CHAPTER 5
PROPERTIES AND TESTS OF EXPLOSIVES

5-1. General Requirements of Explosives for Military Applications.

a. *General.* Numerous compounds are explosive, however the number of compounds that can be used militarily is relatively small. This chapter describes the tests used to cull the usable explosives from the many that are unusable. Many explosive items are designed for a minimum lifespan of ten years. These tests are designed to characterize the explosive as much as possible before deployment to avoid problems during the user phase. The types of tests performed on each explosive depend, to a large degree, on the intended use of the explosive. Most of the tests yield data which are used to rank explosives relative to a standard explosive. The relative rank is then used to determine possible applications. Few tests have absolute ranges that explosives must fall into before use in military items is permitted.

b. *Availability and Cost.* In view of the enormous quantity demands of modern warfare, explosives must be produced from cheap raw materials that are nonstrategic and available in great quantity. In addition, manufacturing operations must be reasonably simple, cheap, and safe.

c. *Sensitivity.* A military explosive must be capable of being detonated and yet be as insensitive as possible. Military requirements for sensitivity are strict. Many compounds that detonate are not used as military explosives because of unfavorable sensitivity characteristics.

d. *Brisance and Power.* The brisance and power of an explosive determine applicability for specific purposes. A bursting charge must be brisant, but a ditching charge needs to be powerful and less brisant.

e. *Stability.* Military explosives must be able to withstand long periods of storage under unfavorable conditions. Storage conditions range from extreme heat and humidity in the tropics to the cold of arctic regions.

f. *Density.* The fixed volume available in a round of ammunition necessitates using explosives of maximum energy density. In general, the greater the density of the explosive the greater the energy available. This is not true, however, for some of the metallo-organic primary explosives. The high density of these compounds is caused by the presence of mercury or lead which does not add to energy content.

g. *Hygroscopicity.* Hygroscopicity, the property of absorbing moisture, can have an adverse effect on the sensitivity, stability, or reactivity of some explosives. Explosives which are hygroscopic must be loaded in moisture-proof containers. This extra precaution is generally undesirable, so explosives which are nonhygroscopic are used. Ammonium nitrate is an exception. Although very hygroscopic, the compound is extremely cheap and readily available.

h. *Volatility.* Volatility can cause loss by evaporation, development of pressure in rounds of ammunition, and separation of ingredients in composite explosives. These undesirable characteristics must be minimized in military explosives.

i. *Reactivity.* A military explosive must be as nonreactive as possible with the materials used in construction of munitions. Compatibility of specific explosives with these materials is discussed in Chapter 8. The reactions, which are accelerated by moisture in many cases, can cause liberation of gaseous products, loss of power, and loss of sensitivity. In some cases, such as with an azide and copper, the metallic salt formed can be dangerously sensitive. When the explosive is to be loaded in contact with or mixed with another explosive or binder, reactivity between the ingredients must be minimized.

j. *Toxicity.* Minimum toxicity is a desirable quality for any military explosive. A discussion of the toxicity of the explosives of military interest is presented in Chapter 12.

k. *Environmental Impact.* The impact of manufacturing and loading operations on the environment must be as small as possible.

l. *Demilitarization.* A military explosive should have favorable demilitarization characteristics. An example is plastic bonded explosives in which a thermally sensitive binder is used. Upon heating, the binder decomposes and the explosive may be totally recovered for reloading.

m. *Vulnerability and Safety During Use.* Explosives must be as invulnerable as possible to conditions that will be encountered during use. The explosives must also be as safe as possible during both manufacture and use.

5-2. Vacuum Stability Test. This test can be made at 100°, 120°, or 150°C or any other desired temperature, but a temperature of 100° or 120°C generally is employed. A weighed 1- or 5-gram sample of the dried explosive is placed in a glass heating tube, so designed that the ground neck can be sealed with mercury after a calibrated capillary tube with a ground stopper end has been connected to the heating tube (figure 5-1). The lower end of the capillary tube is attached to a cup in which about seven milliliters of mercury are placed after the connection of the two tubes has been made. The system is evacuated until the pressure is reduced to about five millimeters of mercury. The level of the mercury in the capillary tube rises to near the top and its exact position is marked and recorded. The junction of the two tubes is sealed with mercury. The heating tube is inserted in a constant temperature bath maintained at the desired temperature ±0.5°C. If an excessive amount of gas (11 + milliliters) is not evolved in less time, heating is continued for 40 or 48 hours. The tube is removed from the bath and cooled to room temperature and the level to which the mercury in the capillary tube has fallen is noted. The volume of gas liberated is calculated from the difference between the initial and final levels, the volume of the capillary per unit of length, the volume of the heating tube, and the atmospheric pressure and temperature conditions at the beginning and end of the test. Vacuum stability test yields reproducible values and when an explosive is subjected to this test at two or more temperatures, a rather complete picture of its chemical stability is obtainable. In some cases, tests at two or more temperatures are required to bring out significant differences in stability between explosives, but a test at 100°C is sufficient to establish the order of stability of an explosive. Vacuum stability test has been found suitable for determining the reactivity of explosives with each other or nonexplosive materials. This is accomplished by making a vacuum stability test of the mixture and determining if the gas liberated is significantly greater than the sum of the volumes liberated by the two materials when tested separately. When used for this purpose, the test generally is made at 100°C.
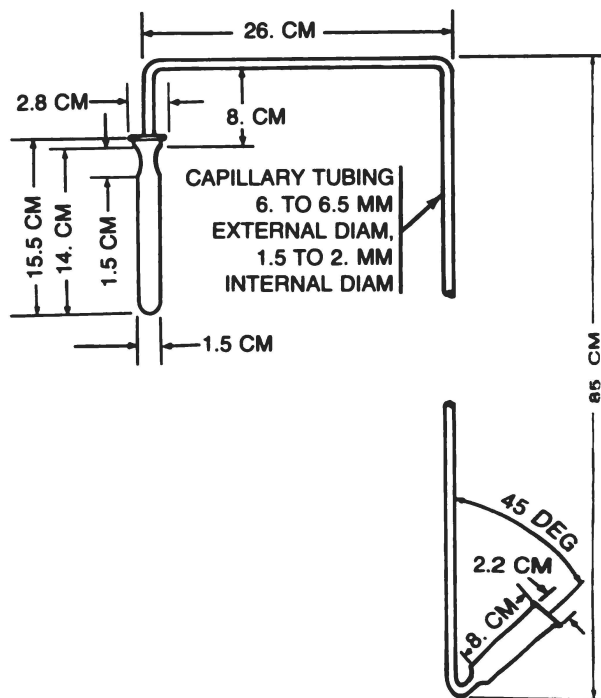

Figure 5-1. Vacuum stability test.

5-3. Impact Sensitivity. There are several different impact sensitivity machines in use. One type, the Explosive Research Laboratory (ERL) machine is shown in figures 5-2 and 5-3. The Picatinny Arsenal apparatus is shown in figures 5-4 and 5-5. The Bureau of Mines apparatus is shown in figure 5-6. The following discussion is relevant to the Bureau of Mines and Picatinny Arsenal apparatus. Sensitivity to impact is expressed as the minimum height of fall of a given weight required to cause at least one explosion in 10 trials, or the minimum height of fall of a given weight to cause explosions in 50 percent of the trials. In such tests, the explosive is ground so as to pass through a No. 50 sieve and be retained on a No. 100 sieve. In carrying out the test with the Picatinny apparatus, a steel die cup is filled with the explosive, covered with a brass cover, surmounted with a steel vented plug, placed in a positioned anvil, and subjected to the impact of a weight falling from a predetermined height. The minimum height, in inches, required for explosion is found after repeated trials. In making the test with the Bureau of Mines apparatus, 0.02 gram of the sample is spread uniformly on a hard steel block, over a circular area one centimeter in diameter. A hard steel tip of that diameter, imbedded in a

steel plunger, is lowered so as to rest on the explosive and turned gently so as to ensure uniform distribution and compression of the explosive. The plunger then is subjected to the impact of a weight falling from a predetermined height. When the minimum height required for explosion is found after repeated trials, this is expressed in centimeters. The Picatinny apparatus can be used for testing explosives having a very wide range of sensitivity, but the Bureau of Mines apparatus cannot cause the explosion of the most insensitive explosives and can be used only for testing explosives no less sensitive than TNT. The Picatinny apparatus can be used for testing solid or liquid explosives. The test with the Bureau of Mines apparatus can be modified so as to be applicable to liquid explosives. This is accomplished by using 0.007 to 0.002 gram (one drop) of the explosive absorbed in a disk of dry filter paper 9.5 millimeters in diameter.
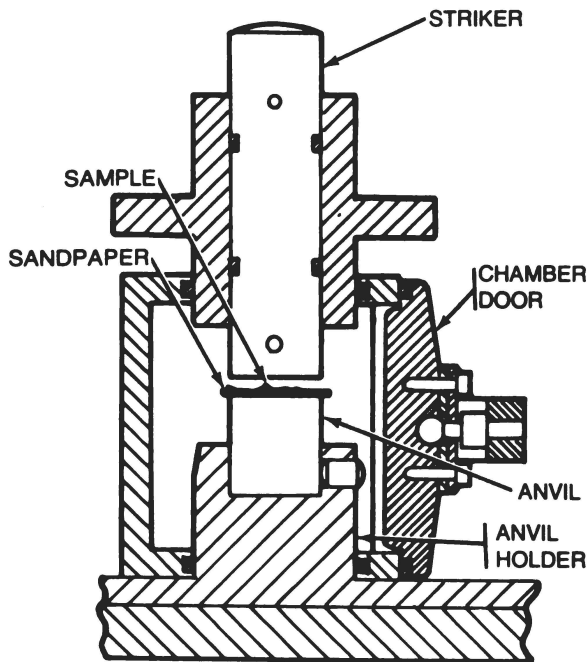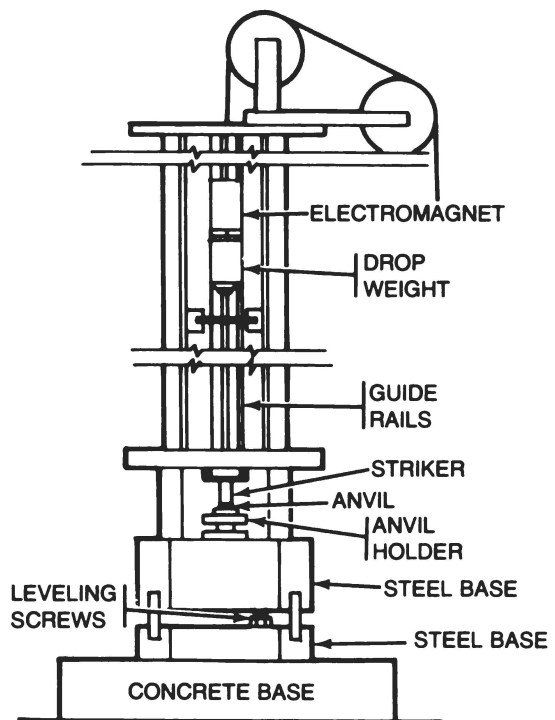

Figure 5-3. Drop weight impact machine, ERL type, type 12 tools.

5-4. Electrostatic Sensitivity. At the present time more than one method is used to determine electrostatic sensitivity. In all of the methods a spark gap is formed between an electrode and the explosive sample. A capacitor is charged to a specific voltage then discharged through the gap. Both the size of the capacitor and the voltage are varied to vary the energy in the spark. Compounds which deflagrate or detonate at spark energy levels less than 0.25 joules are not acceptable.

5-5. Detonation Velocity. Detonation velocity can be determined in any of several ways; the choice of a method probably depends more on the availability of equipment and well tested procedures than on any inherent advantage of a given method.

a. *Chronographic Method.* The chronographic method is widely used. This method depends on the closing of switches either by the conduction of hot gases between two electrodes or by the forcing together of two electrodes by the pressure induced by the detonation. Precision of the measurements depends on the number of switches or pins that is used on the charge and on the precision of the equipment.
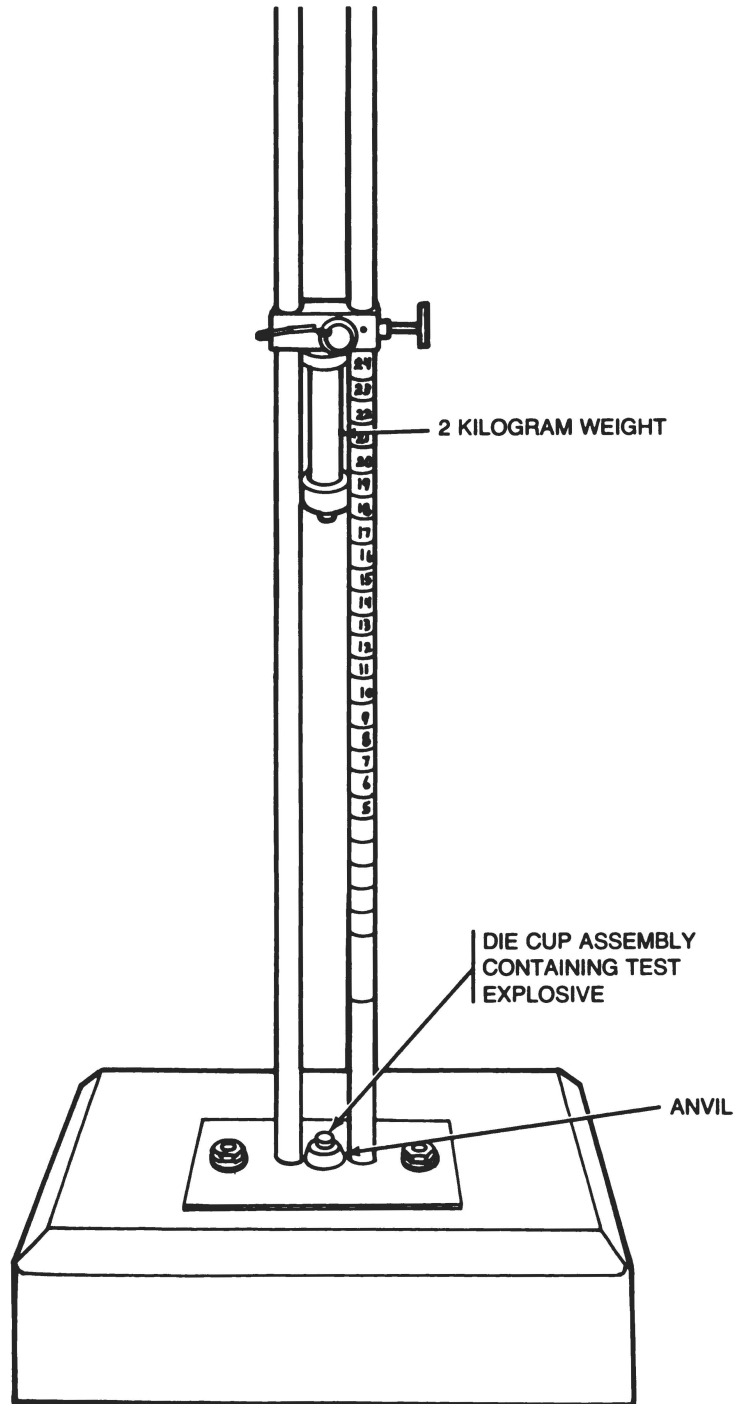

Figure 5-2. Anvil striker arrangement, ERL machine.

2 KILOGRAM WEIGHT

DIE CUP ASSEMBLY
CONTAINING TEST
EXPLOSIVE

ANVIL

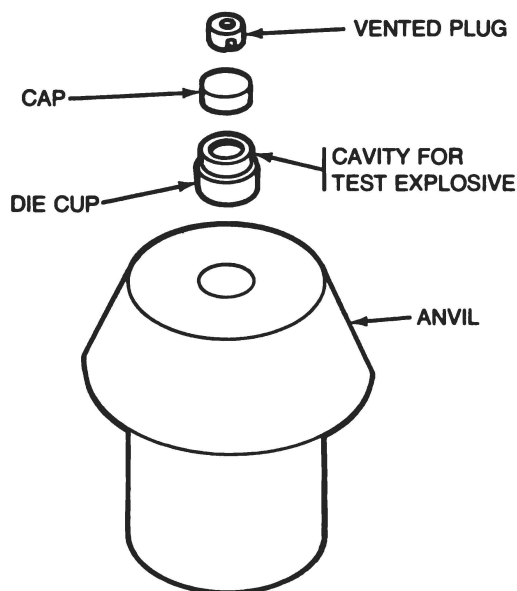Figure 5-4. Picatinny Arsenal impact test apparatus.

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Figure 5-5. Parts of Picatinny Arsenal test apparatus.

b. *Electronic Method.* Another method, which is also entirely electronic, depends on embedding a resistance wire in the explosive. A constant current is maintained in the resistance wire and the return path, which may be a nearby embedded copper wire, a wire or foil on the surface of the charge, or a metal case if the charge is confined. The voltage across the resistance wire is recorded on an oscilloscope. This voltage decreases as the detonation moves along the wire and effectively shortens the wire. This method gives, in effect, the instantaneous position of the detonation front so that the slope of the trace on the record from the oscilloscope is proportional to the detonation velocity. A closely related technique uses a resistance wire which is wound on an insulated wire or other conducting core.

These methods are not recommended for pressed charges. The precision of either version of the resistance technique depends on the quality of the charges, the precision of making the probes, and the precision of the electronics. For smaller diameter charges, the probes and wires may perturb the detonation front so that a true value of the detonation velocity cannot be obtained.

c. *Optical Method.* A commonly used optical method makes use of the streak or smear camera to record the instantaneous position of the detonation front. Because the record gives the instantaneous location of the detonation front, the slope of the streak is proportional to the velocity. Simple data reduction techniques can be used for the application discussed here. The traces are straight so that after digitizing, the data are fitted with a linear relation, the coefficient of the time being the velocity of the detonation. Again, this method can be made to give precise results if sufficient care is taken in preparing the charges and in arranging the experiment.

5-6. Cook-Off Temperature. To determine the cook-off temperature, a sample of approximately five milligrams is placed on a melting point bar. The cook-off temperature is the lowest bar temperature at which the sample flashes off.

5-7. Friction Sensitivity. Friction sensitivity tests are made to determine the relative safety of an explosive during processing. The test may be run on any of several types of machines. In the Picatinny apparatus, a 20 kilogram shoe with an interchangeable face of steel or fiber is attached to a pendulum. The shoe is permitted to fall from a height of one meter and sweep back and forth across a grooved steel friction anvil. The pendulum is adjusted to pass across the friction anvil 18 ± 1 times before coming to rest when no explosive is present. A seven gram sample of the explosive is then spread evenly in and about the grooved portion of the friction anvil, and the shoe is allowed to sweep back and forth over the anvil until it comes to rest. Tests of 10 portions of the sample are made, and the number of snaps, cracklings, ignitions, and/or explosions is noted. As the steel shoe is the more effective in causing explosions, tests with the fiber shoe sometimes will show differences between explosives indicated by the steel shoe to be of the same degree of sensitivity.
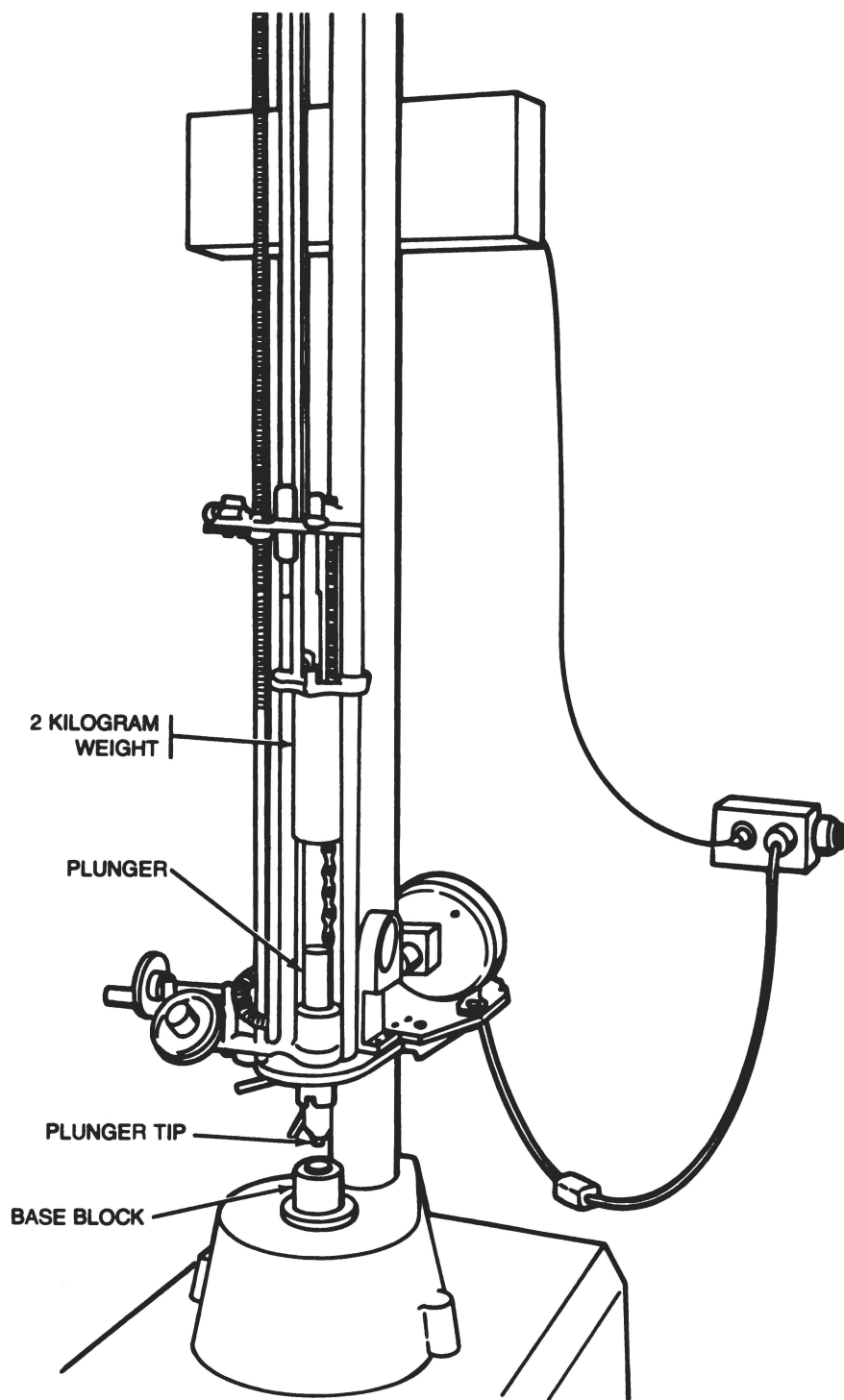
Figure 5-6. Bureau of Mines impact test apparatus.

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5-8. Gap Tests. The gap test is used to measure the sensitivity of an explosive material to shock. The test results are reported as the thickness of an inert spacer material that has a 50 percent probability of allowing detonation when placed between the test explosive and a standard detonating charge. In general, the larger the spacer gap, the more shock-sensitive is the explosive under test. The values, however, depend on test size and geometry and on the sample (the particular lot, its method of preparation, its density, and percent voids). Gap test results, therefore, are only approximate indications of relative shock sensitivity. Tests have been developed covering a wide range of sensitivities for solid and liquid explosives at Los Alamos National Laboratory (LANL), Naval Surface Weapons Center (NSWC), Mason & Hanger-Silas Mason Co., Inc., Pantex Plant (PX), and Stanford Research Institute (SRI). The test configurations are briefly described below. In all cases, detonation of the acceptor charge is ascertained by the dent produced in a "witness plate." While there are many more potential gap test geometries, these are the test configurations for which results are reported in this manual.

a. *NSWC Small Scale Gap Test (SSGT).*

Donor   25.4 millimeters (1 inch) outer diameter ×38.1 millimeters (1.5 inches) long RDX pellet.

Acceptor   25.4 millimeters (1 inch) outer diameter ×38.1 millimeters (1.5 inches) long.

Spacer   25.4 millimeters (1 inch) diameter Lucite disks of different thicknesses.

Results are reported in millimeters.

b. *LANL Small Scale Gap Test (SSGT).*

Donor   Modified SE-1 detonator with PBX-9407 pellet 7.62 millimeter diameter×5.26 millimeters long (0.0300 inch×0.207 inch).

Acceptor   12.7 millimeters diameter×38.1 millimeters long (0.5 inch×1.5 inches).

Spacer   Brass shims in 2.5 millimeter (0.1 inch) increments.

Results are reported in millimeters.

c. *LANL Large Scale Gap Test (LSGT).*

Donor   41.3 millimeters diameter×102 millimeters long (1.625×4 inches) PBX-9205 pellet.

Acceptor   41.3 millimeters diameter×102 millimeters long (1.625×4 inches).

Spacer   41.3 millimeters diameter (1.625 inches) disks of 2020-T4 Dural (aluminum).

Results are reported in millimeters.

d. *PX Gap Test.*

Donor   25.4 millimeters diameter×38.1 millimeters long (1 inch×1.5 inches) LX04 pellet.

Acceptor   25.4 millimeters×25.4 millimeters (1×1 inch) right cylinder.

Spacer   25.4 millimeter (1 inch) diameter brass shims in 0.25 millimeter (0.1 inch) increments.

Results are reported in millimeters.

5-9. Flying Plate Test. The flying plate test is used to measure the vulnerability of an explosive to high velocity impact. A steel plate is propelled by the detonation of an explosive at the sample under test. The velocity of the plate is adjusted by varying the size of the explosive charge.

5-10. Transportation Vibration. This test is performed on an end item to determine if the explosive is satisfactory for that specific application. The test consists of vibrating explosive components according to a specified schedule of frequencies, amplitudes, and durations while being maintained under prescribed temperate conditions.

5-11. Temperature and Humidity. This test consists of exposing end items containing explosives to conditions of cycling temperature and humidity.

5-12. Jolt. In this test an end item containing explosives is attached to the end of a pivoted arm. The arm is raised to a prescribed height and allowed to drop freely. The end item strikes a leather padded anvil. The test is repeated a prescribed number of times with the end item in a number of different orientations to the anvil.

5-13. Jumble. In this test an end item containing explosives is placed in a wood lined steel box. The box is then rotated about two diagonal corners at a speed of 30 revolutions per minute. The rotation is continued for 3,600 revolutions.

5-14. Forty Foot Drop Test. In this test, explosive components, such as bombs, are dropped 12.2 meters (40 feet) onto a hard impact surface. The impact surface consists of a steel plate on a concrete pad. The impact area is surrounded by walls of sufficient height and strength to contain the component during rebound. The component is dropped a number of times so different areas of the item are exposed to the impact. This test is used to determine the safety of both the component case and the contained explosive. No cracks, breaks, deformation, or displacement should occur in the component case. No explosion, burning, or charring of the explosive should occur.

5-15. Growth and Exudation Characteristics.
When explosives contain liquids as impurities, they often undergo irreversible dimensional changes when subjected to many temperature cycles between −54°C and +71°C. In explosives containing TNT, the dinitro-toluenes form low-melting liquid eutectics which cause problems. Mononitrotoluenes added as anti-cracking agents give large irreversible growth in TNT explosives. In the use of pure TNT explosives, one solution to the cracking problem is the use of pure TNT with addition of high melting point eutectic formers which reduce crack-ing without introducing objectionable irreversible dimensional change during the normal temperature variations encountered. Another cause for irreversible dimensional change is the solid polymorphic transition such as occurs with ammonium nitrate. (Refer to ammonium nitrate in Chapter 8.) Procedures for solids include measuring any cylindrical sample at least 1.27 centimeters in diameter by 1.27 centimeters in height, temperature cycled between −54°C and +60°C for 30 cycles or more. If no exudation or excessive growth is noted, an additional test can be made for exudation by placing two cylinders together inside a sealed can. These should be held together by parallel steel face plates and clamped together at an initial pressure of 413.7 kilopascals. The sealed unit is subjected to 30 cycles from ambient to 140°F, maintaining each tem-perature long enough for the entire sample to reach the temperature of the oven. The sample is then observed for exudation. Any exudate is removed and weighed.

5-16. Rifle Bullet Impact Test. Rifle bullet impact tests may use a .30 or .50 caliber bullet. Results reported in this manual use a .30 caliber bullet. In the .30 caliber test a bomb is prepared by screwing a closing cap to one end of a piece of cast iron pipe 7.62 centime-ters long, 5.08 centimeters in diameter, and threaded at both ends. The bomb is filled with the cast, pressed, or liquid explosive and is closed by screwing on a closing cap. With the loaded bomb in a vertical position, a caliber .30 bullet is fired through it from a distance of 30 yards, so that the bullet strikes between the two closing caps and at a right angle to the axis of the bomb. Five or more such tests are made and the percentage of explo-sions is noted. Those explosives which do not detonate, deflagrate, or burn are considered highly desirable. Those which burn but do not detonate are still generally satisfactory, but those which detonate are used only in applications where detonation from projectile impact is unlikely because of protection, high altitude release, or other considerations.

5-17. SUSAN Test. The SUSAN Sensitivity Test is a projectile impact test. The projectile head contains about 0.45 kilograms of explosive and the target is armor-plate steel. Figure 5-7 shows the projectile used in this test. The results of the tests are expressed as a sensitivity curve in which the relative point-source deto-nation energy released by the explosive on impact is plotted as a function of the projectile velocity. The rela-tive point-source detonation energy can be derived from a transit-time measurement of the air shock from the point of impact to a pressure gauge three meters (10 feet) from the point of impact. The results determined in this manner are somewhat subjective, particularly when the reaction level shows a large but relatively slow increase with time. The currently preferred way to determine the point-source detonation energy is to relate it to the overpressure measured by the pressure gauge. This method gives much more reproducible data and is not subject to many of the errors of the transit-time measurements. On the figures in Chapter 8, the energy scale ranges from zero (no chemical reaction) to about 100 for the most violent detonation-like reactions (all explosive consumed). Less violent burning reactions that appear to consume all of the explosive can give values as low as 40, whereas the energy equivalent of TNT fully reacted as a point source would be 70. In the test material of Chapter 8 details of the impact process pertinent to the impact safety of an explosive are given. Remarks about probabilities of large reactions are rele-vant to unconfined charges in the 11 kilogram (25 pound) class. Smaller unconfined charges show a trend of decreasing reaction level as the charge size decreases. References to the "pinch" stage of impact refer to the terminal stage of the test when the nose cap has completely split open longitudinally and has peeled back to the steel projectile body, which is rapidly brought to a halt.
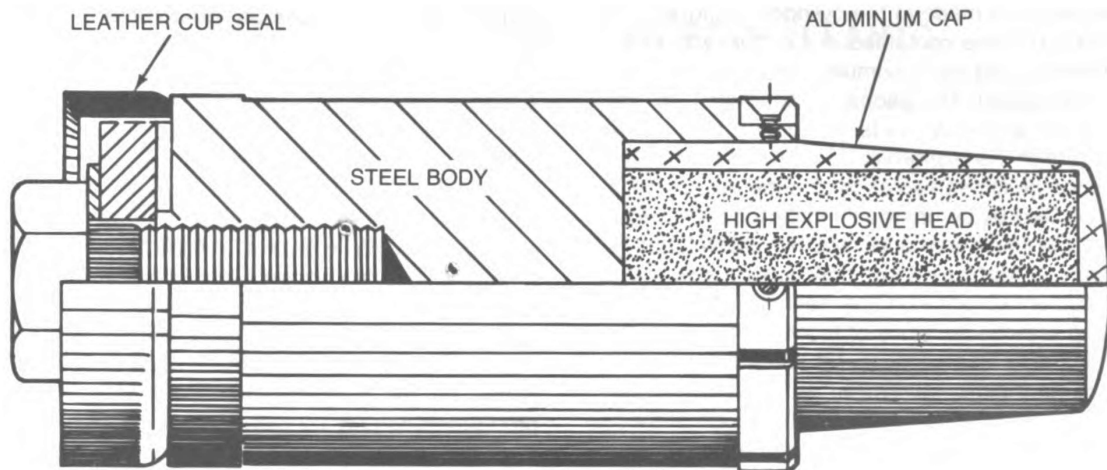
Figure 5-7. *Scaled drawing of the SUSAN projectile. The high explosive head is 4 in. long and 2 in. in diameter (.102 m ×0.051 m).*

5-18. Skid Tests. A combination of friction and impact is a frequent cause of accidents where large pieces of an explosive can be dropped a few feet. The skid test measures the sensitivity of an explosive material hitting a rigid surface at glancing angle. In one testing configuration a sample of the explosive is dropped vertically onto a hard surface inclined at 45 degrees. In another testing configuration the explosive sample is attached to the end of a pendulum. The pendulum is allowed to swing from a predetermined height.

5-19. Adiabatic Sensitivity Test. In the adiabatic sensitivity test a sample of the explosive is placed in an airtight holder. The top of the holder has an air compressing piston that decreases the volume and thus increases the pressure in the test chamber when struck by a falling weight. The results of the test are reported as the height the weight must fall, thus the degree of compression, to produce detonation in 50 percent of the cases.

5-20. Fragmentation Test. In the fragmentation test a charge of the explosive under test is loaded into a cylinder or artillery shell and detonated in a pit filled with sand or sawdust. The fragments are separated magnetically and categorized by weight. This test also gives an indication of the brisance of the explosive.

5-21. Cylinder Expansion Test.

a. An important problem faced by the designer of fragmentation warheads is that he must maximize the energy which is transferred from explosive to metal during the detonation. The most frequently encountered configuration is that of an explosive-filled metal cylinder detonated by a wave moving axially. The best scaling law that has been devised for this condition is that of Gurney, who disregarded detonation conditions and shock effects in the metal and assumed implicitly that all the energy of the explosive is conserved. His equation for the cylinders is

$$v = \sqrt{2\,E \left(\frac{C/M}{1 + 0.5\ C/M} \right)}$$

where v is the velocity to which the metal is accelerated by the explosive, E is unit energy content of the explosive, C is the weight of the explosive, and M is the metal weight. This expression of velocity in terms of C/M implies that weight-ratio scaling of explosive and metal is of prime importance and that dimensional scaling need not be considered at all. The term $2\,E$ has the dimensions of a velocity as was pointed out by Gurney in his original report.

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b. Determination of the Gurney constant of a warhead explosive is made in the cylinder expansion test where the explosive contained in a metal cylinder is end-detonated and the maximum lateral velocity of the metal is measured. The geometry resembles that of most fragmentation warheads, particularly as to lateral confinement of the explosive. The dimensions of the cylinder can be chosen so as to give the full run-up to detonation velocity before reaching the location of fragment velocity measurements, and the end-release effects can be kept far enough downstream so as not to affect fragment velocities. Other techniques for evaluating explosives, while of full value in their own contexts, are all less applicable to the prediction of effects in the fragmentation warhead. The plate-push test transfers only about one-fourth as much of the energy of the explosive to the metal as does the cylinder expansion; also, the air cushion between explosive and plate is highly unrepresentative of the warhead configuration. Other rating tests such as the plate dent, ballistic mortar, and the Trauzl lead block are even more unrepresentative geometrically.

c. The cylinder expansion test is any test performed where a metal cylinder (relatively thin walled) is loaded with an explosive and this explosive charge is detonated. As the detonation occurs, the expansion of the cylinder wall is observed and recorded in such a way that the rate at which the wall moves outward can be followed up to the point where the expanding cylinder wall is obscured by the reaction products as they break through the wall.

d. The method for observing the wall's expansion varies. It has been recorded through the use of electronic pin probes and raster oscilloscope recording systems as well as with flash X-ray techniques. It has also been accomplished by the use of streak cameras and framing cameras. The Lawrence Radiation Laboratory method uses a streak camera for the recording of the wall velocity and a pin probe method for determining the detonation velocity of the explosive while it is expanding the walls of the test-cylinder. The Atomic Weapons Research Establishment, UK, uses both electronic pin probe and streak camera methods to record the wall expansion, and pin probes for the detonation velocity. There is some reason to believe that, perhaps in the early stages of the expansion, the pin probe method may be more accurate, but the data reduction is also a bit more difficult in some respects than with the streak camera record.

e. When various explosives are rated in the standard geometry, the relative performance of these explosives becomes readily apparent. This permits the warhead design engineer to select an explosive compound for a specific feature of its performance.

f. It has been demonstrated that cylinder expansion test results scale up or down over a wide range of sizes.

CHAPTER 6
PROPERTIES AND TESTS OF PROPELLANTS

6-1. Introduction. The tests performed on propellants can be divided into three classes: mandatory, prescribed, and optional. The mandatory tests, covered in paragraphs 6-2 through 6-13, are safety tests. These tests must be run on each propellant formulation. The prescribed tests, covered in paragraphs 6-14 through 6-17, provide useful information about a propellant formulation. These tests are generally run on propellant formulations after the mandatory tests. The optional tests, covered in paragraphs 6-18 through 6-23, are only run if warranted by the intended application of the propellant formulation. Tests in which a propellant formulation is heated are called accelerated aging tests.

6-2. Compatibility. Compatibility can be measured by any of three methods: Taliani test, vacuum stability test, and differential thermal analysis. The propellant and the inert material being tested for compatibility are mixed together in some ratio which may vary from equal parts of propellant and test material to 10 parts propellant and 1 part inert material. In the vacuum stability test, increased reactivity is indicated by the mixture evolving more than five milliliters of gas over the sum of the amount of gas produced by the ingredients tested separately. In a differential thermal analysis, increased reactivity is indicated by an upward displacement of the curve. In the Taliani test, increased gas production also indicates more reactivity. Increased reactivity is considered evidence of incompatibility.

6-3. External Heat. In this test, also called the bonfire test, the propellant formulation is loaded into a standard cartridge assembly or storage container. The sample is mounted 30.5 centimeters (one foot) above a fire which is allowed to burn for 30 minutes. The test is recorded using a 16 millimeter movie camera. The film record of the test is examined to determine if any detonation occurred. No detonation reaction is considered the acceptable criteria for a propellant formulation.

6-4. Deflagration to Detonation Transition. In this test, an igniter is placed in the bottom of a tall test container which is then filled with the sample material. Propellants must not undergo detonation when ignited in this manner.

6-5. Heat Tests. Heat tests are performed at 134.5°C for single-base propellants and 120°C for double- and triple-base propellants. These tests measure the stability of the propellant. Specimens of the propellant are placed into the bottom five centimeters (two inches) of a glass test tube. A piece of methyl violet indicator paper is placed vertically in the tube so that the lower end of the paper is 25 millimeters from the specimen. The tube is corked and set into a constant temperature block or a constant temperature reflux bath. The temperature must be maintained to within 0.5°C. The result of the test is reported as the time required for the test paper to change color to salmon pink. For the propellant to pass the test, the color change cannot occur in less than 40 minutes or 60 minutes, depending on the propellant formulation, and the sample may not explode in less than five hours.

6-6. Vacuum Stability. Vacuum stability tests are performed at 100°C for single-base propellants and 90°C for double- and triple-base propellants. This test determines propellant stability on the basis of the volume of gas liberated on heating the propellant under vacuum. The propellant specimen is placed in a heating tube which is then connected to a capillary tube. Mercury is placed in a cup on the other end of the capillary tube. The system is then evacuated to approximately five millimeters. The mercury is then allowed to enter the capillary. The heating tube is then placed in a constant temperature reflux bath. The volume of gas liberated during the test is determined by observing the mercury level. If rate data is desired, the volume of gas is observed at regular intervals. If the volume of condensable gases is desired, the volume of gas is calculated based on measurements before the tube is removed from the constant temperature bath. Although there is no specific pass-fail criteria established for this test, the test is stopped when the gas volume reaches 11 + mil.

6-7. Closed Bomb. The standard closed bomb is a thick-walled cylindrical vessel capable of withstanding gun pressures. The bomb is equipped with firing electrodes to affect ignition, a pressure transducer, a gas release valve, a thermocouple, and temperature controlled water jacket. The result of the test is a pressure-time plot. There is no pass-fail criteria for this test.

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6-8. Surveillance. In the surveillance test, a 45 gram sample of the propellant is placed in a 237 milliliter (eight ounce) glass, stoppered bottle which provides an essentially airtight seal. The bottle consists of a special colorless resistance glass which has no more than 0.02 percent alkalinity calculated as potassium hydroxide. The test is performed at 65.5°C. The bottle and contents are placed in a chamber and the temperature is regulated to within one degree centigrade. After 24 hours of heating, the stopper is reseated. Daily observations are then made to check for the appearance of reddish fumes which indicate the presence of oxides of nitrogen. Single-base propellants, when new, should last for fifteen hundred days before fuming. Double-base propellants should last at least 400 days. This test does not yield reliable data for triple-base propellants. For these propellants, the stabilizer content is analyzed at regular time intervals. The rate of stabilizer depletion gives an indication of the maximum storage life of the propellant. A stabilizer depletion test can also be performed on single- and double-base propellants.

6-9. Card Gap. The card gap test measures the sensitivity of a propellant formulation to detonation by a shock wave. A sample of the propellant is placed in a cardboard tube with a booster explosive. The explosive and sample are separated by a series of 0.254 millimeter (0.01 inch) cellulose acetate cards. The test results are reported as the number of cards necessary to prevent detonation of the sample. Three successive trials with no detonation are required. Seventy cards represent the dividing line between an explosive and fire hazard material.

6-10. Cap. This test determines whether a propellant formulation can be detonated by a shortened number eight blasting cap. The sample and blasting cap are placed on top of a lead cylinder. Whether a detonation occurs is determined by the degree of compression of the cylinder. The test results are reported as either a detonation, sample burned, sample fragmented but no reaction, or no reaction. To pass this test, the propellant must not detonate.

6-11. Electrostatic Discharge Sensitivity. This test determines the sensitivity of a propellant formulation to energy from an electrostatic discharge. A test sample of not more than 50 milligrams is placed on a test plate. A capacitor is charged to the desired energy level with a 5,000 volt power source and discharged into the sample through a steel needle. Results are reported as the maximum energy which can be applied without decomposing the sample. Twenty consecutive negative results are required at the specified energy level. High

sensitivity material yields results in the range of 0.001 to 0.00875 joules, medium sensitivity material in the range of 0.00875 to 0.0125 joules, and low sensitivity material in the range of 0.0125 to 12.5 joules.

6-12. Friction Sensitivity. This test is performed on an apparatus which consists of a metal sliding block, a stationary metal wheel that is attached to a hydraulic ram, and a weighted pendulum. The sample, amounting to no more than 50 milligrams, is placed on the block under the wheel. Pressure is applied using the hydraulic ram. The pendulum is raised to a 90 degree position and dropped. Results are reported as the maximum force which can be applied to the wheel without causing the sample to decompose. Normally, 20 consecutive negative results must be obtained. The results of this test are compared to those obtained for other propellants. Most standard propellants have values of about 4,360 Newtons.

6-13. Impact Sensitivity. This test may be performed on any of the standard impact sensitivity devices. The results of the test are compared with data obtained for other standard propellants.

6-14. High Loading Rate Compression. In this test, propellant grains are subject to compressive loading at about the same rate and in the same time frame as occurs in the chamber during firing. The propellant grains are machined to give flat parallel ends with a length to diameter ratio of approximately one. The machined samples are compressed perpendicular to the flat ends using a high rate hydraulic servo. The servo is computer controlled. The results of the test are the maximum compressive strength, the strain at the maximum compressive strength, stress-strain curves, the time to maximum compressive strength, and whether the mode of failure was brittle or ductile. A drop tower apparatus may also be used to obtain higher strain rates.

6-15. Low Loading Rate Compression. For this test, propellant grains are machined to give flat parallel ends usually with a length to diameter ratio of one. Solid grains are usually extruded to yield a diameter of approximately 1.27 centimeters (0.5 inches). The device used for this test is a mechanically driven, electronically controlled tester capable of continuously recording the load exerted on a test specimen. The compressive effect on the sample is also measured. The result of the test is a load-displacement curve. From this curve the strain at maximum compressive strength and maximum stress are computed.

6-16. Taliani. The Taliani test is used to determine the stability of a propellant. A dry sample of the propellant is placed in a tube, heated to a specified temperature (usually 110°C), and the tube is evacuated. The composition of the atmosphere above the sample is controlled by alternately filling with nitrogen or another gas and evacuating a specified number of times. The pressure is then reduced and heating is continued. The pressure in the tube is measured with a manometer. The increase in pressure as the test progresses is a measure of the rate of decomposition of the sample. The test result is a graph of the time versus the pressure in the tube. The following data is usually reported: the time in minutes required for the pressure to reach 100 millimeters of mercury, the slope of the line at 100 millimeters of mercury, and the slope of the line at 100 minutes.

6-17. Explosion Temperature. In this test, a sample of the propellant formulation is loaded into a gilding metal tube and then immersed in a woods metal bath which has been raised to a specified temperature. The time to ignition is recorded. Ignition is detected by noise, flash, or smoke. The ignition time is obtained at several temperatures. A time-temperature plot is made. The result that is reported, the temperature required to ignite the propellant in five seconds, is obtained by extrapolation of the time-temperature plot.

6-18. Strand Burner. In this test a strand of propellant that is 17.8 centimeters (seven inches) long and 3.2 millimeters (one-eighth of an inch) in diameter is placed in a bomb in which the temperature and pressure can be regulated. The strand is placed vertically in a jig and ignited at the top. Vertical burning is ensured by coating the strand with a compound that does not interfere with the burning of the propellant. Two wires are inserted through the jig, one 6.4 millimeters (one-quarter of an inch) from the top of the strand and the other 12.7 centimeters (five inches) below the first. As the propellant burns, an electronic circuit through the two wires is broken and an automatic timer is used to determine the burning time. The rate is calculated from the strand length and burning time. The effect of initial temperature and pressure on the burning rate is measured.

6-19. 90°C Dutch Weight Loss Test. In this test, a four gram sample of a propellant is placed in a stoppered tube and inserted in a heating block which is maintained at 90°C. Every second day the stoppered tube is removed and cooled to room temperature for 30 minutes. The stopper is then briefly lifted and closed again. The tube is weighed to the nearest milligram and reinserted in the heating block. The test results are then plotted as weight loss percentage versus the time in days, as shown in figure 6-1. The initial bump in the curve, which results from loss of volatiles, is ignored. The results reported are the number of days coinciding with the kink in the curve, which indicates the onset of instability.
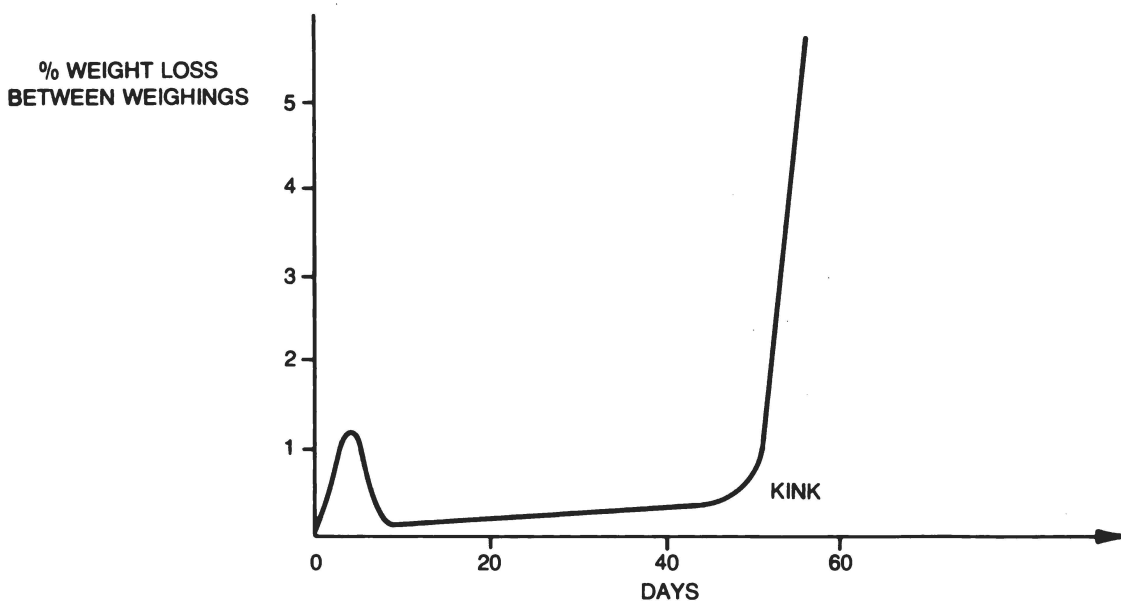

Figure 6-1.   90°C Dutch weight loss test results.

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6-20. Shaped Charge Jet Impact. This is a vulnerability test. The propellant is loaded into a standard cartridge. The cartridge is placed behind a 1.27 centimeter (one-half inch) steel plate. A shaped charge jet is fired through the steel plate directly at the cartridge. Video tape and film are used to record the reaction of the propellant in the cartridge. The results are compared to the results for other propellants.

6-21. Shaped Charge Jet Spall. This is a vulnerability test. The propellant is loaded into a standard cartridge. The cartridge is placed behind a 1.27 centimeter (one-half inch) steel plate. A shaped charge is aligned so that the jet does not impact the cartridge shell when fired through the plate, but the spall from the plate does. Video tape and film are used to record the reaction of the propellant in the cartridge.

6-22. Single Fragment Impact. This is a vulnerability test. The propellant is loaded into a standard cartridge. Standard .50 caliber 208 grain fragments are fired into the cartridge at a velocity of about 1,585 meters per second (5,200 feet per second). The velocity of the fragments before impact is recorded and video tape and film are used to record the reaction of the propellant in the cartridge.

6-23. Multiple Fragment Impact. This is a vulnerability test. The propellant is loaded into a standard cartridge. Fragments are explosively launched at a velocity of about 2,286 meters per second (7,500 feet per second) in a pattern such that each cartridge is impacted by at least two fragments. The velocity of the fragments before impact is recorded and video tape and film are used to record the reaction of the propellant in the cartridge.

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CHAPTER 7
UNITED STATES PRIMARY EXPLOSIVES

7-1. Introduction. This chapter contains discussions of military primary explosives. The chemical, physical, thermochemical, sensitivity, performance, and stability characteristics of each explosive are covered. The method of manufacture is also given. If known, the chemical structure of each compound is shown. This chapter also contains a discussion of priming compositions.

7-2. Lead Azide.

a. Lead azide, $Pb(N_3)_2$, is a salt of hydrazoic acid, HN_3. The compound is white, has a nitrogen content of 28.86 percent and a molecular weight of 291.26. At the melting point, 245°C to 250°C, decomposition into lead and nitrogen gas occurs. The pure compound has two crystal modifications: an orthorhombic form and a monoclinic form. The orthorhombic form, which is also called the alpha form, has a density of 4.68 grams per cubic centimeter and unit cell dimensions of a=11.31 Angstroms, b=16.25 Angstroms, and c=6.63 Angstroms. The monoclinic form, which is also called the beta form, has a density of 4.87 grams per cubic centimeter and unit cell dimensions of a=18.49 Angstroms, b=8.84 Angstroms, and c=5.12 Angstroms. The compound is usually prepared as colorless, needlelike crystals. The orthorhombic form is very sensitive. During manufacture, the production of this crystal form must be avoided. Lead azide is soluble in acetic acid and almost insoluble in ether, acetone, alcohol, ammonia, or organic solvents. In water the solubility is 0.02 percent at 18°C and 0.09 percent at 70°C. Lead azide may be dissolved in monoethanolamine or in a 50/50 mixture of monoethanolamine/ammonia. Recovery can be accomplished by adding dilute acetic acid, but the product obtained will be impure. The heat of formation at constant pressure is −112 to −126.3 kilocalories per mole. The calculated heat of detonation is 0.367 kilocalories per gram. Lead azide is used extensively as an ingredient in initiating compositions.
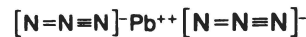
$$[N=N\equiv N]^- Pb^{++} [N=N\equiv N]^-$$

Figure 7-1. Structural formula for lead azide.

b. The forms of lead azide used for military purposes include the following types. Table 7-1 compares the properties of the types of lead azide.

Table 7-1. Various Types of Lead Azide

Properties	DLA (type I, US)	SLA	CLA (type II, US)	PVA-LA (US)	RD-1333	DCLA
Color	Buff	White	White	White to buff	-	-
Lead azide, percent	92.7	98.1	99.9	96.0	98.7	95.3
Total lead, percent	69.3	71.5	71.67	71.6	71.06	69.99
Particle size, mean, microns	24.5	55.0	3.4	19.0	34.5	1.74
Apparent density in grams per cubic centimeter	1.83	-	0.85	-	-	-
Density, pressed at 103,425 kilopascals, (15,000 psi) in grams per cubic centimeter	3.14	3.31	-	3.81	-	-
Sand test values	13.8	-	15.0	-		

Table 7-1. Various Types of Lead Azide (Continued)

Properties	DLA (type I, US)	SLA	CLA (type II, US)	PVA-LA (US)	RD-1333	DCLA
Five second explosion temperature	340	350	344	340	345	-
Impact sensitivity Picatinny Arsenal apparatus with 2 kilogram weight, in inches	4-6	2	2-3	4-5	5	3-6
Charge weight in milligrams	28	37	25	30	23	18
Bureau of Mines apparatus with 2 kilogram weight in centimeters	13-28	30	-	13-16	15	-
Picatinny Arsenal apparatus with 500 gram weight in inches	12	-	6	18	15	-
Charge weight in milligrams	28	-	-	31	21	-
Bureau of Mines apparatus with 500 gram weight in centimeters	100 +	-	35	100 +	100 +	-
Minimum charge in milligrams required to initiate 60 milligrams of RDX in an M47 detonator	90	25	-	30	25	-
Vacuum stability in milliliters per gram						
100° C, gas evolved	0.32	-	-	0.20	-	-
120 °C, gas evolved	0.46	-	-	0.44	0.43	-
100°C Heat test:						
Loss in sample wt in 8 hrs, %	-	0.11	0.12	0.30	-	-
Loss in sample wt in 48 hrs, %	0.34	0.08	-	0.13	0.30	-
Loss in sample wt in 96 hrs, %	0.39	0.16	-	-	0.30	-
Explosion in 100 hrs	None	None	-	None	None	-
Hygroscopicity at room temperature and 90% relative humidity for 56 hours	1.18	0.07	0.02	0.03	-	-

(1) Dextrinated Lead Azide (DLA) is also known as type I lead azide. Dextrin is used as a colloiding agent which prevents the formation of large, sensitive crystals and regulates crystal shape during manufacture.

(2) Service Lead Azide (SLA) consists of lead azide crystals each containing a nucleus of lead carbonate. This form of lead azide is used extensively in the United Kingdom. The method of manufacture of this compound is confidential. SLA is practically nonhygroscopic and is superior to DLA in functioning characteristics. Storage under water is considered hazardous due to the possibility of growth of the crystals and formation of agglomerates which detonate spontaneously. Other long term storage tests dispute this result.

(3) Colloidal Lead Azide (CLA) is also known as type II lead azide. CLA is nondextrinated lead azide of very small particle size. The size of the particles is in the range of three to four microns. CLA is not suited for uses requiring good flow characteristics, but, because of the very fine particle size, is ideal as a spot charge and a priming charge in low energy, electric initiators. CLA successfully replaced the milled DLA formerly used for this purpose, thus eliminating the milling operation which was always considered dangerous, even under carefully controlled conditions. In preparing a spot charge for a low energy, electric detonator, dry CLA is mixed with a concentrated solution of nitrocellulose in ether, alcohol, or other organic solvent, and a small quantity of the resulting paste is placed on the bridgewire to form a droplet called a spot. For a type of detonator in which the bridgewire is located inside a cavity, the charge of CLA can be made in the form of a pellet by pressing wet CLA into the cavity.

(4) Polyvinylalcohol Lead Azide (PVA-LA) consists of lead azide crystals coated with polyvinylalcohol. PVA-LA possesses practically the same sensitivity to impact as DLA, but is much more efficient in detonators and is practically nonhygroscopic. The ignitability is about the same as for straight lead azide and better than for DLA. The normal lead azide content is 93 to 96 percent. Other substances, such as polyethylene glycols and ureaformaldehyde polymer, can be used to produce mixtures with properties very similar to PVA-LA.

(5) RD-1333 lead azide is an insensitive form of lead azide. The method of manufacture as well as some properties of RD-1333 are confidential.

(6) Dextrinated Colloidal Lead Azide (DCLA) is essentially DLA with a very small particle size. The particle size is in the range of one to two microns.

c. In the manufacture of DLA two stock solutions must be prepared. Solution A is prepared by dissolving about 73.9 kilograms (169 pounds) of lead nitrate in about 750 liters of water treated by the permutit demineralization process. Care must be taken to remove all grit and insoluble matter. The pH of this solution is in the range of 4.2 to 4.6. To neutralize this acidity 25 to 30 grams of sodium hydroxide in dilute solution are added. The sodium hydroxide will neutralize the occluded acid and the acid formed by the hydrolysis of the lead nitrate. An excess of sodium nitrate must be avoided to prevent the production of elongated crystals which are very sensitive. About 4.08 kilograms of potato dextrin that was previously dissolved in about 100 liters of water is then added and the solution is brought to 7.325 ± 0.07 percent lead nitrate content. Solution B is prepared by diluting a refined solution of 27 percent sodium azide to 3.175 ± 0.02 percent sodium azide content. Then 794 grams of sodium hydroxide in the form of pellets are added. The sodium hydroxide is added to neutralize most of the free acid formed during the interaction of solutions A and B. This quantity of sodium hydroxide is also just sufficient to control the purity of the finished lead azide by precipitating a small quantity of lead as $Pb(OH)_2$ or $Pb(OH)N_3$. The solution is then adjusted to 3.175 ± 0.025 percent sodium azide content. Solution A is then heated to between 57.5°C and 60°C with agitation and 50 liters of solution B are added at the rate of two liters per minute. The slow rate of mixing these two very dilute solutions inhibits the formation of the orthorhombic crystalline polymorph. After solution B has been added, the temperature is lowered to 90°C or lower with continued agitation. When agitation stops the lead azide settles out. The precipitate is caught on filter cloths under vacuum and washed with four changes of

water to remove the acidity. To manufacture colloidal lead azide, a solution of four percent sodium azide is maintained at 25°C. Then a solution of lead acetate or lead nitrate is added with agitation. The lead nitrate or acetate is in slight excess of the amount required by the equation:

$$2NaH_3 + Pb(NO_3)_2 \longrightarrow Pb(N_3)_2 + 2NaNO_3$$

The resulting slurry is then filtered and the precipitate washed with several changes of water and dried.

d. The specifications for dextrinated lead azide, type I, and collodiol lead azide, type II, are:

Properties	Type	
	I	II
Color	White to buff	White to buff
Form, dimension maximum	Free from needle shaped crystal	-
Purity, minimum	91.5%	99.0%
Acidity	None	None
Solubility in water, maximum	1.0%	-
Particle size geometric mean, micron maximum	-	5
Largest micron maximum	-	10

A needle shaped crystal is defined as a crystal having a length to diameter ratio of 7 to 1 or greater. Needle shaped crystals are more sensitive than crystals of normal shape and tend to detonate under pressure. RD-1333 lead azide must be precipitated from a solution of sodium carboxymethyl cellulose which is used as the crystal growth agent. The color shall be white to buff. The aggregates shall contain no well defined translucent crystals when examined microscopically. The particles shall be opaque and irregular in size and shape and the powder shall be free flowing. RD-1333 lead azide must have a minimum bulk density of 1.1 grams per milliliter, be 98.5 percent pure, have a pH in the range of 7.5 to 5, and have a maximum solubility of one percent in water. In nitric acid, the insoluble material shall be no more than 0.05 percent and none of the material shall be retained on a US standard sieve 230. In addition there shall be no more than trace quantities of iron, copper, chlorides, nitrates, and acetates. Carboxymethyl cellulose may be present in concentrations of 0.6 to 1.20 percent. Another specification for special use lead azide has the same requirements as stated for RD-1333, except there is no limitation for trace quantities of iron, copper, chlorides, nitrates, and acetates.

e. Dextrinated lead azide is less sensitive to impact than mercury fulminate, lead styphnate, diazodinitrophenol, tetracene, or crystalline lead azide. The small aggregates that pass through a No. 325 sieve are slightly less sensitive than those that pass through a No. 230 sieve and are retained on a No. 270 sieve. When wet with water or 95 percent ethanol, lead azide has the comparative sensitivity values shown by table 7-2. The impact test results are from the Picatinny Arsenal apparatus with a two kilogram weight.

Table 7-2. Sensitivity of Dry and Wet Lead Azide

Composition, percent			Impact test inches	Pendulum friction test			
				Fiber shoe		Steel shoe	
Lead azide	Water	Ethanol		Trials	Detonation	Trials	Detonation
100	-	-	4	1	1	-	-
80	20	-	9	10	0	4	1
80	-	20	4	1	1	-	-
75	25	-	9	10	0	12	0

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The five second explosion temperature is 315°C to 345°C for pure lead azide and 275°C for dextrinated lead azide. These temperatures are much greater than the corresponding values for mercury fulminate, lead styphnate, diazodinitrophenol, and tetracene and reflect the greater difficulty in igniting lead azide in practical use. The maximum static discharge for which no ignition takes place is 0.01 joules.

f. When subjected to the sand test, dextrinated lead azide is 95 percent as brisant as the pure crystalline material and 40 percent as brisant as TNT. At maximum density, the rate of detonation is 5,400 meters per second. The rate of detonation for samples with densities of 3.8 and 4.6 grams per cubic centimeter are 4,500 and 5,300 meters per second, respectively. Slightly higher values than these have been reported. The temperature developed on detonation is between 3,420°C and 3,484°C and the pressure developed on detonation is 94,930 kilograms per square centimeter. When lead azide detonates, 308 milliliters of gas are evolved per gram of explosive with the lead produced in the gaseous form. Trauzl lead block tests have shown dextrinated lead azide to be 89 percent as powerful as the pure compound but only 80 percent as powerful as mercury fulminate and 40 percent as powerful as TNT.

g. Lead azide is an excellent initiating agent for high explosives. While not superior to mercury fulminate for detonating the less sensitive explosives such as TNT, lead azide is markedly superior as an initiator for the more sensitive explosives such as tetryl, RDX, and PETN. Unlike diazodinitrophenol, lead azide cannot initiate the detonation of ammonium picrate or cast TNT.

h. The stability of dextrinated as well as pure lead azide is exceptional. This is indicated by 100°C heat and vacuum stability tests and also by storage tests. No change is found with respect to purity or brisance after storage for 25 months at 50°C or under a water-ethanol mixture at ordinary temperature. Storage at 80°C for 15 months caused no decrease in brisance and, after such storage, a priming composition containing lead azide showed no decrease in sensitivity to stab action. The beta form is considerably less stable than the alpha form and undergoes decomposition much more rapidly. Low X-ray dosages cause lead azide crystals to decrepitate with heat and increase in hardness. Higher X-ray dosage produces severe damage. Ninety-eight percent destruction of an SLA sample was observed after an X-ray dose of 3.5×10^8 röntgen. Lead azide corrodes copper with the formation of cupric azide. Cupric azide is highly sensitive, so tools of brass, bronze, or copper cannot be used with lead azide. Figure 7-2 shows the DTA curve for lead azide.

7-3. Mercury Fulminate.

a. Mercury fulminate, $Hg(ONC)_2$, is a salt of fulminic or paracyanic acid. The acid undergoes polymerization very rapidly in both aqueous and ethereal solutions, and so cannot be isolated. The structure of fulminic acid, and thus the salts of this acid, is undetermined. Mercury fulminate has an oxygen balance to CO_2 of -17 percent, an oxygen balance to CO of -5.5 percent, a nitrogen content of 9.85 percent, and a molecular weight of 284.65. When mercury fulminate is crystallized from water, a hydrate, $Hg(ON:C).1/2H_2O$, is formed that has a nitrogen content of 9.55 percent and a molecular weight of 293.64. The anhydrous form, which is crystallized from alcohol, is white when pure but normal manufacturing yields a gray product of only 98 to 99 percent purity. The crystals formed are octahedral but are usually truncated. Only the smaller crystals are fully developed. The crystal density is 4.43 grams per cubic centimeter. Table 7-3 shows the density of mercury fulminate as a function of loading pressure.

Table 7-3. Loading Density of Mercury Fulminate

Pressure in kilopascals	Pressure in pounds per square inch	Density in grams per cubic centimeter
20,685	3,000	3.0
68,450	10,000	3.6
137,900	20,000	4.0
344,750	50,000	4.3

Pressures of more than 172,375 to 206,850 kilopascals (25,000 to 30,000 pounds per square inch) cause mercury fulminate to be desensitized to the extent of becoming dead pressed. Such material merely ignites and burns when subjected to contact with flame. The dead pressed material can be detonated by a strong blasting cap. If a layer of loose or only slightly pressed mercury fulminate covers the dead pressed material, the ensemble can be detonated by ignition. When the dead pressed material is detonated, the velocity of detonation is greater than for material that has not been dead pressed. Mercury fulminate has a melting point of 160°C, but explodes at that temperature. The solubility in one liter of water is 0.71 grams at 12°C, 1.74 grams at 49°C, and 7.7 grams at 100°C. The solubility in ethanol is slight. Because of these slight solubilities, mercury fulminate can be stored underwater or, if there is danger of freezing, under a mixture of equal volumes of water and ethanol or methanol. After such storage the compound can be dried easily. Aqueous ammonium
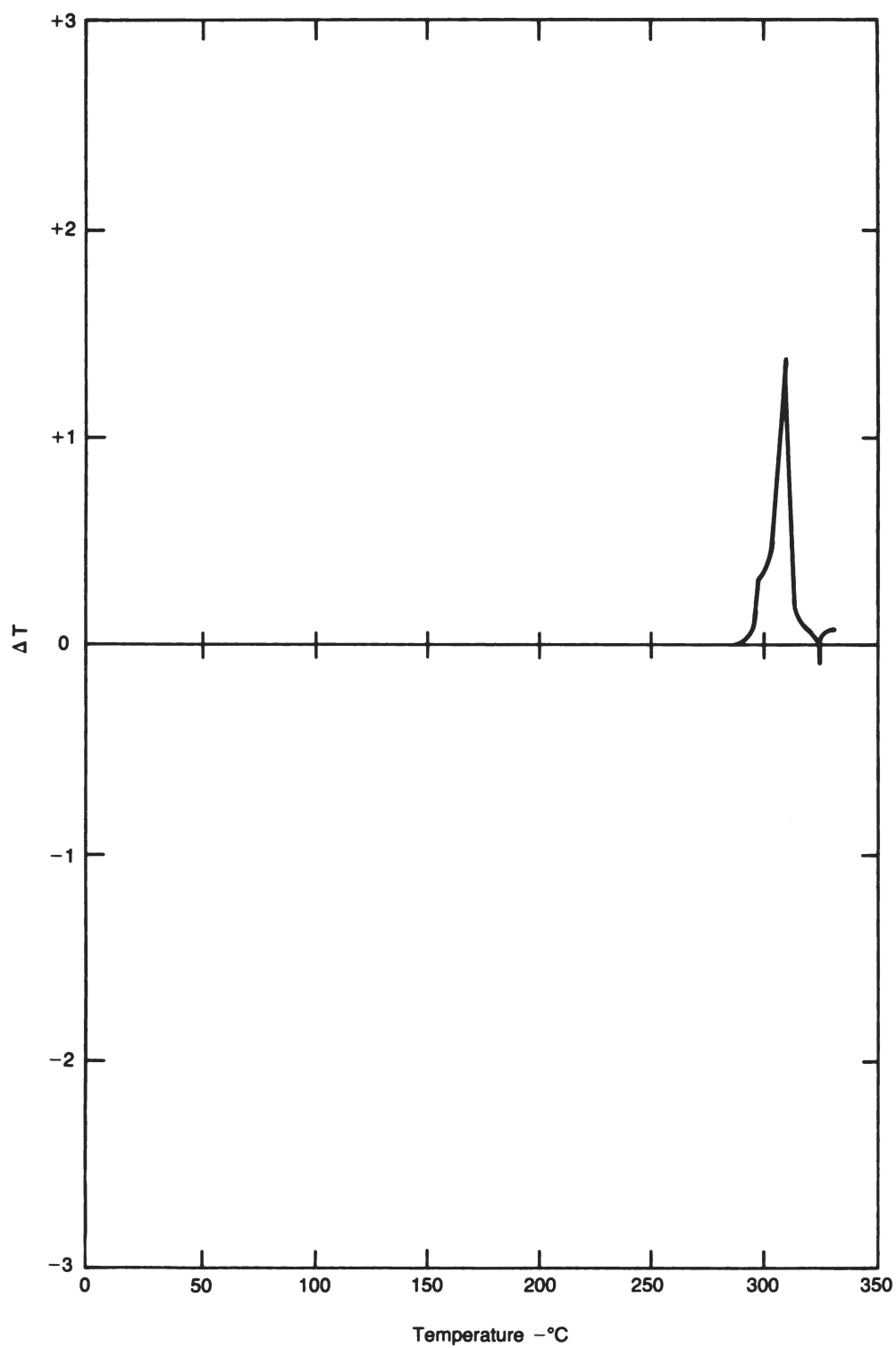
Figure 7-2.   DTA curve for lead azide.

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hydroxide, aqueous potassium cyanide, and pyridine dissolve mercury fulminate. The compound can be recovered by treating the ammonium or potassium solution with acid and the pyridine solution with water. The heat of formation is 221 to 226 calories per gram, heat of combustion is 938 calories per gram, and the heat of explosion is 427 calories per gram. Mercury fulminate was used extensively as an initiator, however, poor stability has prompted replacement of this compound by such initiators as lead azide.

b. Mercury fulminate reacts with concentrated hydrochloric acid to produce hydroxylamine, H_2N,OH, and formic acid, HCOOH. The reaction with sodium thiosulfate in aqueous solution forms mercury tetrathionate according to the equation:

$$Hg(ONC)_2 + 2Na_2 S_2O_3 + H_2O \longrightarrow$$
$$HgS_4O_6 + 2NaOH + NaCN + NaNCO$$
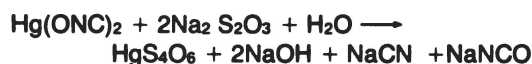
If allowed to stand, a secondary reaction occurs with the formation of sulfate and thiocyanate according to the equation:

$$HgS_4O_6 + 2NaOH + NaCN + NaNCO \longrightarrow$$
$$HgSO_4 + Na_2SO_4 + 2NaNCS + H_2O$$
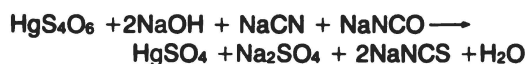
The first reaction can be used for the determination of the purity of mercury fulminate. Even in the presence of 0.5 percent moisture, pure mercury fulminate does not react with any of the common metals. However, the standard grade of the compound may contain as much as one percent free mercury, formed by exposure to light or elevated temperatures. The free mercury readily forms amalgams with copper, brass, or bronze, so components containing these metals must be protectively coated if used with mercury fulminate.
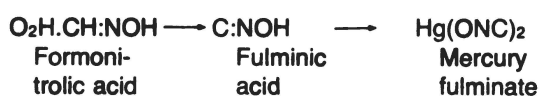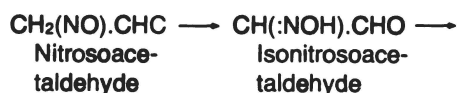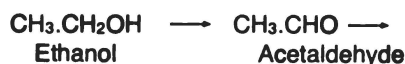
c. Mercury fulminate is manufactured in relatively small quantities. About one pound of redistilled mercury is added to an open, earthenware vessel or five liter flask that contains eight to ten pounds of nitric acid with a specific gravity of 1.4. The nitric acid is in excess of the amount required by the equation:

$$3Hg + 8HNO_3 \longrightarrow 3Hg(NO_3)_2 + 2NO + 4H_2O$$

A large number of such charges are usually prepared and allowed to stand overnight until the mercury is completely dissolved. The charges are then poured into a large balloon flask which contains eight to ten pounds of 95 percent ethanol. The flask rests in a bath of running, cold water. This installation has to be either outside or in a building provided with an exhaust system. The flask is fitted with a reflux condenser. About two to three min-

utes after the acidic solution of mercury nitrate is added to the ethanol, a violent reaction starts and the liquid boils with the evolution of white fumes. Most of these fumes are recovered by the condenser. As the reaction approaches the end point, the fumes change color to brownish-red because of the decomposition of nitric acid by heat. A small quantity of dilute alcohol is added at this point to moderate the reaction and prevent the decomposition of the mercury fulminate by the heat of reaction. The reaction normally takes about an hour and a half. The reaction mix is then allowed to cool to room temperature, at which time all the mercury fulminate has settled out. The mercury fulminate crystals are then caught on a screen and washed with cold water until free of acid and five impurities known as fulminate mud. The washed mercury fulminate is then drained and packed into cloth bags which are stored in tanks of water until required for use. The acid mother liquor and the water washings are neutralized with alkali, evaporated to recover the alcohol, and treated to recover any mercury or mercury salts. The yield of the process is 120 to 130 parts per 100 parts of mercury.

d. In the manufacturing process ethyl nitrate $(C_2H_5.ONO_2)$, ethyl nitrite $(C_2H_5.ONO)$, and nitroethane $(C_2H_5NO_2)$ also are produced. The intermediate products of oxidation and nitration involved in the preparation of mercury fulminate are as follows:

$CH_3.CH_2OH \longrightarrow CH_3.CHO \longrightarrow$
Ethanol   Acetaldehyde

$CH_2(NO).CHC \longrightarrow CH(:NOH).CHO \longrightarrow$
Nitrosoace-   Isonitrosoace-
taldehyde   taldehyde

$CH(:NOH).COOH \longrightarrow$
Isonitrosoacetic acid

$C(NO_2)(:NOH).COOH \longrightarrow$
Nitroisonitrosoacetic acid

$O_2H.CH:NOH \longrightarrow C:NOH \longrightarrow Hg(ONC)_2$
Formoni-   Fulminic   Mercury
trolic acid   acid   fulminate

The product so obtained is not more than 99 percent pure. The material can be purified so as to have a fulminate content of 99.75 percent or more by dissolving the impure material in concentrated ammonium hydroxide, filtering the solution, cooling the filtrate, and reprecipitating slowly adding concentrated nitric acid with rapid agitation while keeping the temperature below 35°C. Conditions can be established so that the

precipitated fulminate is of essentially the same granulation as the impure material. The precipitated pure fulminate is washed with distilled water until free of acid. The yield is 80 to 87 percent.

e. Mercury fulminate for military use consists of one grade. The requirements applying are:

Appearance:	Crystals of sparkling appearance that are white, gray, or light gray with a yellowish tint.
Granulation:	A maximum of 15 percent retained on a No. 100 and a maximum of 75 percent passing through a No. 200 sieve.
Sand test:	0.400 gram shall crush a minimum of 44 grams of sand.
Mercury fulminate:	Minimum, 98.0 percent.
Acidity:	None.
Insoluble matter:	Maximum, 2.0 percent.
Free mercury:	Maximum, 1.0 percent.
Chlorine:	Maximum, 0.05 percent.

The chlorine content requirement is due to the occasional use of a small quantity of cupric chloride, $CuCl_2$, for the purpose of improving the color of the product. The chloride is added to the solution of mercury in nitric acid. While this improves the color, there is also a decrease in the purity of the product. The insoluble matter represents decomposition products, which are formed as the result of side reactions.

f. The impact sensitivity on the Bureau of Mines apparatus with a 20 milligram sample is five millimeters and on the Picatinny Arsenal apparatus with a nonstandard 2.2 kilogram weight is four inches. This indicates mercury fulminate is more sensitive to impact than lead azide and lead styphnate. Being of the same sensitivity to impact as diazodinitrophenol and tetracene, these three compounds are the most sensitive initiating explosives used in military ammunition. Mercury fulminate is more sensitive to friction than lead azide and lead styphnate, exploding with both the steel and fiber shoe. The five second explosion temperature is 210°C which indicates mercury fulminate is more sensitive to heat than lead azide or lead styphnate, but less sensitive than diazodinitrophenol and tetracene. The sensitivity of mercury fulminate to percussion is one of the compound's most advantageous characteristics. Mercury fulminate is highly sensitive to electric spark. A spark from a person charged to less than 5,000 volts causes ignition. This condition is possible in plant operations. The sensitivity to electrostatic discharge is reported to be 0.025 to 0.07 joules.

g. The sand test indicates mercury fulminate is 27.3 to 59 percent as brisant as TNT. The rate of detonation of a charge with a density of 2.0, 3.0, and 4.0 grams per cubic centimeter is 3,500, 4,200, and 5,000 meters per second. When ignited, a single crystal will burn rapidly with a flash, but detonation does not take place. When a layer of crystals is ignited, high order detonation takes place. The Trauzl test indicates a power of 37 to 50 percent of TNT. Mercury fulminate is distinctly more powerful than lead azide.

h. Although mercury fulminate is not as efficient an initiator of detonation as lead azide and diazodinitrophenol, satisfactory results are obtained when used in conjunction with tetryl, RDX, or PETN, the most generally used booster explosives. The number of grams of mercury fulminate required for complete detonation of TNT is 0.25 to 0.36, for tetryl is 0.20 to 0.29, for RDX is 0.19, for PETN is 0.17, and for explosive D is 0.85.

i. Mercury fulminate is no longer used by the United States military because of poor stability. The usual stability tests are not applicable to mercury fulminate, due to explosion in a relatively short time at temperatures above 85°C. The products of deterioration are nonexplosive solids rather than gases. When the purity of mercury fulminate is reduced to about 92 percent, the initiating efficiency is destroyed although the material will explode when ignited. When purity has been reduced to 95 percent, the stability of mercury fulminate must be considered seriously impaired. Table 7-4 gives a summary of the approximate times of storage required to cause deterioration to 92 percent and 95 percent. Mercury fulminate gains 0.02 percent when exposed to 90 percent relative humidity at 30°C. When dry, mercury fulminate reacts rapidly with aluminum and magnesium and reacts slowly with copper, zinc, brass, and bronze. When wet, mercury fulminate reacts immediately with aluminum and magnesium and rapidly with copper, zinc, brass, or bronze. Dry or wet, the compound does not effect iron or steel.

Table 7-4. Deterioration of Mercury Fulminate

Storage temperature °C	Time required to reduce purity to					
	95 percent			92 percent		
	Days	Months	Years	Days	Months	Years
80	0.5	-	-	1	-	-
50	-	8	-	-	11	-
30-35	-	-	1.7	-	-	5.8
20	-	-	7	-	-	9
10	-	-	8	-	-	10

7-4. Diazodinitrophenol (DDNP).

a. This explosive is also known as 4,5-dinitrobenzene-2-diazo-1-oxide, dinol, diazol and may be referred to as DADNP. The compound (figure 7-3) is a greenish yellow to brown solid with tabular crystals. DDNP has a crystal density of 1.63 to 1.65 grams per cubic centimeter at 25°C and a molecular weight of 210.108. DDNP is not dead pressed even at a pressure of 896,350 kilopascals (130,000 pounds per square inch). The solubility of DDNP in various solvents is shown in table 7-5.
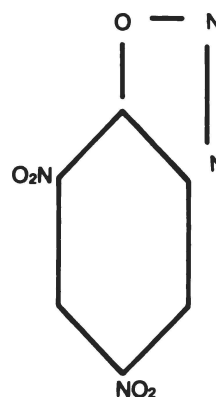
Table 7-5. Solubility of Diazodinitrophenol

	Solubility, grams per 100 grams of solvent at-	
	25°C	50°C
Water	0.08	-
Benzene	0.09	0.23
Methanol	0.57	1.25
Ethanol	0.84	2.43
Ether	0.04	-
Chloroform	-	0.11
Ethylene chloride	0.29	-
Acetic acid	1.40	-
Ethyl acetate	-	2.45
Acetone	6.0	-

DDNP is also soluble to some extent in nitroglycerin, nitrobenzene, aniline, pyridine, and concentrated hydrochloric acid. DDNP is nearly insoluble in carbon tetrachloride and carbon disulfide. The heat of formation is 956 calories per gram and the heat of explosion is 820 calories per gram. DDNP is used as an ingredient in priming compositions and in commercial blasting caps.

Figure 7-3. Structural formula for DDNP.

b. At ordinary temperatures DDNP does not react with water, but the mixture of the two is less sensitive than DDNP alone. DDNP is darkened rapidly by exposure to sunlight, probably because of oxidation at the surface.

c. The process used commercially for the manufacture of DDNP is not available, but the compound can be prepared by the diazotization of picramic acid by means of sodium nitrite and hydrochloric acid. The reactions involved are shown in figure 7-4. Picramic acid may be prepared by evaporating a mixture of an alcoholic solution of ammonium picrate and ammonium sulfide and purifying the product. Ten grams of picramic acid are suspended in 120 milliliters of a five percent aqueous solution of hydrochloric acid. The mixture is cooled with an ice bath and stirred rapidly. A solution of 3.6 grams of sodium nitrite in 10 milliliters of water is added all at once and stirring is continued for 20 minutes. The dark brown, granular material that separates

7-9

is caught on a filter and washed with ice water until the washings give no indication of hydrochloric acid or sodium chloride. If this material is dissolved in hot acetone and a large volume of ice water added to the agitated solution, the DDNP is precipitated as a bright yellow, amorphous powder. Recrystallization from a solvent is used to produce the tabular crystals that comprise specification grade material. After manufacture, the DDNP is kept wet with water until used.

d. Only one grade of DDNP is used for military purposes. This complies with the following requirements:

Color: Greenish yellow to brown.

Form: Tabular crystals having a maximum length of 0.2 millimeter.

Granulation: 100 percent shall pass through a No. 100 US standard sieve.

Bulk density: Minimum, 0.4 grams per milliliter.

Acidity: Maximum, 0.01 percent as hydrochloric acid.

Sand test: 0.40 gram shall crush not less than 33 grams of sand.

e. DDNP is less sensitive to impact than lead azide or mercury fulminate. The friction sensitivity is approximately the same as lead azide but less than mercury fulminate. The five second explosion temperature is 195°C. A mixture of DDNP and water is desensitized to the extent that a number eight blasting cap cannot cause detonation. DDNP detonates when struck with a sharp blow. An unconfined sample burns with a flash if ignited but even the slightest confinement causes a transition from burning to detonation. A charge of DDNP undergoes detonation when ignited if pressed into a blasting cap shell with a reinforcing cap and a piece of black powder safety fuse crimped in the shell. A spark falling into the open end of such a blasting cap causes only ignition and flashing of the DDNP. The maximum energy of a static discharge that does not cause ignition is 0.25 joules.

f. The sand test indicates DDNP is 94 to 105 percent as brisant as TNT. DDNP is considerably more brisant than mercury fulminate, lead azide, lead styphnate, and tetrazene. At a density of 1.58 grams per cubic centimeter DDNP and TNT have the same velocity of detonation, 6,900 meters per second. At densities of 0.9 and 1.63 grams per cubic centimeter the detonation velocities are 4,100 and 7,100 meters per second, respectively. The Trauzl test and ballistic mortar test indicate that DDNP is 110 percent and 95 percent as powerful as TNT, respectively. The gas volume produced on detonation is 856 liters per kilograms.
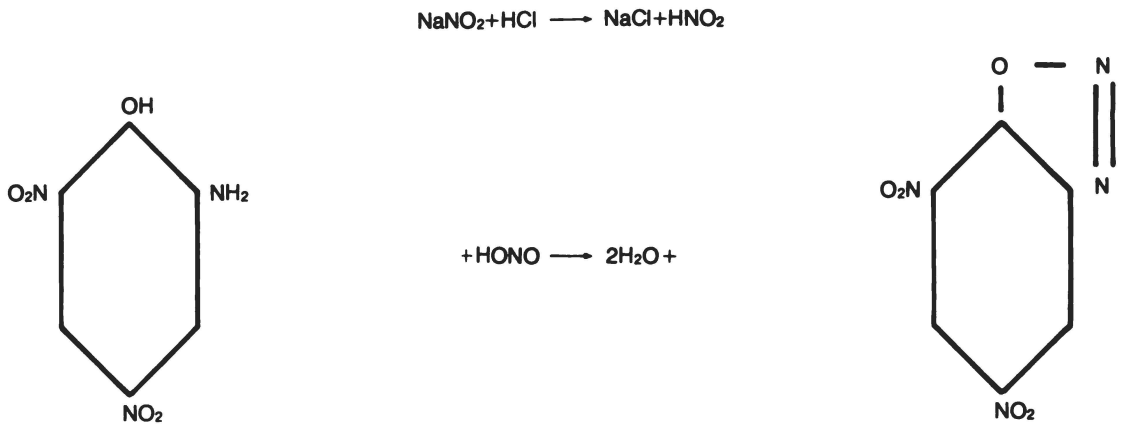
$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

Figure 7-4. Preparation of DDNP.

000110

g. The sand test indicates DDNP is a better initiator of detonation than mercury fulminate or lead azide for less sensitive high explosives. The most marked evidence of this is the ability of DDNP to initiate the detonation of ammonium picate and cast TNT. For initiation of the more sensitive high explosives, DDNP is not superior to lead azide. Comparative values showing relative initiating efficiencies are given in table 7-6.

Table 7-6. Efficiency of Initiating Compounds

	Minimum detonating charge, gram of initiator required to detonate		
	Tetryl	TNT	Ammonium picrate
Lead azide	0.10	0.26	No detonation
Mercury fulminate	0.19	0.24	No detonation
Diazodinitrophenol	0.12	0.15	0.28

h. In the vacuum stability test at 100°C, 7.6 cubic centimeters of gas are evolved from a five gram sample in 40 hours. In the 100°C heat test, 2.10 percent is lost in the first 48 hours, 2.20 percent in the second 48 hours, and no explosions occur in 100 hours. These results indicate DDNP is not as stabile as lead azide, but is markedly more stabile than mercury fulminate. Storage tests have shown dry DDNP to withstand storage at 50°C for at least 30 months, as compared with nine months for mercury fulminate. When stored under water, DDNP is of unimpaired brisance for 24 months at ordinary temperature and for 12 months at 50°C. The stability of DDNP, therefore, is considered satisfactory for commercial and military use, and DDNP and lead azide have replaced mercury fulminate in blasting caps to a large extent. DDNP is hygroscopic to the extent of 0.04 percent in an atmosphere of 90 percent relative humidity at 30°C.

7-5. Lead Styphnate.

a. Two forms of lead styphnate are used as primary explosives: basic (figure 7-5) and normal (figure 7-6). Basic lead styphnate has a nitrogen content of six percent and a molecular weight of 705.53. The compound has two crystal forms: yellow needles with a density of 3.878 grams per cubic centimeter and red prisms with a density of 4.059 grams per cubic centimeter. The apparent density is 1.4 to 1.6 grams per cubic centimeter. Normal lead styphnate has a nitrogen content of nine percent and the monohydrate has a molecular weight of 468.38. The compound has yellow orange or reddish brown, rhombic, needle like crystals with a density of 3.02 grams per cubic centimeter at 30°C. The anhydrous salt has a density of 2.9 grams per cubic centimeter. Both forms of lead styphnate are soluble in aqueous ammonium acetate. Basic lead styphnate is practically insoluble in water; normal lead styphnate is only soluble to the extent of 0.04 percent at room temperature. Normal lead styphnate is even less soluble in methanol and ethanol than in water. Both forms of lead styphnate are insoluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, toluene, concentrated hydrochloric acid, and glacial acetic acid. Normal lead styphnate has a heat of formation of 92.3 calories per gram, a heat of combustion of 1,251 calories per gram, and a heat of detonation of 460 calories per gram. Both forms of lead styphnate are used as ingredients in priming compositions. When used alone, despite a favorable rate of detonation and good power characteristics, lead styphnate is a relatively poor initiator of detonation. Detonation of 60 percent dynamite and sometimes gelatin dynamite is possible. However, of the military high explosives, only unpressed PETN can be detonated. The minimum detonating charge for unpressed PETN is 0.55 gram, as compared to 0.30 gram of mercury fulminate or 0.40 gram of lead azide. The ease of ignition of the compound has led not only to use in priming compositions, but also use as a cover charge for igniting lead azide.
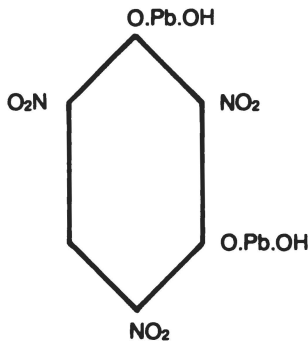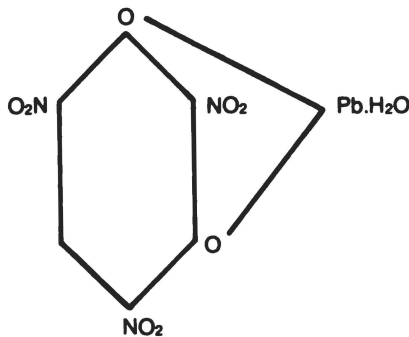
Figure 7-5.   Basic lead styphnate.

Figure 7-6.   Normal lead styphnate.

b.   Lead styphnate can be prepared by the reaction of lead nitrate or acetate with either sodium or magnesium styphnate in the presence of an acid. In commercial production, the magnesium salt is used. This is prepared by the reaction of magnesium oxide and styphnic acid (2,4,6-trinitroresorcinol). In one procedure, a boiling solution of lead nitrate is added to a boiling solution of sodium styphnate acidified with acetic acid. In another procedure, solutions of magnesium styphnate and lead acetate are caused to react at 70°C to form a precipitate of basic lead styphnate, which is converted into the normal salt by the addition of dilute

nitric acid. The insoluble product is filtered off and washed with water until free of acid. Like other initial detonating compounds, lead styphnate is kept under water or under a water-isopropyl alcohol mixture until used.

c.   For military use basic lead styphnate must comply with the following requirements:

Appearance:	The material shall be free from visible impurities and aggregates of crystals. Type I shall be yellow to orange yellow in color. Type II shall be yellow brown to brown in color.
Crystal form:	Type I material shall consist of discrete crystals in the form of needles. Type II material shall consist of discrete crystals.
Crystal dimensions:	95 percent of the type I crystals shall have a maximum dimension between 7 and 20 microns. The length of the crystal shall not be greater than five times the width of the crystal. 95 percent of the type II crystals shall have lengths between 7 and 35 microns.
Granulation:	100 percent of the type I and II material shall pass through a US standard number 325 sieve.
Apparent density:	The apparent density of the type I material shall be 0.3 to 0.5 grams per milliliter and for the type II material, 1.40 to 1.60 grams per milliliter.
Acidity:	The pH shall be 5.0 to 6.0 in a one percent solution for the type I material, 6.0 to 7.0 for the type II material.
Material insoluble in ammonium acetate:	0.2 percent, maximum, for both type I and II material.
Material soluble in ether:	0.1 percent, maximum, for both type I and II material.
Lead content:	59.6 to 60.2 percent for both type I and II material.
Nitrogen content:	5.97 to 6.17 percent for both type I and II material.
Instantaneous flash point:	330°C to 350°C for both type I and II material.

d. For military use normal lead styphnate must comply with the following requirements:

Appearance:	The material shall be free from visible impurities and aggregates of crystals and be yellow brown to brown in color.
Crystal form:	The material shall consist of the discrete crystals of the monoclinic system and the longest dimension of any crystal shall not be greater than three times the next longest axis. Hexagonal plates are acceptable.
Crystal dimension:	The largest dimension of any crystal shall not exceed 0.5 millimeter.
Granulation:	100 percent of the material shall pass through a US standard number 100 sieve.
Apparent density:	1.30 to 1.60 grams per cubic centimeter.
Acidity:	The pH shall be between 5.0 and 6.0 in a one percent solution.
Material insoluble in ammonium acetate:	0.3 percent, maximum
Material soluble in ether:	0.1 percent, maximum
Lead content:	43.2 to 44.3 percent
Nitrogen content:	8.87 to 9.07 percent
Instantaneous flash point:	310°C to 330°C

e. Normal lead styphnate is slightly less sensitive to impact than mercury fulminate or diazodinitrophenol, but is more sensitive than lead azide. The friction sensitivity is less than that for mercury fulminate or lead azide. The five second explosion temperature is 282°C, less than that for lead azide but much greater than those of mercury fulminate and diazodinitrophenol. Normal lead styphnate is much more easily ignited by flame or electric spark than mercury fulminate, lead azide, and diazodinitrophenol. The sensitivity to electrostatic static discharge is 0.001 joules. When ignited, the rate of detonation is less than the maximum rate. The calculated activation energy for the decomposition of lead styphnate is 61.5 kilogram-calories per gram molecule as compared with a value to 25.2 kilogram-calories for mercury fulminate.

f. When subjected to the sand test with ignition by a black powder fuse, the brisance of normal lead styphnate (10.5 grams of sand crushed) is much less than that of lead azide (16.7 grams of sand crushed). However, when initiated with a small charge of mercury fulminate or lead azide, the brisance (24 grams of sand crushed) is greater than that of lead azide or mercury fulminate. The range of brisance reported is from 27 to 53 percent of TNT. When initiated with blasting caps, lead styphnate pressed to a density of 2.9 has a rate of detonation of 5,200 meters per second, which is greater than the rate of detonation of either lead azide or mercury fulminate at the same density. Trauzl lead block tests, with large and small blocks, show lead styphnate to be more powerful than lead azide and 42 percent as powerful as TNT.

g. Normal lead styphnate is of a high order of stability as indicated by vacuum stability tests at 100°C and 120°C. In both tests 0.4 cubic centimeters of gas are evolved in 40 hours. The loss of 1.5 percent in the 100°C heat test may be attributable to the removal of the water of crystallization, which is present to the extent of 3.84 percent. Storage at 80°C caused no change in the 120°C vacuum stability test value, although the explosion temperature and sand test values were increased slightly. These changes also may be attributable to loss of the water of crystallization. The stability of lead styphnate is the same as lead azide and better than that of mercury fulminate or diazodinitrophenol. Figure 7-7 shows the DTA curve for lead styphnate and figure 7-8 shows the TGA curve.
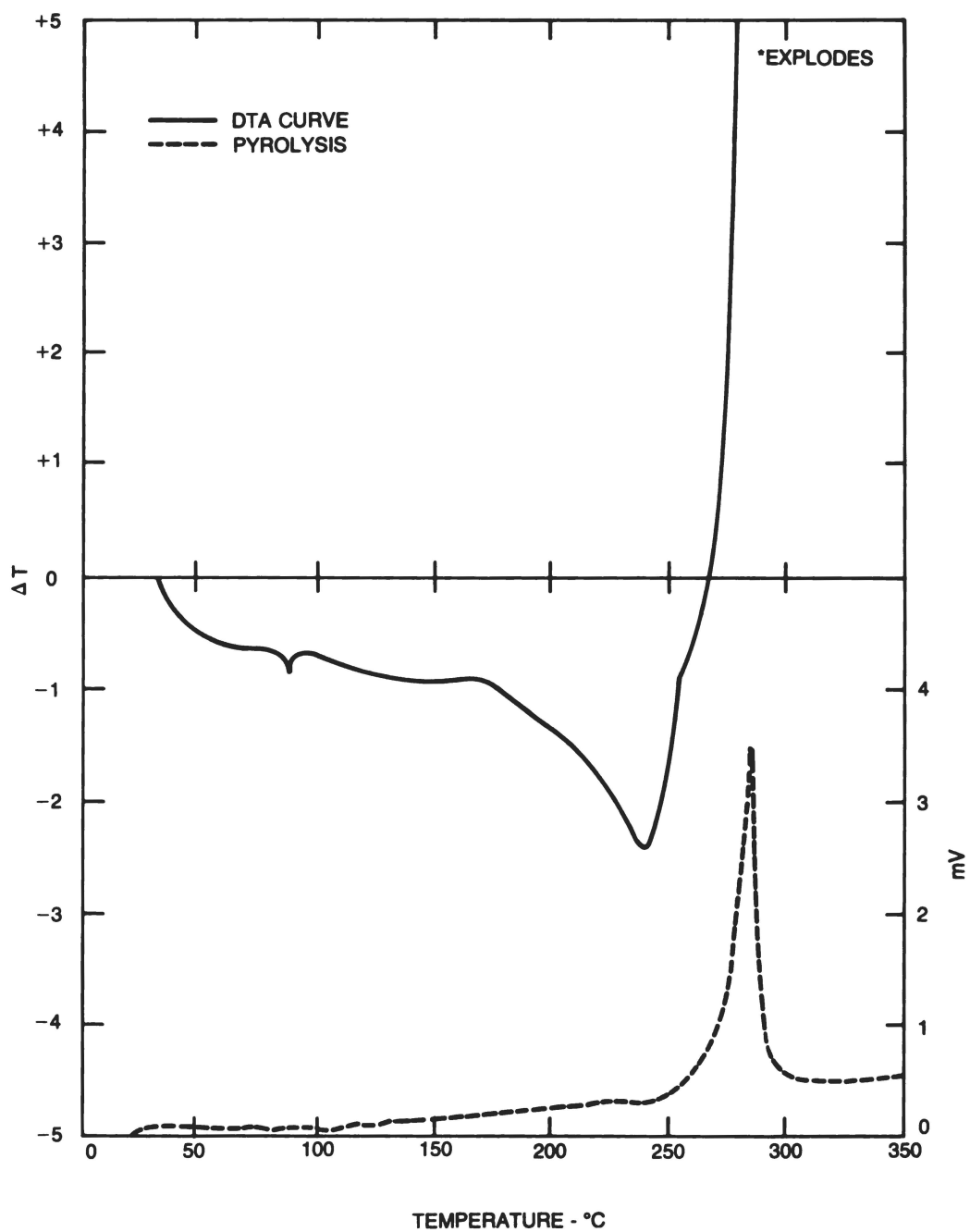
000113

Figure 7-7. DTA curve for lead styphnate.

000114

per gram and the heat of detonation is 658 calories per gram. Tetracene can be used in detonators when initiated by another primary explosive. In such cases, the tetracene functions as an intermediate booster or as a sensitizer to flame or heat. In some cases, tetracene is used in primers where as little as two percent tetracene in the composition results in uniformity of percussion sensitivity.
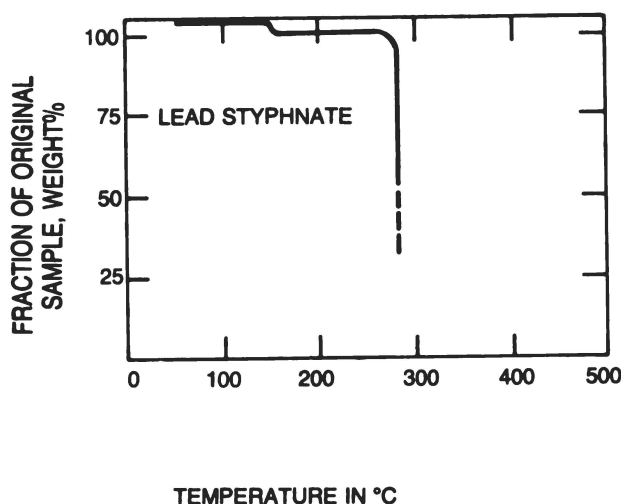

Figure 7-8. TGA curve for lead styphnate.

7-6. Tetracene.

a. Tetracene is also known as guanyldiazoguanyl tetrazene and 4-guanyl-1-(nitrosoaminoguanyl)-1-tetrazene. The compound (figure 7-9) is a colorless to pale yellow, fluffy material with needle crystals, an oxygen balance to CO_2 of -57.6 percent, an oxygen balance to CO of -43 percent, a nitrogen content of 74.4 percent, and a molecular weight of 188.15. Tetracene forms a hydrate with three molecules of water. The melting point of the pure compound is between 140°C and 160°C accompanied by decomposition and explosion. The apparent density is only 0.45 grams per cubic centimeter. When compressed at 20,685 kilopascals (3,000 pounds per square inch), the density is 1.05 grams per cubic centimeter. The crystal density is 1.7 grams per cubic centimeter. The compound can be easily dead pressed. Tetracene is practically insoluble in water and ethanol and so can be stored wet with water or a mixture of water and ethanol. The compound is also insoluble in ether, benzene, acetone, carbon tetrachloride, and ethylene dichloride. Tetracene is soluble in dilute nitric acid or strong hydrochloric acid. In a solution with hydrochloric acid, the hydrochloride is precipitated by the addition of ether. Tetracene may then be recovered by treatment with sodium acetate or ammonium hydroxide. The heat of formation is 270 calories
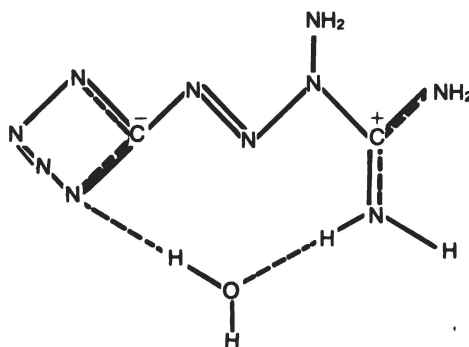

Figure 7-9. Structural formula for tetracene.

b. Boiling water decomposes tetracene liberating two molecules of nitrogen per molecule of tetracene. Hydrolysis with sodium hydroxide yields ammonia, cyanamide, and triazonitrosoaminoguanidine ($N_3C(:NH).NH.NH.NO$). Tetracene reacts with an excess of silver nitrate to form the double salt $C_2H_7N_{10}OAg.AgNO_3.3H_2O$ and forms explosive salts such as the perchlorate.

c. To prepare tetracene, 34 grams of aminoguanidine carbonate are dissolved, with warming, in a mixture of 2.5 liters of water and 15.7 grams of glacial acetic acid. After the solution has been filtered and cooled to 30°C, 27.6 grams of solid sodium nitrite are added. The sodium nitrite is dissolved by stirring. After standing for three or four hours, the solution is shaken to start precipitation and the mixture is allowed to stand for about 20 hours longer. The precipitate of tetracene is separated and washed with water until free from acid. An alternate method is to dissolve five grams of aminoguanidine dinitrate in 30 milliliters of distilled water, cooling to 0°C, and mixing with a solution of 2.5

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grams of sodium nitrite in 15 milliliters of water. While maintaining the temperature at 10°C, 0.5 grams of glacial acetic acid is added to precipitate the tetracene. After allowing the slurry to stand, at least overnight, the precipitate is washed by decantation with several portions of water and then transferred to a filter to be washed more thoroughly with water using suction. Then the product is air dried at room temperature. Another method for the preparation of tetracene uses aminoguanidine sulfate and sodium nitrite in distilled water.

d. Tetracene must meet the following requirements for military use:

Color and appearance:	Tetracene shall be white to light yellow and under the microscope shall appear as needle shaped crystals.
Melting and explosion point:	130 ± 2°C.
Granulation:	100 percent shall pass through a US number 45 standard sieve.
Specific gravity:	1.65 ± 0.05.
Heavy metals:	There shall be no heavy metals present.
Nitrogen content:	74.5 ± 1 percent.

e. Tetracene is of the same order of sensitivity as mercury fulminate and diazodinitrophenol. Using the Bureau of Mines apparatus with a two kilogram weight, the result obtained is seven centimeters as compared to five centimeters for mercury fulminate. Using the Picatinny Arsenal apparatus with a 226.8 gram (eight ounce) weight, the result obtained is eight inches, as compared to nine to ten inches for mercury fulminate. The five second explosion temperature (160°C) is relatively low as compared with the other initial detonating agents. This ease of ignition along with a relatively high heat of explosion and large gas volume produced makes tetracene useful in priming compositions and with lead azide in explosive rivets. When exposed to contact with a flame, tetracene undergoes mild explosion with the production of much black smoke. The minimum detonating charge of mercury fulminate is 0.40 grams.

f. In the sand test, loose tetracene crushes 13.1 grams of sand, but when loaded under a pressure of 20,685 kilopascals (3,000 pounds per square inch), only two grams of sand are crushed. However, tetracene pressed at 20,685 kilopascals crushes 21.1 grams of sand when initiated with mercury fulminate. This

maximum brisance is equal to that of mercury fulminate. The range of brisance values reported are 40 percent to 70 percent of TNT. The volume of gas developed on explosion is 1,190 cubic centimeters per gram. The Trauzl test indicates tetracene has a power of 51 to 63 percent of TNT.

g. Unpressed tetracene, when ignited by a flame, can cause the detonation of loose or pressed PETN, but pressed tetracene does not detonate PETN. Unpressed tetracene can cause low order detonation of tetryl. The unpressed material, however, cannot detonate TNT even when primed with mercury fulminate. Tetracene, therefore, does not have sufficient initiating efficiency to be used with military high explosives.

h. Tetracene is relatively stable at temperatures not greater than 75°C. However, in the 100°C heat test, extreme decomposition occurs in the first 48 hours. The reactivity with water and the slightly high 75°C international test value (0.5 percent) indicate an order of stability approximating that of mercury fulminate. Tetracene gains only 0.77 percent in an atmosphere with 90 percent relative humidity at 30°C.

7-7. Potassium Dinitrobenzofuroxane (KDNBF).

a. KDNBF (figure 7-10) is a red crystalline solid with a nitrogen content of 21.21 percent and molecular weight of 264.20. The oxygen balance of the compound to CO_2, H_2O, and K_2O is −42.4 percent. The anhydrous salt has a density of 2.21 grams per cubic centimeter and a melting point, with explosive decomposition, of 210°C. KDNBF is soluble to the extent of 0.245 grams per 100 grams of water at 30°C. Between the temperatures of −50C to 50°C the specific heat is 0.217 calories per gram per degree centigrade. KDNBF is used in primary compositions.

b. Using a .45 kilogram (one pound) weight in the Picatinny Arsenal impact apparatus, the drop height is only six inches. In the pendulum friction test, KDNBF explodes with both the steel and fiber shoes. The minimum charge required for initiation is 0.30 grams of mercury fulminate or 0.10 grams of lead azide. The sensitivity of KDNBF is between that of mercury fulminate and lead azide.

c. In the sand test, 44.8 grams of sand are crushed, which indicates a brisance of 93 percent of TNT. The volume of gas developed on explosion is 604 cubic centimeters per gram.

d. In the 100°C heat test, the weight loss in the first 48 hours is 0.03 percent and in the second 48 hours 0.05 percent with no explosions in 100 hours. At 30°C and 90 percent relative humidity KDNBF is hygroscopic to the extent of 0.27 percent.
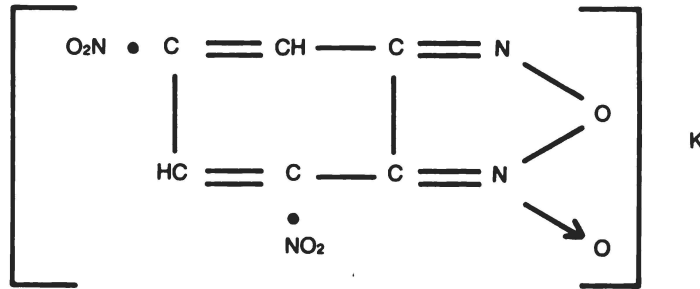
Figure 7-10. Structural formula for KDNBF.

e. The specifications for KDNBF are:

Color:	Light orange to dark red.
Bulk density:	0.2 grams per milliliter, minimum.
Forms:	KDNBF shall be in the form of plate-like crystals. In addition, the dried KDNBF powder shall be easily dispersible.
Granulation:	Through a No. 50 US standard sieve, 98 percent minimum.
	Retained on a No. 100 US standard sieve, 4 percent maximum.
	Retained on a No. 200 US standard sieve, 10 to 75 percent.
	Retained on a No. 270 US standard sieve, 85.0 to 100 percent.
Vacuum stability:	Not more than 1.0 milliliters of gas shall be evolved at $120° \pm 0.5°C$ in 40 hours.
Nitrogen content:	19.75 percent ± 0.20 percent.
Differential thermal analysis:	The DTA graph of the tested KDNBF sample shall show only one major exotherm and that exotherm shall occur between 210°C and 225°C.
Nuclear magnetic resonance:	The NMR spectra of the tested KDNBF sample shall have five distinct peaks one each at 5.77, 5.93, 6.13, 6.27, and 8.63 ppm. The average amplitude of the peaks at 5.93 and 6.13 ppm shall be greater than

thirty percent of the peak at 8.63 ppm. In addition, there shall be no peak at 9.22 ppm greater than five percent of the peak at 8.63 ppm.

7-8. Lead Mononitroresorcinate (LMNR).

a. LMNR (figure 7-11) has a nitrogen content of 3.89 percent, an NO_2 content of 12.77 percent, a lead content of 57.51 percent, and a molecular weight of 360.30. The compound forms microscopic reddish brown crystals. LMNR has slow burning properties and a low combustion temperature. The compound is used in electric detonators with DLA as the spot charge to initiate a PETN base charge, as an upper charge, and as an ingredient in primary compositions.
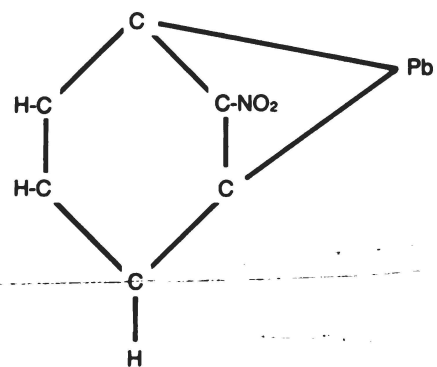

Figure 7-11. Structural formula for LMNR.

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b. LMNR is prepared by mononitrating recorcinol then allowing the slurry of mononitrorecorcinol to react with $Pb(OH)_2$ at elevated temperatures. The LMNR is stored and transported under water with not less than 10 percent denatured alcohol.

c. LMNR must meet the following requirements for military use:

Color and appearance:	LMNR shall be light brown in color.
Apparent density:	0.20 to 0.35 grams per milliliter.
Acidity:	The pH shall be between 5.0 and 6.5 for a solution of one gram of the material in 150 milliliters of water.
Lead content:	70.5 to 72.5 percent.
Nitro group content:	7.2 to 7.6 percent.
Vacuum stability at 120°C:	0.4 milliliters of gas in 40 hours with a 2.3 gram sample, maximum.

7-9. Primary Compositions.

a. Primary compositions are mixtures of primary explosives, fuels, oxidizers, and other ingredients used to initiate detonation in high explosive charges or ignite propellants and pyrotechnics. The ingredients and the portions of the ingredients for individual priming compositions are determined empirically from the use the composition is intended for. Fuels commonly used in priming compositions are lead thiocynate, antimony sulfide, and calcium silicide. The last two also serve to sensitize the composition to friction or percussion. Oxidizing agents include potassium chlorate and barium nitrate. Other ingredients include primary explosives and binders. The major determining factor in ingredient selection is the impetus which is to detonate the priming composition. The types of impetus commonly used are percussion and electrical.

b. Percussion type primers are used extensively for the ignition of propellants. In the early 1900's this type of priming composition contained mercury fulminates. At the present time, however, mercury fulminate has been replaced by more stable compounds. Potassium chlorate was used in this type of priming composition from about 1917 through World War II. Except for special applications, the use of this compound has been discontinued because of the corrosive action of potassium chloride, a decomposition product of potassium chlorate, on gun barrels. Potassium chlorate is still used in high temperature priming compositions. Table 7-7 lists the composition of two such mixtures. The percentages listed are by weight. Table 7-8 lists several commonly used percussion priming compositions.

Table 7-7. High Temperature Percussion Primers

	G-11	G-16
Potassium chlorate, %	53	53
Antimony trisulfide, %	25	30
Calcium silicide, %	12	17
Temperature resistant explosive, %	10	-

Table 7-8. Percussion Priming Compositions

	FA959	Composition FA982	FA956
Normal lead styphnate, %	35	36	37
Tetracene, %	3.1	12	4
Barium nitrate, %	31	22	32
Antimony sulfide, %	10.3	7	15
Powdered zirconium, %	10.3	9	-
Lead dioxide, %	10.3	9	-
PETN	-	5	5
Aluminum, %	-	-	7
Gum arabic	-	-	0.2 (added)
Autoignition temperature	199°C	240°C	184°C
Decomposition temperature	209°C	262°C	193°C

Table 7-8. Percussion Priming Compositions (Continued)

	FA959	Composition FA982	FA956
Density in grams per cubic centimeter	1.3-2.3(bulk)	1.4-2.4	1.3-2.4
Fuel to oxidizer ratio	0.5 to 1	0.52 to 1	0.69 to 1
Gas volume produced	5-10 milliliters per gram	5-10 milliliters per gram	5-10 milliliters per gram
Electrical spark sensitivity	< 0.05 joules	-	-
Friction sensitivity	yes	-	-

The output of percussion type primers includes hot gases, hot particles, thermal radiation, and a pressure pulse. In some cases the pressure pulse may be a shock wave.

c. Stab detonators are used to directly initiate secondary explosives. As the name implies, a stab detonator is initiated by penetration of a firing pin. The mechanical energy of the firing pin is converted to heat, which causes detonation. Rather than using one homogenous priming mixture as percussion type primers do, stab detonators contain three layers of charges; primary, intermediate, and base. Priming compositions used in the primary charge are shown in table 7-9. The intermediate charge is an energetic material such as lead azide or black powder. The base charge may be lead azide, black powder, or a more brisant explosive such as RDX or PETN. The base charge initiates the secondary explosive.

d. Electrical primers are of several types:

(1) exploding bridge wire

(2) hot wire bridge

(3) film bridge

(4) conductive mixture

(5) spark gap

Table 7-9. Stab Detonator Priming Compositions

	NOL 130	Composition PA101	NOL 60
Lead azide, %	20	-	-
Basic lead styphnate, %	40	53	60
Tetracene, %	5	5	5
Barium nitrate, %	20	22	25
Antimony sulfide, %	15	10	10
Powdered aluminum, %	-	10	-
Autoignition temperature	274°C	196°C	210°C
Decomposition temperature	280°C	215°C	227°C
Density in grams per cubic centimeter	1.85 (loading)	1.3-2.0	1.3-2.0
Fuel to oxidizer ratio	0.75 to 1	0.91 to 1	0.4 to 1
Gas volume produced	10-25 milliliters per gram	5-10 milliliters per gram	5-10 milliliters per gram
Electrical spark sensitivity	0.0022 joules	<0.05 joules	0.0022 joules
Friction sensitivity	yes	yes	yes
Hygroscopic	yes	yes	yes

In an exploding bridge wire detonator, a large current is passed through a wire which causes the wire to burst. The bursting of the wire causes a shock wave that is of sufficient strength to cause detonation. With this type of primer no priming composition is used; the wire is placed directly in a charge of RDX or PETN. Hot wire bridges and film bridges use priming compositions.

Examples are listed in table 7-10. In these detonators the wire or film is heated by an electric current. The heat causes ignition of the charge which may then undergo a deflagration to detonation transfer. The functioning of a conductive mixture or spark gap primer is readily apparent from the name. These two types of primers are not commonly used.

Table 7-10. *Electric Priming Compositions*

	Composition					
	I	II	III	IV	V	VI
Potassium chlorate, %	8.5	55	25	60	66.7	66.7
Lead mononitroresorcinate, %	76.5	-	-	-	-	-
Nitrocellulose, %	15.0	-	-	-	-	-
Lead thiocynate, %	-	45	-	-	-	-
DDNP, %	-	-	75	20	-	-
Charcoal, %	-	-	-	15	-	-
Nitrostarch, %	-	-	-	5	-	-
Titanium, %	-	-	-	-	33.3	-
Aluminum, %	-	-	-	-	-	33.3
Autoignition temperature	244°C	203°C	396°C	396°C	475°C	446°C
Decomposition temperature	296°C	240°C	451°C	442°C	486°C	465°C
Density in grams per cubic centimeter	1.9-2.6	1.6-2.2	1.6-2.2	1.6-2.4	2.16-2.36	0.6
Fuel to oxidizer ratio	0.9 to 1	0.82 to 1	0.3 to 1	0.25 to 1	0.5 to 1	0.5 to 1
Gas volume produced	-	-	148 milliliters per gram	96 milliliters per gram	286 milliliters per gram	150 milliliters per gram

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, $\gamma-$ 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.
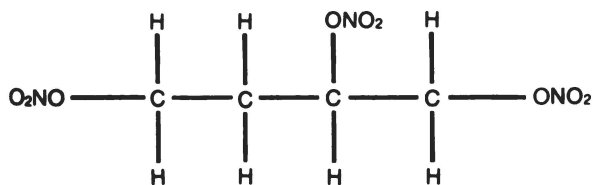
b. *Diethyleneglycol Dinitrate (DEGN).*

(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.
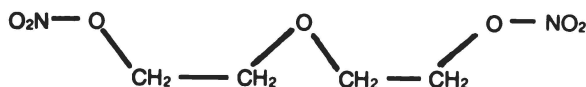

Figure 8-2. Structural formula for DEGN.

Figure 8-1. Structural formula for BTN.

000121

(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.
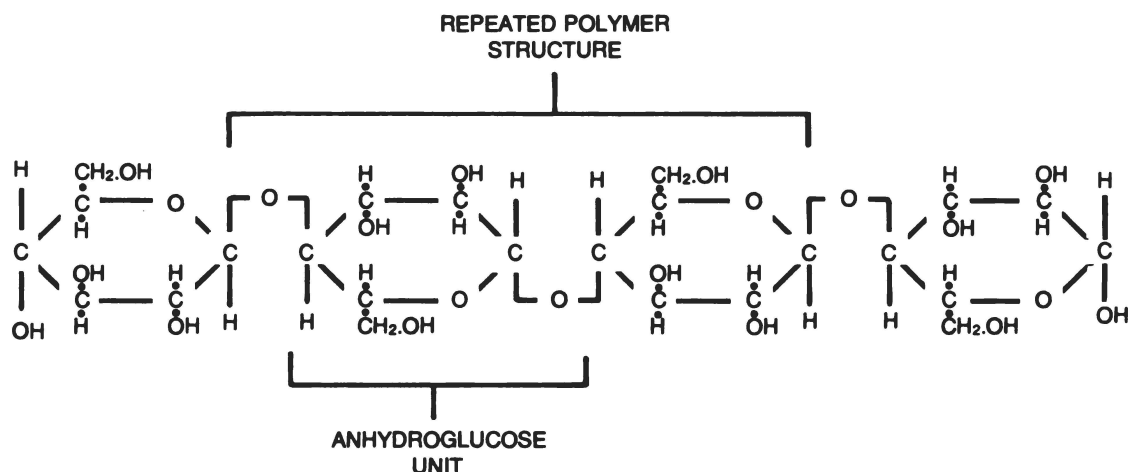
REPEATED POLYMER
STRUCTURE

ANHYDROGLUCOSE
UNIT

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 nitro-

gen 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:

$$(C_6H_7O_2)(OH)_3 + xHNO_3(C_6H_7O_2) \rightleftharpoons (OH)_{3-y} (ONO_2)_y + xH_2O$$
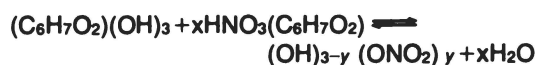
where y varies between 0 and 3 over the length of the polymer. Therefore, an equilibrium exists for each concentration of nitrating acid, which corresponds to a definite degree of nitration, provided all other conditions, such as temperature and pressure, remain the same. This means that if the concentration 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

ORIGINAL MICELLE
°ANHYDROGLUCOSE RING
°OH

PARTIALLY REACTED MICELLE
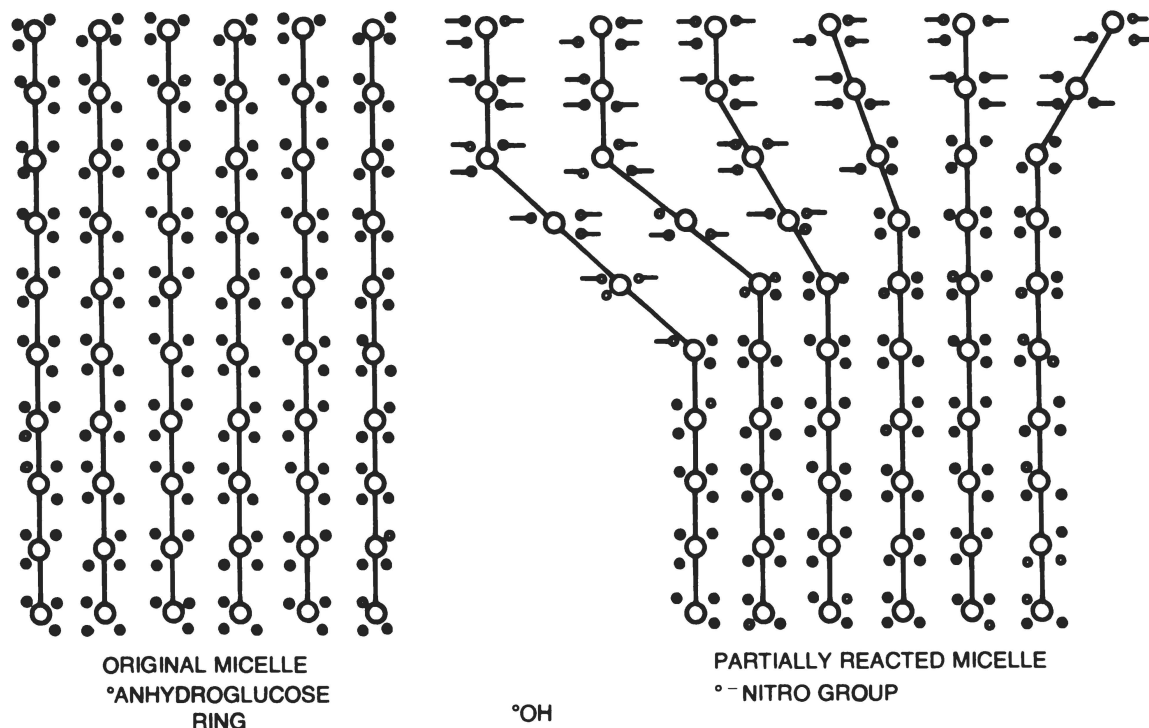° ‾ NITRO GROUP

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.
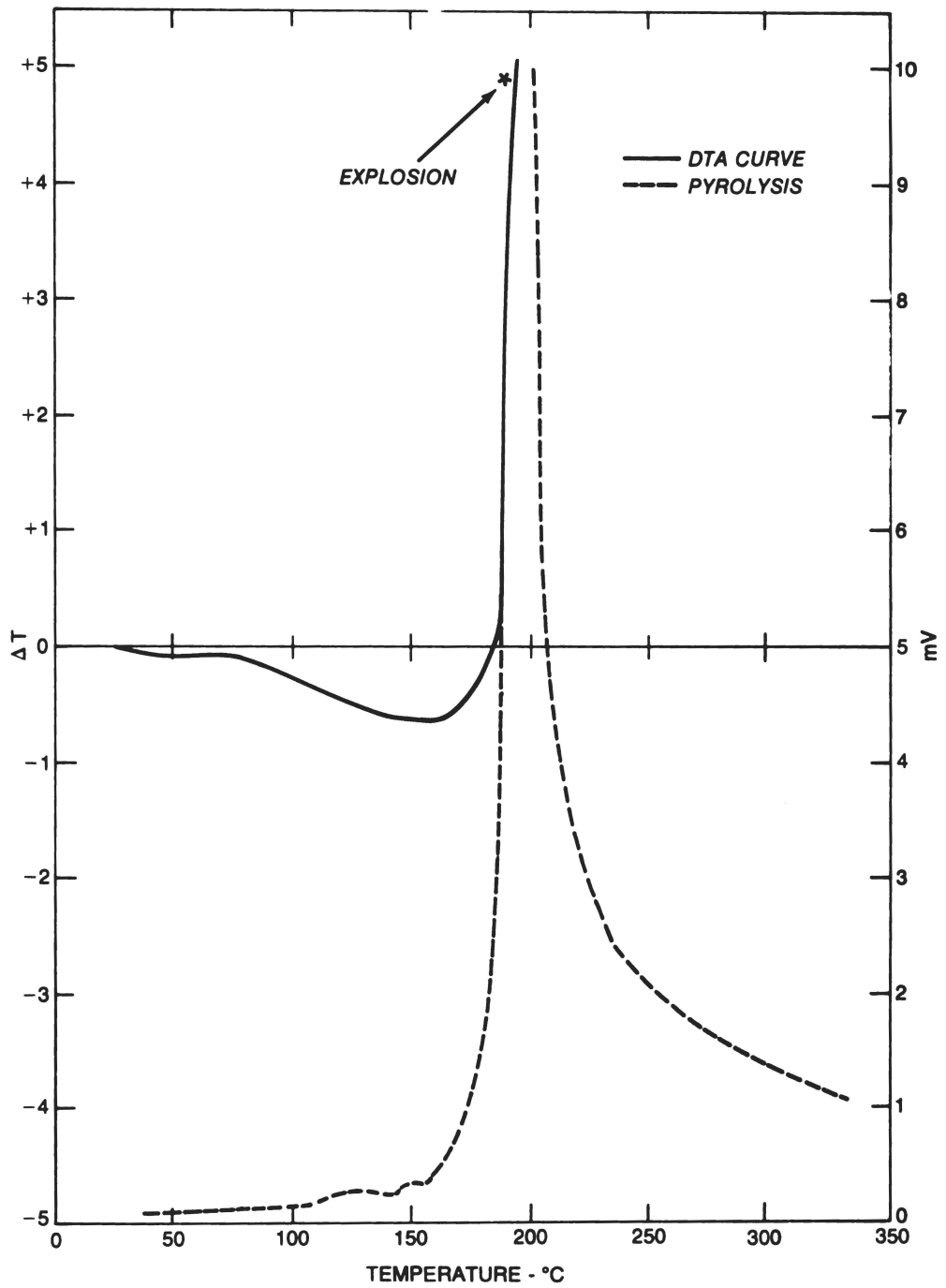
Figure 8-5.   DTA curve for nitrocellulose.

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(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.
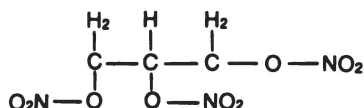

Figure 8-6. Structural formula for nitroglycerin.

(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 milliliters/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.
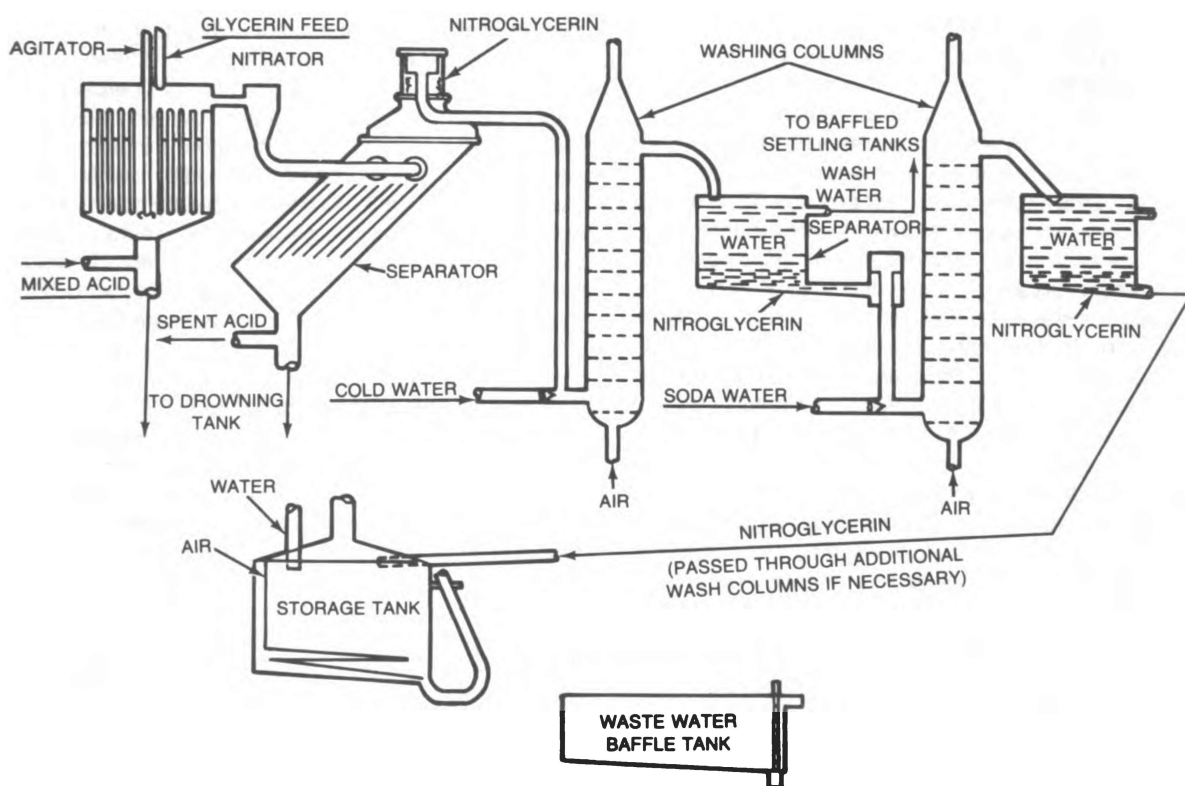

Figure 8-7. Schmid-Meissner continuous method for manufacturing nitroglycerin.

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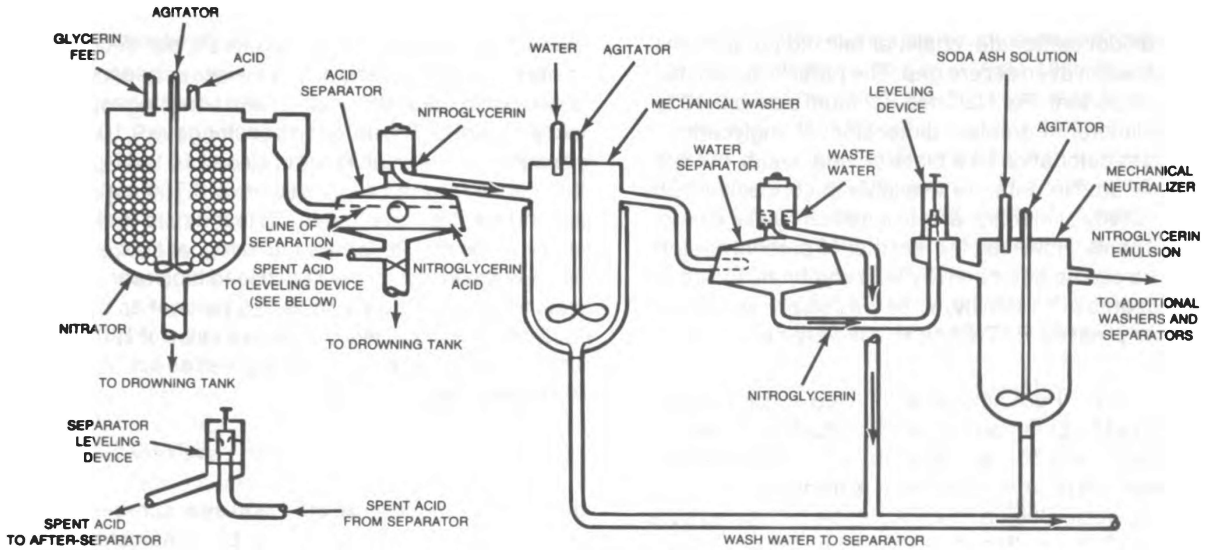
Figure 8-8. Biazzi continuous method for manufacturing nitroglycerin.

(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,

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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:

$$y = 162N/(1400-45N)$$

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 nitro-penta 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 crys-tals 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 inter-atomic 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 pres-sure at temperatures above 210°C, PETN decomposes rapidly and in some cases detonates. The vapor pres-sure of solid PETN can be found by the empirical equa-tion:

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

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:

$$C = 0.257 + (5.21 \times 10^{-4})T \text{ for } T \leq 140°C$$
and $C = 0.239 + (8.0 \times 10^{-4})T$
$$\text{for } 32°C < T < 127°C$$

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.
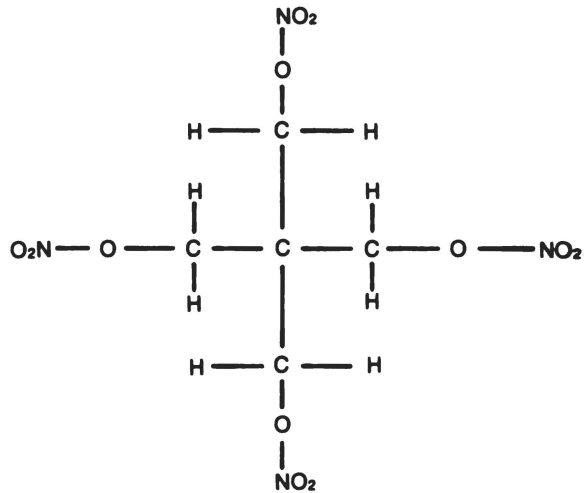
Figure 8-9.   Structural formula of PETN.

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:

$$C(CH_2OH)_4 + 4HNO_3 \longrightarrow C(CH_2NO_3)_4 + 4H_2O$$

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 $(HOH_2C)_3C.CH_2O.CH_2C(CH_2OH)_2.CH_2O.$
$$CH_2C(CH_2OH)_3.$$
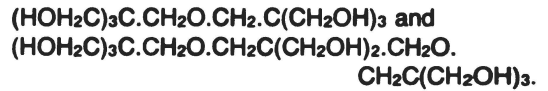
PETN produced on a large scale contains corresponding amounts of the hexanitrate and octanitrate of these compounds, respectively.

(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.

$$D = 2.14 + 2.84p \qquad p < 0.37$$
$$D = 3.19 + 3.7(p - 0.37) \qquad 0.37 < p < 1.65$$
$$D = 7.92 + 3.05(p - 1.65) \qquad p > 1.65$$

000140

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 cri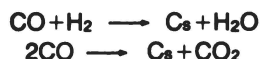tical diameter becomes smaller as the density of the charge is increased. Since confinement effects parallel the diameter effects, the detonation velocity of PETN is not greatly affected by confinement for any particular charge size. This is also indicated by table 8-9. Detonation, or Chapman-Jouguet, pressure is shown as a function of packing density in table 8-10.

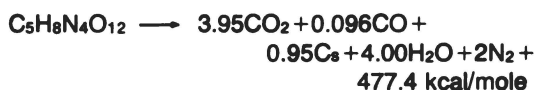*Table 8-10. PETN Detonation Pressures Versus Density*

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.
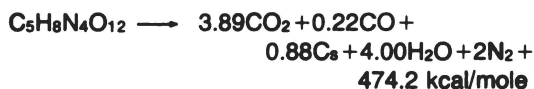
(8)   The products obtained upon detonation of PETN depend on the density of the explosive. The four equations listed in subparagraphs (a) through (d) are valid at the density given. The subscript s refers to soot. The soot is produced in the Chapman-Jouguet region by the reactions:
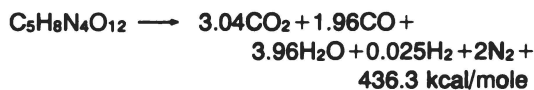
$$CO + H_2 \longrightarrow C_s + H_2O$$
$$2CO \longrightarrow C_s + CO_2$$

(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:

$$C_5H_8N_4O_{12} \longrightarrow 3.04CO_2 + 1.96CO + 3.94H_2O + 0.050H_2 + 1.99N_2 + 0.02NO + 436.3 \text{ kcal/mole}$$
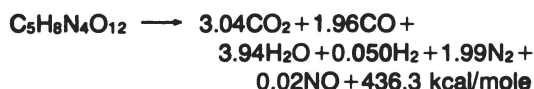
and minor amounts of NH_3, H, OH and CH_4.

(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.
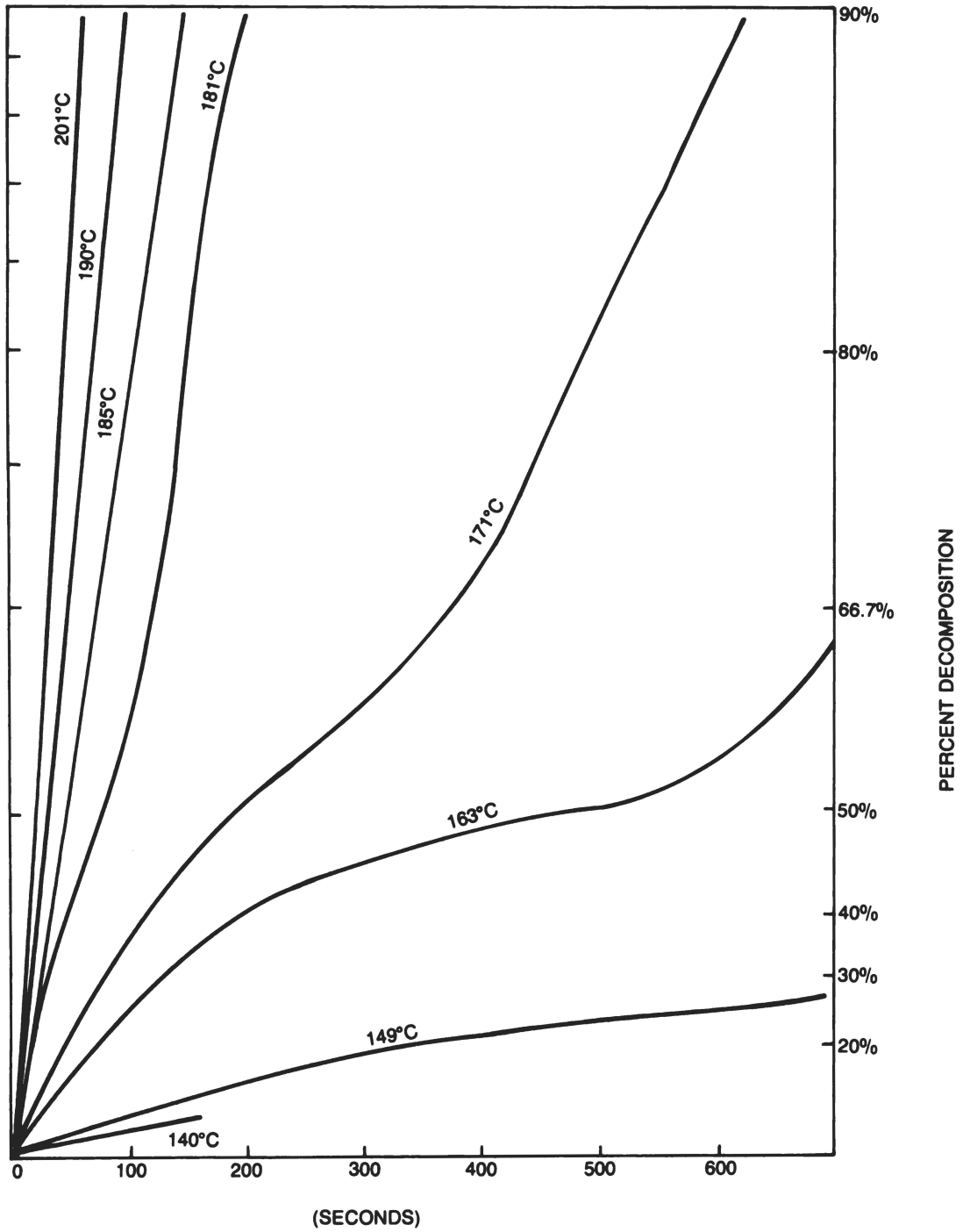
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Figure 8-10. Thermal decomposition of PETN.
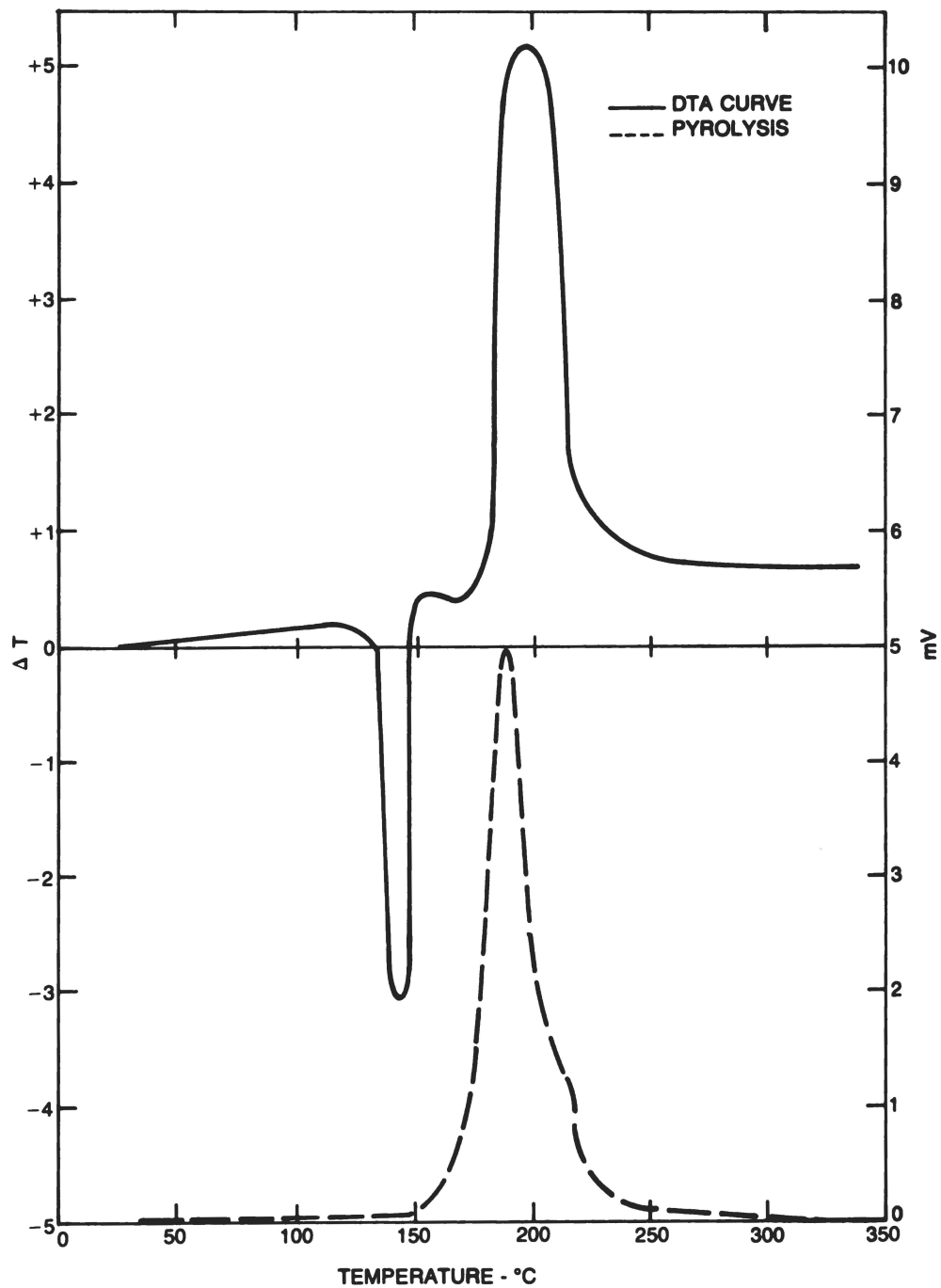
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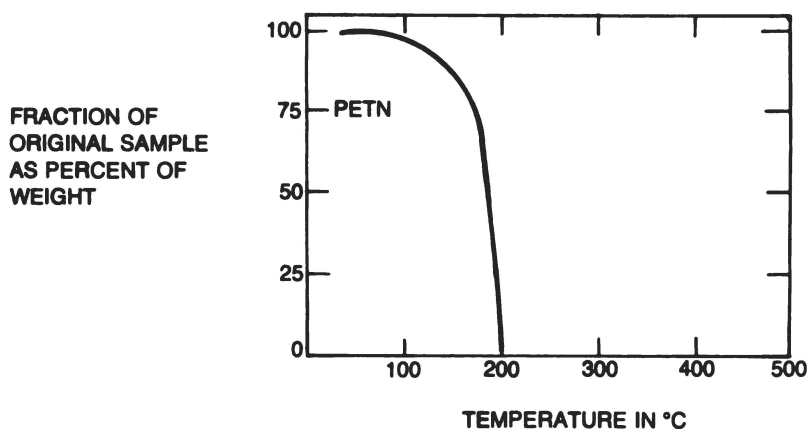Figure 8-11.   DTA curve for PETN.
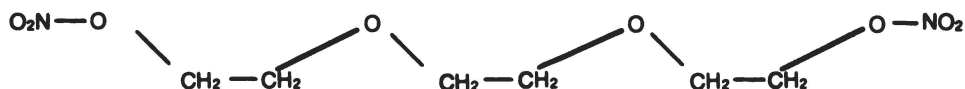
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Figure 8-12. TGA curve for PETN.

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.
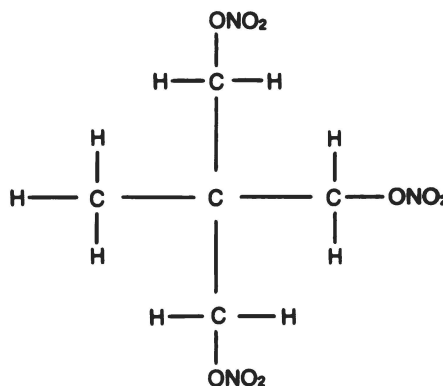

Figure 8-14. Structural formula for TMETN.

(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.
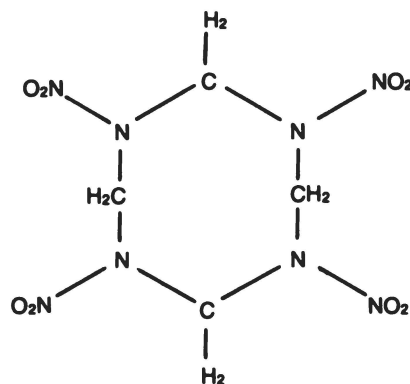
Figure 8-15. Structural formula for HMX.

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.

000147

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:

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

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 tempera-
ture of 44°C ±1°C. All part measurements in this dis-
cussion are by weight. The solution is held at that tem-
perature throughout the subsequent steps of the pro-
cess. 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 anhy-
dride are added simultaneously, continuously, and
equivalently. The mixture is aged for 15 minutes. In the
second stage of the reaction, 320 parts of acetic anhy-
dride 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 per-
cent. 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 man-
ufacturing.

(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

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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

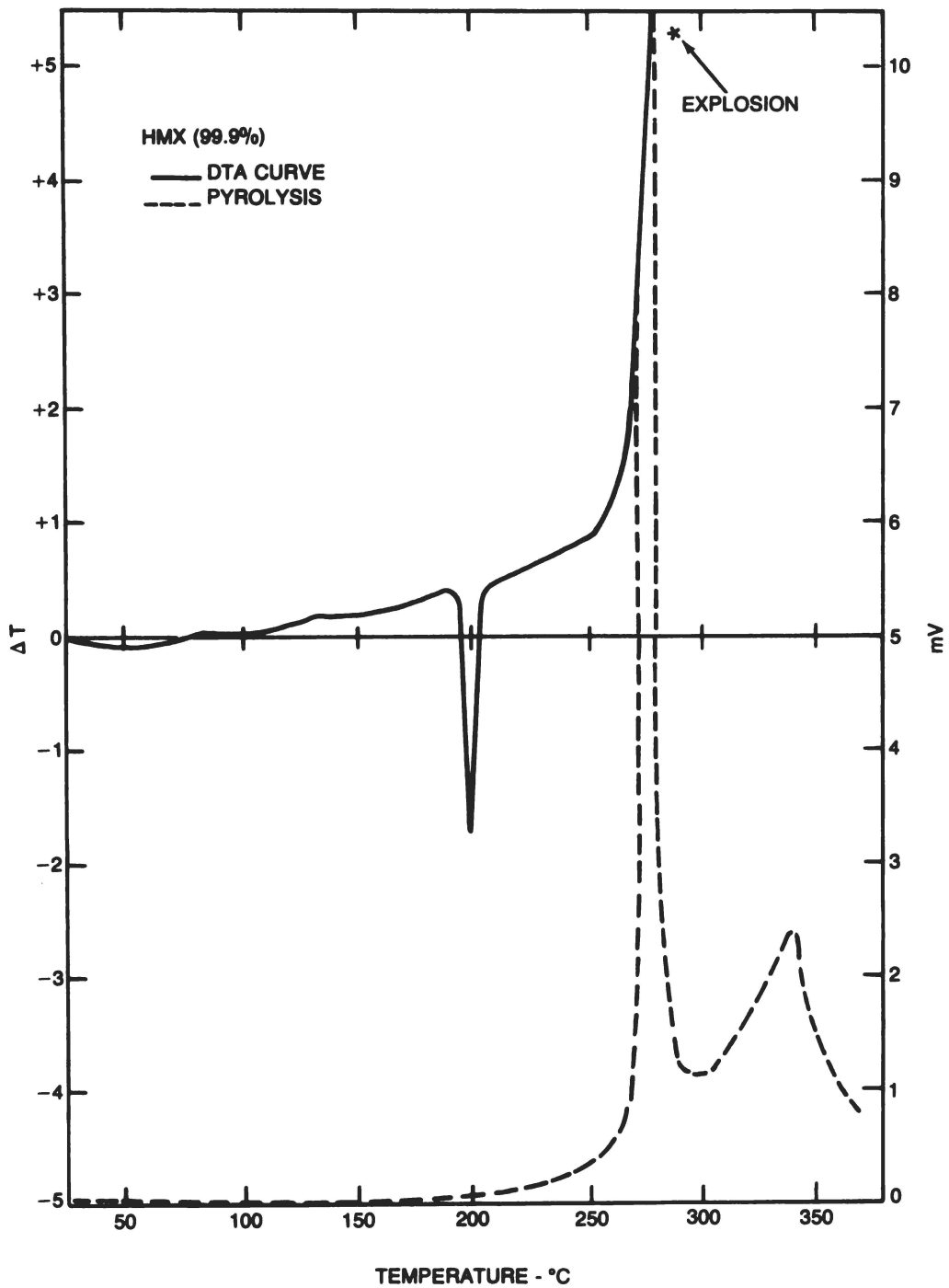| Pressure kilopascals	Pressure pounds per square inch	Density grams per cubic centimeter
34,475	5,000	1.52
68,950	10,000	1.60
137,900	20,000	1.68
172,375	25,000	1.70
206,850	30,000	1.72

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:

$$(CH_2.NNO_2)_3 \longrightarrow 2CO + CO_2 + 2H_2O + H_2 + 3N_2$$
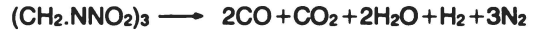
The temperature developed on explosion is 3380°C. There are two grades specified for RDX: types A and type B. Type A contains no HMX and type B has a constant impurity of from 8 to 12 percent HMX. Types A and B are produced by different manufacturing processes. Type A RDX melts between 202°C and 203°C; type B RDX melts between 192°C and 193°C. The vapor pressure of RDX is given by the equation:

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

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.
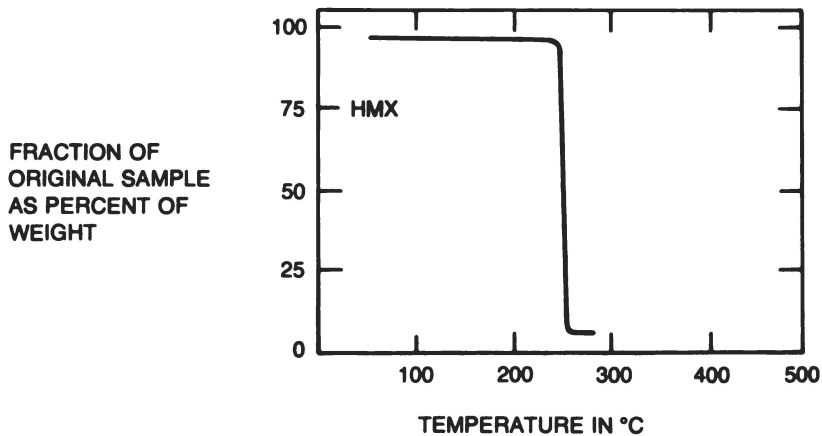

Figure 8-17. TGA curve for HMX.

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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
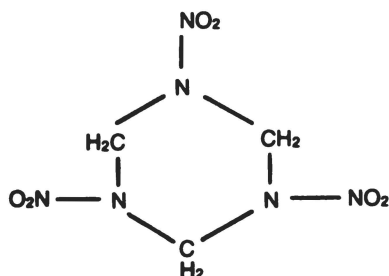
Figure 8-18. Structural formula for RDX.

(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 per-

cent 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.
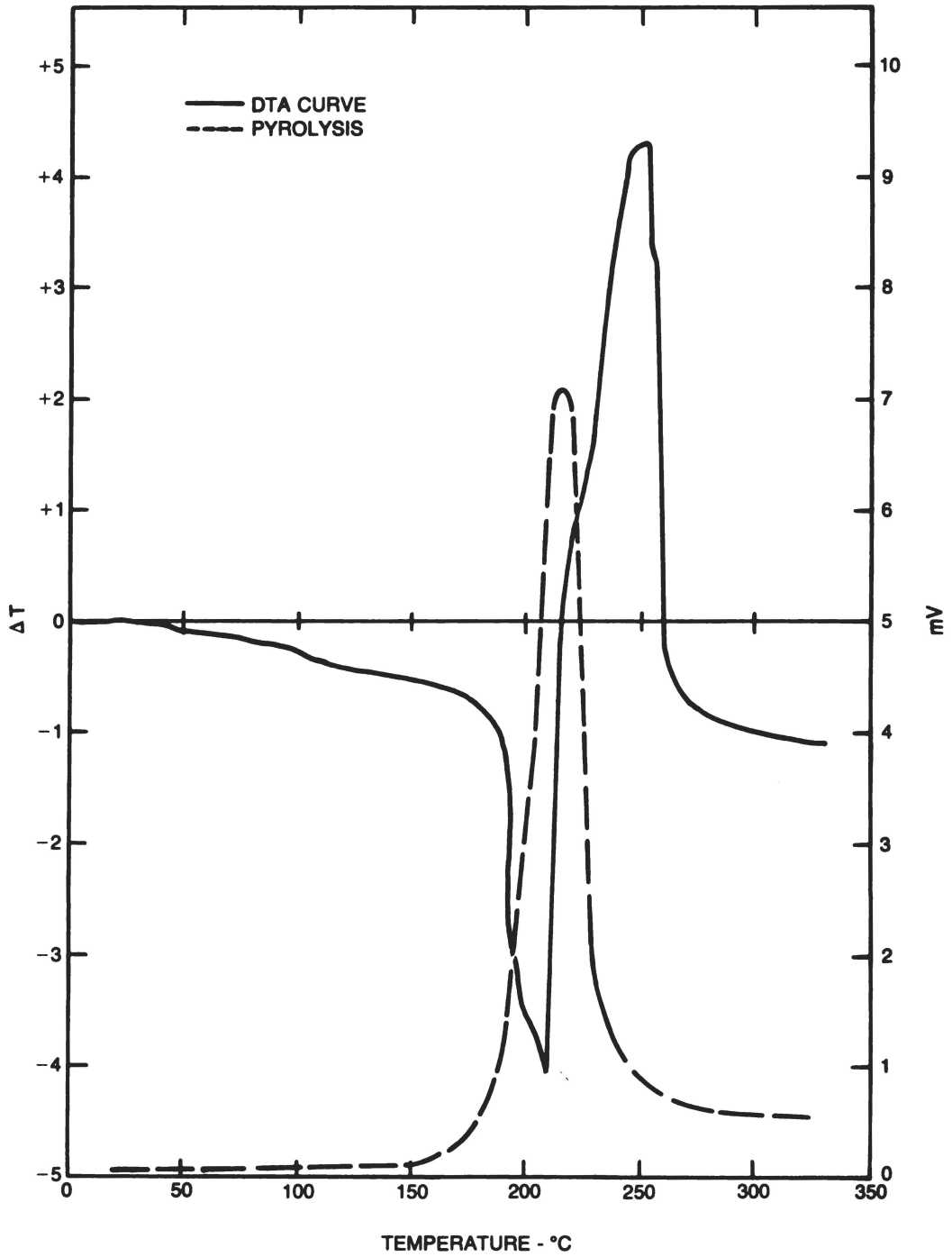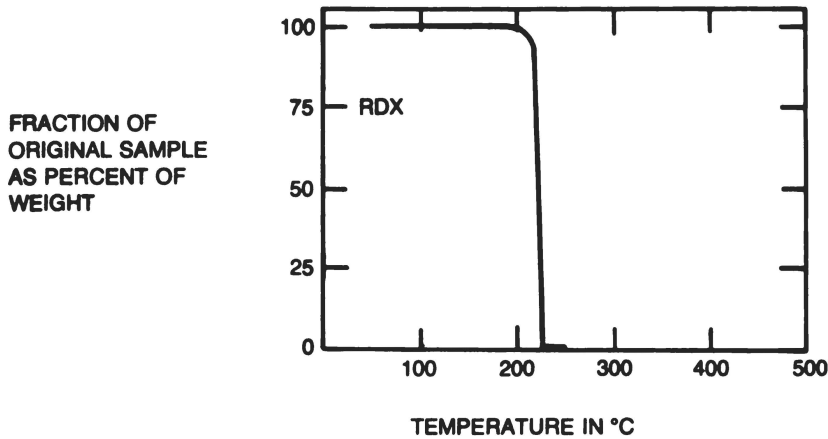
Figure 8-19.   DTA curve for RDX.

000156

FRACTION OF
ORIGINAL SAMPLE
AS PERCENT OF
WEIGHT

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

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