 to 99 percent as brisant as RDX and 122 percent as brisant as TNT. As judged by plate dent test values, cast torpex is 120 percent as brisant as TNT. Fragmentation tests of shell charges indicate torpex to be 126 percent as brisant as TNT and, therefore, inferior to composition B in this respect. The rate of detonation of cast torpex is 110 percent that of TNT. The heats of combustion and explosion are 3,740 calories per gram and 1,800 calories per gram, respectively. Trauzl tests for the heat of explosion indicate torpex to be 161 to 162 percent as powerful as TNT, but the ballistic pendulum test gives torpex a superiority of only 34 percent. Torpex has a great blast effect. The following blast comparisons are relative to TNT as 100:

	Air	Air, confined	Underwater
Peak pressure	122	-	116
Impulse	125	116	127
Energy	146	-	153

(e) Vacuum stability tests show torpex to be of the same order of stability as composition B. Storage at 75°C for one month or 65°C for 13 months has no effect on the stability of torpex. In the 100°C heat test there is no weight loss in the first 48 hours, 0.10 percent weight loss in the second 48 hours, and there is no explosion in 100 hours. Torpex, therefore, has high stability. However, moisture reacts with the ingredients in torpex causing the evolution of gas which can cause rupture of the ammunition component or cause an increase in the sensitivity of torpex to shock. For this reason all moisture must be removed during manufacture.

(f) The composition of torpex can be determined by extracting a weighed sample with cold benzene or toluene that has been saturated with RDX. The residue is dried and weighed and the loss in weight is calculated to percentage of TNT. The dried residue is extracted with hot acetone, dried, and weighed. The loss in weight is calculated to percentage of RDX. The weight of the final residue is calculated to percentage of aluminum.

(g) The shaped charge efficiency of torpex relative to TNT as 100 is:

	Glass cones	Steel cones
Hole volume	150	145
Hole depth	127	131

c. *Quanternary Mixtures.*

(1) Depth bomb explosive (DBX) is the only explosive covered under quanternary mixtures. DBX consists of:

TNT	40 percent
RDX	21 percent
Ammonium nitrate	21 percent
Aluminum	18 percent

DBX was developed to replace the more sensitive torpex. As the name indicates, the primary use of DBX is in depth charges. The mixture is a grey solid that is slightly hygroscopic and, except for the aluminum, is soluble in acetone. The density of the cast material is from 1.61 grams per cubic centimeter to 1.76 grams per cubic centimeter. The method of manufacture is similar to that of torpex except that casting is done at 90°C to 95°C.

(2) The impact sensitivity of DBX is slightly less than that of TNT; 10 inches on the Picatinny Arsenal apparatus versus 14 inches for TNT. In the rifle bullet impact test about 49 percent of the samples exploded from the impact of a 30 caliber bullet at a distance of 2,743 meters (90 feet). The five second explosion test value is 200°C. The minimum detonating charge is 0.20 grams of lead azide and 0.10 grams of tetryl.

(3) The sand test results indicate a brisance of 112 percent of TNT. The detonation velocity is 6,630 meters per second for a density of 1.65 grams per cubic centimeter and 6,800 meters per second at a density of 1.76 grams per cubic centimeter. By the ballistic mortar test the power of PBX is 146 percent of TNT. For the 100°C vacuum stability test, 0.6 cubic centimeters of gas are evolved in 40 hours. The energy of the air blast is 138 percent of TNT and the energy of the water blast is 143 percent of TNT.

d. *Plastic Bonded Explosives (PBX).*

(1) PBX is a term applied to a variety of explosive mixtures which have high mechanical strength, good explosive properties, excellent chemical stability, relative insensitivity to handling and shock, and high thermal input sensitivity. The detonation velocity of PBX's is usually above 7,800 meters per second, the average autoignition temperature is above 250°C and the shock sensitivity is usually 10 to 40 percent above that required for detonating the basic explosive. PBX's contain a large percentage of basic explosives such as RDX, HMX, HNS, or PETN in intimate mixture with a polymeric binder such as polyester, polyurethane, nylon, polystyrene, various types of rubbers, nitrocellulose, or teflon. In some instances a plasticizer such as dioctylphthalate (DOP), DPA, or butyldinitrophenylamine (BDNPA) is included in the ingredients as well as a fuel such as powdered aluminum or iron.

(2) Much of the advantage stemming from the use of PBX lies in the simplicity of the technique of end item manufacture. About half of the developed PBX composites are used to directly cast end items. For this procedure no elaborate melting equipment or controlled cooling cycles are required. All operations may be conducted at ambient temperatures or, in some instances, can even be carried out in the field. However, where extraordinary mechanical strength is required or where complicated shapes are desired, a pressing or injection technique is applied using a molding powder or slurry of the PBX. The final PBX product not only exhibits excellent technical properties but also has the economical advantages of low processing costs and the ready availability of all constituents from commercial sources. In currently evolved compositions, recycling and disposal present no special difficulties because thermally degradable binders are used. Ideally, the binders undergo controlled thermal degradation so that the material can be easily removed from explosive casings for the purpose of efficient recycling of the base explosive or low pollution disposal of the entire item.

(3) Several manufacturing procedures are currently used to produce PBX's. One of these techniques is that of casting. This procedure, at first glance, merely involves combining a dried explosive, such as HMX, with binder constituents and curing initiators in a mixing vessel, blending to desired homogeneity, then casting into a given warhead or other ordnance item. Unfortunately, there are hazards associated with the drying of large quantities of explosives such as HMX or RDX. Hence, a desensitizing procedure must be added for production-scale operations. This procedure involves coating the water wet HMX or RDX with the alkyd or polyester portion of the binder. The resulting lacquer is added slowly to an aqueous slurry of the HMX or RDX. Agitation at 250 revolutions per minute in the presence of water causes the resin to precipitate onto the surface of the HMX or RDX, producing an insensitive powder which may be safely dried, handled, shipped, and stored until ready for use in the final PBX composition. The precoated explosive is then combined in a mixing kettle with sufficient copolymer to constitute the final binder composition. At this point an accelerator such as cobalt naphthenate is added. The mixture is then stirred until homogeneous, at first under ambient pressure and finally in a partial vacuum to remove entrapped air. A curing agent such as methyl ethyl ketone peroxide is then added. After another short mixing period, the explosive composition is poured into the desired mold. Vacuum casting has not been found necessary to obtain good density provided that the mold design is not too intricate or the height-to-diameters ratio not too great. Another method of casting is called injection molding. This method is used to produce intricate shaped or small diameter castings. The PBX usually employed with this technique has a high solid content of explosive such as PETN, which provides for steady state detonation in small cross-sectional channels or tubes. This method was developed by the Navy to provide explosive logic links of less than .25 centimeters in diameter. Figure 8-91 illustrates the injection molding process. The technique of injection molding involves movement of explosive material at room temperature into a cavity or tubing from a reservoir. This is accomplished by applying about 82,740 kilopascals (12,000 pounds per square inch) to the piston. This forces the explosive into the cavity or tube. When the accepting device is full, pressure on the piston is relaxed and flow stops. The device is then removed and set aside to allow the explosive to polymerize into an elastic, rubber-like solid. A second manufacturing technique produces a molding powder which is pressed into the desired end item shape under pressure in excess of 206,850 kilopascals (30,000 pounds per square inch). A slurry method can be used to prepare RDX type PBX's. In this method 42.5 grams of polystyrene and eight cubic centimeters of dioctylphthalate were dissolved in 200 cubic centimeters of toluene in a lacquer dissolver. Steam is introduced into the jacket until the temperature is 65°C. The lacquer is agitated constantly then added to a granulator. This lacquer contains a four to one ratio of plastic-plasticizer to toluene. The granulator which is agitated at 400 revolutions per minute, contains 450 grams of RDX and 4,500 grams of water which has been heated to 75°C. The lacquer solution is poured into the granulator followed by a solution of gelatin in water. Mixing is continued for five minutes to insure the RDX is well dispersed. Granulation takes place at this point. Steam is introduced into the jacket again to distill the solvent until the temperature reaches 98°C. Cooling water is then run into the jacket to cool the batch to 40°C. The coated material from the granulator is collected on a Buchner funnel and dried in a tray at 70°C for 24 hours.

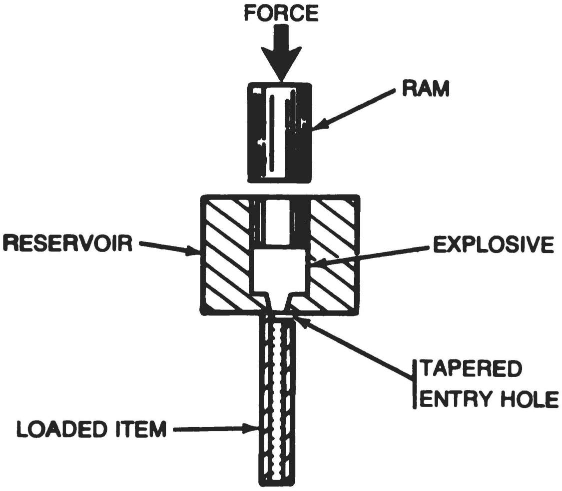


Figure 8-91. Injection loading operation.

(4) Table 8-76 lists the composition of the PBX's currently produced and used for military purposes.

Table 8-76. PBX Compositions

Designation	Composition
PBXN-4	94 percent DATB 6 percent nylon
PBXN-5	95 percent HMX 5 percent copolymer of vinylidene fluoride and hexafluoropropylene
PBXN-6	95 percent RDX 5 percent copolymer of vinylidene fluoride and hexafluoropropylene
PBXN-201	83 percent RDX 12 percent copolymer of vinylidene fluoride and hexafluoropropylene 5 percent polytetrafluoroethylene (teflon)
PBX-0280	95 percent RDX 5 polyethylene binder
PBX Type I	90 percent RDX 8.5 percent polystyrene 1.5 percent Dioctylphthalate (DOP)
PBXC-116	86 percent RDX 14 percent elastomeric binder
PBXAF-108	82 percent RDX 16 percent plasticizer 2 percent binder

PBXN-5 is also known as LX-10-0. This compound has blue-green spots on a white background. The theoretical maximum density is 1.896 grams per cubic centimeter with a nominal density of 1.86 to 1.87 grams per cubic centimeter. The melting point, with decomposition, is greater than 250°C, and the heat of formation is −31.4 calories per gram. The heat of detonation with liquid water is 1.55 kilocalories per gram and the heat of detonation with gaseous water is 1.42 kilocalories per gram. In the LANL small scale gap test a hot pressed charge of density 1.872 grams per cubic centimeter and a pressed charge of density 1.857 grams per cubic centimeter had 50 percent points of 2.25 ± .25 millimeters and 2.29 millimeters, respectively. Figure 8-92 shows the DTA curve for PBXN-5.

e. *Industrial Explosives.*

(1) Dynamites.

(a) Military operations frequently necessitate excavation, demolition, and cratering operations for which the standard high explosives are unsuited. Recourse is made to commercial and special compositions. Commercial blasting explosives, with the exception of black powder, are referred to as dynamites although in some cases they contain no nitroglycerin.

(b) Nobel gave the name dynamite to mixtures of nitroglycerin and kieselguhr, the strength of the dynamite being indicated by the percentage of nitroglycerin in the mixture. Kieselguhr is a chemically inert but porous material. Nitroglycerin absorbed by kieselguhr is much safer to handle than the unabsorbed material. Later, even stronger dynamites were made by substituting sodium nitrate and a combustible absorbent, such as wood pulp, for the kieselguhr. The resulting composition was called an active dope dynamite. Subsequently, the replacement of part of the nitroglycerin and sodium nitrate by ammonium nitrate brought into existence the less costly ammonia dynamites that are notable for their great heaving rather than shattering effects. The replacement of nitroglycerin in dynamite by nitrostarch resulted in the development of a class of dynamites free from some of the objectionable characteristics of nitroglycerin dynamites. While the active dope and ammonia dynamites are hygroscopic and desensitized by water, necessitating a moistureproof wrapper, a waterproof composition termed blasting gelatin is obtained by colloiding nitrocellulose with nitroglycerin. When mixtures are made of 88 to 92 percent of nitroglycerin and 8 to 12 percent of nitrocellulose having a nitrogen content of about 12 percent, a relatively tough material is formed. Blasting gelatins are particularly adapted to deep-water blasting. By including some nitrocellulose in the compositions of active dope dynamites, the so-called gelatin dynamites were formulated.

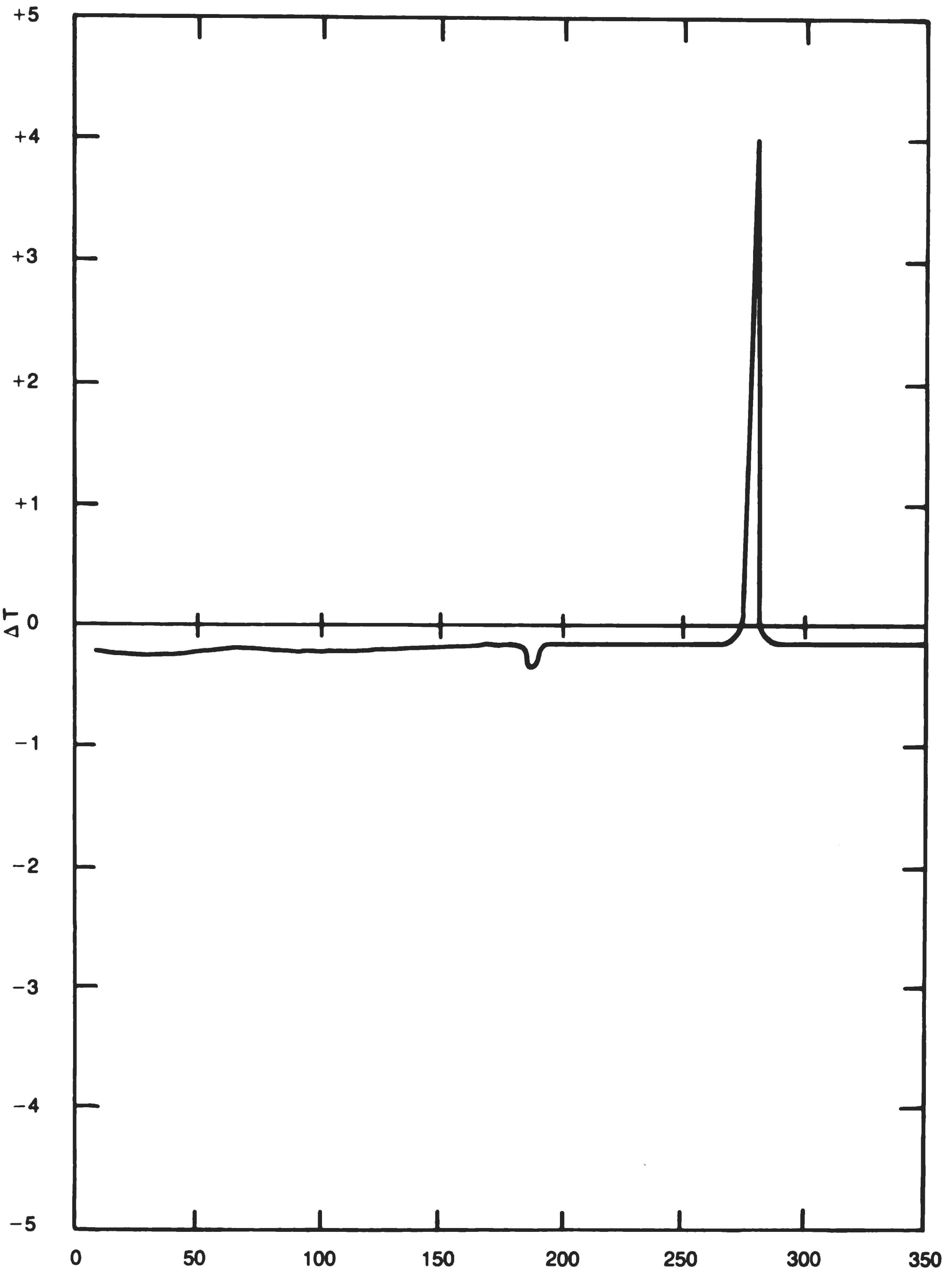


Figure 8-92. DTA curve for PBXN-5.

These possess greater density and water resistance than straight active dope dynamites and so are more suitable for use under wet conditions.

(c) The cost of glycerin and the tendency of nitroglycerin to freeze at some atmospheric temperatures prompted the partial replacement of nitroglycerin by antifreeze materials such as nitrated diglycerin, sugars, and glycols. Antacid materials such as calcium carbonate or zinc oxide have been added to most dynamite compositions to neutralize any acidity developed during storage. The inclusion of special purpose ingredients such as sulfur, ferrosilicon, alum, nitrotoluenes, sodium chloride, copper sulfate, etc and the substitution of starch, ground peanut hulls, vegetable ivory, etc, for wood pulp have further increased the complexity of dynamite compositions. Usually, they are formulated so as to have certain rate of detonation and heaving force values that render them suitable for various types of blasting operations. At the same time care must be taken that the compositions are oxygen balanced when the paraffined paper wrapper is taken into consideration. Compositions overbalanced with respect to oxygen produce nitrogen oxides on detonation while underbalanced compositions produce some carbon monoxide instead of carbon dioxide. While many of the commercial dynamites are given strength designations on a percentage basis, this no longer means that they contain that percentage of nitroglycerin or have the same characteristics as a mixture of kieselguhr and nitroglycerin containing that percentage of nitroglycerin. Representative compositions and characteristics of the various types of dynamite are given in table 8-77.

Table 8-77. Compositions[1] and Characteristics of Dynamites

Strength of dynamite, percent	20	30	40	50	60	100
Straight dynamites:						
Nitroglycerin	20.2	29.0	39.0	49.0	56.8	-
Sodium nitrate	59.3	53.3	45.5	34.4	22.6	-
Carbonaceous fuel	15.4	13.7	13.8	14.6	18.2	-
Sulfur	2.9	2.0	-	-	-	-
Antacid	1.3	1.0	0.8	1.1	1.2	-
Moisture	0.9	1.0	0.9	1.2		
Rate of detonation, m/sec	3,600	4,300	4,800	5,150	5,900	-
Ballistic pendulum, percent TNT	83	90	94.5	102.5	114	-
Ammonia dynamites:						
Nitroglycerin	12.0	12.6	16.5	16.7	22.5	-
Sodium nitrate	57.3	46.2	37.5	25.1	15.2	-
Ammonium nitrate	11.8	25.1	31.4	43.1	50.3	-
Carbonaceous fuel	10.2	8.8	9.2	10.0	8.6	-
Sulfur	6.7	5.4	3.6	3.4	1.6	-
Antacid	1.2	1.1	1.1	0.8	1.1	-
Moisture	0.8	0.8	0.7	0.9	0.7	-
Rate of detonation, m/sec	2,700	-	3,300	3,900	4,600	-
Ballistic pendulum, percent TNT	81	-	91	99	109	-
Gelatin dynamites:						
Nitroglycerin	20.2	25.4	32.0	40.1	49.6	91.0[2]
Sodium nitrate	60.3	56.4	51.8	45.6	38.9	-
Nitrocellulose	0.4	0.5	0.7	0.8	1.2	7.9
Carbonaceous fuel	8.5	9.4	11.2	10.0	8.3	-
Sulfur	8.2	6.1	2.2	1.3	-	-
Antacid	1.5	1.2	1.2	1.2	1.1	0.9
Moisture	0.9	1.0	0.9	1.0	0.9	0.2
Rate of detonation, m/sec	4,000	4,600	5,150	5,600	6,200	7,400
Ballistic pendulum, percent TNT	70 - 74	79	84.5 - 86	90.5 - 93	99 - 101	143

Table 8-76. Compositions[1] and Characteristics of Dynamites (Cont)

Strength of dynamite, percent	20	30	40	50	60	100
Ammonia gelatin dynamites:						
Nitroglycerin	-	22.9	26.2	29.9	35.3	-
Sodium nitrate	-	54.9	49.6	32.0	33.5	-
Ammonium nitrate	-	4.2	8.0	13.0	20.1	-
Nitrocellulose	-	0.3	0.4	0.4	0.7	-
Carbonaceous fuel	-	8.3	8.0	8.0	7.9	-
Sulfur	-	7.2	5.6	3.4	-	-
Antacid	-	0.7	0.8	0.7	0.8	-
Moisture	-	1.5	1.4	1.6	1.7	-
Rate of detonation, m/sec	-	4,400	4,900	5,300	5,700	-
Ballistic pendulum, percent of TNT	-	83	88	92	97.5	-

[1] Percent by weight

[2] Blasting gelatin

(d) In addition to military dynamite (h below), dynamites of the types described may be used for military operations and are procured as commercial items. A composition having great heaving force and relatively low rate of detonation is preferable for blasting soft rock or earth, while a gelatin dynamite of low heaving force and high rate of detonation is used for hard tough rock.

(e) A special demolition explosive standardized shortly before World War II is based on nitrostarch instead of nitroglycerin. The explosive is pressed into 1/4-pound pellets which are covered with paper and one pound packages of the pellets are wrapped in paper with markings indicating the location of holes for blasting caps in the pellets. The composition used is as follows:

	Percent
Nitrostarch	34.5 ±2.5
Barium nitrate	43.5 ±1.5
TNT	15.0 ±2.0
Aluminum	3.0 ±1.0
Graphite	2.0 ±1.0
Coal dust	1.5 ±0.5
Paraffin	0.6 ±0.6
Dicyandiamide	1.0 ±0.5
Moisture	0.75±0.75

The barium nitrate is coated with the paraffin before the ingredients are mixed together and pressed into pellets. The composition must not undergo ignition or explosion when heated at 100°C for 48 hours and must have a density of 1.75±0.10 when pressed.

(f) Nitrostarch demolition explosive is sensitive with respect to crumbling or breaking action. No explosions occur in the pendulum friction test but explosions do occur in the rifle bullet impact test. The initiation sensitivity is slightly greater than that of TNT. The sand test indicates a brisance of 90 percent of TNT and the ballistic pendulum test indicates a power of 96 percent of TNT. The explosive is hygroscopic to the extent of 2.1 percent when exposed to air of 90 percent relative humidity at 30°C. Long term storage tests indicate a satisfactory stability. Some volatilization, rather than decomposition, occurs in the 100°C heat test in 96 hours. A weight loss of one percent with no signs of deterioration is reported in the 75°C international test.

(g) During World War II, a cratering explosive with the following composition was used.

	Percent
Ammonium nitrate	86.6
Dinitrotoluene	7.6
Ferrosilicon	5.7
Red dye	0.1

This inexpensive and easily manufactured explosive is very insensitive to shock and initiation, has a low rate of detonation but high heaving force value, and is very stable. As it is somewhat hygroscopic in spite of the moistureproofing action of the dinitrotoluene, the explosive is packed in hermetically sealed containers.

(h) Military dynamite M1, M2, and M3 is a medium velocity (6,096 meters per second) blasting explosive in three cartridge sizes. Military dynamite M1, M2, and M3 has been standardized for use in military construction, quarrying, and service demolition work. The explosive composition is packaged in standard dynamite cartridge waxed-paper wrappers. The models differ only in the cartridge size. Cartridges are 1 1/4 inches in diameter by 8 inches long for the M1, 1 1/2 inches in diameter by 8 inches long for the M2, and 1 1/2 inches in diameter by 12 inches long for the M3. The composition used is:

	Percent
RDX	75±1.0
TNT	15±0.5
Grade SAE No. 10 engine oil plus polyisobutylene	5±0.5
Cornstarch	5±0.5

Desensitized RDX, which is coated with engine oil before mixing with the other ingredients, and grained TNT are used in the manufacture of the dynamite. Military dynamite M1, M2, and M3 is equivalent in strength to 60 percent commercial dynamite. The military dynamite is safer to transport, store, and handle than 60 percent straight nitroglycerine commercial dynamite and is relatively insensitive to friction, drop impact, and rifle bullet impact. The composition remains plastic at −57°C after 24 hours. Military dynamites are odorless, free from nitroglycerin toxicity, nonhygroscopic, and chemically stable when exposed to 80 percent relative humidity at 71°C for one month. No freezing occurs in cold storage or exudation in hot storage. Turning of shipping containers during storage is not necessary.

(2) Ammonium nitrate fuel oil explosives (ANFO).

(a) When ammonium nitrate is mixed with approximately 5.6 percent of a combustible material such as fuel oil, the heat liberated on detonation is increased by almost three-fold. The reaction proceeds according to the equation:

$$3NH_4NO_3+(CH_2)_n \longrightarrow 3N_2+7H_2O+CO_2+102.5 \text{ kilocalories per gram}$$

(b) Extremely insensitive to initiation, ANFO requires a high explosive booster containing 50/50 pentolite, composition B, or other similar high explosive. Sensitivity does vary somewhat with oil content. The maximum sensitivity is at about two to four percent, with a substantial reduction for greater concentrations of oil. Sensitivity is decreased by the presence of water, but decreasing the particle size or density of the ammonium nitrate prills increases sensitivity.

(c) The energy produced upon detonation is comparable to the energy produced by some of the less powerful military explosives, however, the detonation velocity is only about 4,300 meters per second in large diameter charges. With six percent oil, the detonation velocity is at maximum, but maximum energy is obtained with 5.5 percent oil. Increased charge diameter, up to about 13 centimeters, and confinement causes an increase in the velocity of detonation.

(3) Water gel and slurry explosives.

(a) Along with ANFO explosives, the water gel and slurry explosives have virtually replaced dynamite in mining operations. Water gel and slurry explosives have a higher energy content than ANFO, smaller critical diameter, and can be used in wet conditions. The gel explosives consist of ammonium nitrate with or without other oxidizing agents, explosive or nonexplosive sensitizers, fuels, and gelatin forming compounds in an aqueous medium. Slurry explosives contain the same ingredients with additional compounds that bond the solid particles and prevent water from defusing in and out of the slurry. The explosive sensitizers are such compounds as pentolite, TNT, methylamine nitrate, smokeless powder, and nitrostarch. Nonexplosive sensitizers can be finely granulated aluminum, gas bubbles in suspension, gas contained in small glass spheres, and porous solids. The fuels include coal dust, urea, sulfur, and various types of hydrocarbons. The gelatin forming compounds include guar gums, carboxymethyl cellulose, resins, and synthetic thickeners. The viscosity of the mix can be altered by the addition of cross linking agents like sodium tetraborate and potassium dichromate. Glycerol, methanol, and diethylene glycol may be added as antifreezes.

(b) The detonation characteristics of the water and slurry explosives vary considerably with the composition of the slurry. Detonation velocities vary from 4,300 to 6,050 meters per second and detonation pressures vary from 60 to 104 kilobar.