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HEADQUARTERS DEPARTMENT OF THE ARMY Washington, DC 20 September 1984

Technical Manual

No. 9-1300-214

MILITARY EXPLOSIVES

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CHAPTER 1 INTRODUCTION

1-1. Purpose. This manual is intended for use as a text for instruction or as a reference source in the field of energetic materials. Only the materials of interest in conventional armaments are covered; nuclear armaments are not.

1-2. Scope. Chapter 2 is a history of the field of energetic materials. Chapter 3 divides the energetic materials field into three categories: explosives, propellants, and pyrotechnics. Chapter 4 discusses the principles of chemistry and physics pertinent to the energetic materials field. Chapter 5 is a description of the tests used to evaluate explosives. Both mandatory safety tests and tests used in the selection of particular compounds among the many explosive compounds are covered. Chapter 6 contains a description of the tests used to evaluate propellants. Chapter 7 presents detailed information about the compounds that are used by the United States as initiating explosives. A discussion of priming compositions is also included. Chapter 8 presents detailed information about the compounds that are used by the United States as booster and secondary explosives. Chapter 9 provides a discussion of those mixtures of materials that are used as propellants. Chapter 10 discusses the field of pyrotechnics. Foreign energetic materials are covered in Chapter 11. Safety and toxicity considerations are discussed in Chapter 12. Basic methods used to identify and detect energetic materials are presented in Chapter 13. Chapter 14 presents information pertinent to the packing, marking, storing, and shipping of energetic materials. Chapter 15 discusses disposal, destruction, decontamination, and demilitarization of energetic materials. Pertinent data on explosives and propellants are tabulated in Appendix A. Tables A-1 through A-8 allow rapid comparison of the important characteristics of the material. The bibliography is contained in Appendix B. An index for all material covered, referencing both paragraph and page numbers, concludes the contents of this manual.

CHAPTER 2 HISTORICAL DEVELOPMENT OF ENERGETIC MATERIAL

2-1. Introduction.

a. *Purpose*. This chapter describes the development of energetic material in chronological order.

b. Scope. This history is mainly concerned with military applications of energetic material, however some important nonmilitary uses are also discussed.

c. Relationship of Development to Science and Technology. Developments in the energetic material field are generally the result of a close relationship between basic research and technology. Advances in basic research provide new materials and new applications. The use of the new materials and new methods of application, as well as ideas from other fields, advance technology or even create new technology. The advancement of technology gives an impetus to further research. For example, the shaped charge effect was discovered in 1888. Little use of the principle was made until World War II, when technological advances made the tank a major battle weapon. At the present time, significant progress is being made in lessening the effect of a shaped charge on armor. This will require further development in energetic materials and their applications to defeat the newer types of armor.

d. Interrelationship Among Explosives, Ammunition, and Weapons.

(1) Explosives are the materials that detonate. They may be used independent of, or form a part of, ammunition. For military management purposes, the two are controlled as one category of weapons or armaments.

(2) Weapons are instruments of any kind used in fighting. We may consider weapons as the tools used in warfare. The development of these tools is the art or science of weaponry. Weaponry includes use of clubs, stones, slings, axes, spears, darts, javelins, bows and arrows, shields, body armor, etc. for hunting and fighting. Later, siege weapons such as catapults and ballista (the forerunners of cannon) were developed to hurl large stones and other missiles at fortifications. Better weapons created the need for a special group of artisans called metalworkers and metallurgists. The metalworkers began shaping the weapons from metals. The metallurgists practiced the art or science of extracting metals from their ores, refining them, and preparing them for use. e. Discoveries, Inventions, Developments. Historians often disagree as to who was the first to discover, invent, develop, or use a new theory, characteristic, device, or material. Authenticating this information is a difficult task, for the records and terminology used to record these facts may be misleading. What has been published and used as an official source in subsequent documents may have been taken from an unreliable source. The history of energetic materials is particularly full of such examples. For example, who invented black powder or gunpowder? And, when was gunpowder first used? Sometimes the answer is that several or many people or nations were all involved at the same time.

2-2. Early Use of Flame, Incendiaries, and Smoke.

Flame and Incendiaries. Flame and incena. diaries are the oldest chemical weapons dating back to the caveman's use of flames and burning coals to drive off animals and enemies. In Biblical times, armies attacking and defending fortified cities threw upon each other burning oils and flaming fireballs consisting of resin and straw. In 424 BC, the Spartans successfully employed a prototype of the flamethrower against a Greek fort in Delium. Attaching a pot filled with burning pitch, coals, and sulfur to a hollow log, they used bellows to blow a hot jet of flame which set fire to the city walls and routed the defenders. Incendiary compositions of pitch, sulfur, hemp or flax, and resinous wood were used in the Trojan Wars about 360 BC. Centuries later, the Romans used similar materials in fire bombs or fire pots, which they catapulted over the walls of besieged towns. To set fire to wooden forts they used hollow, perforated arrows filled with incendiary materials, which were ignited just before being shot. The most famous of the incendiary mixes was "Greek Fire," which was prepared by Kallinikos of Heliopolis in Syria to enable the Byzantine fleet to defeat the Caliphate Navy in 668 AD. The exact formula for Greek Fire is unknown. However, the formula is believed to be a mixture of sulfur, naptha, pitch, resin, and quicklime, which ignited and burned fiercely upon contact with water. The Greek Fire was apparently forced by water, under high pressure, through tubes or siphons. The violent reactions and high pressure ejected the burning incendiary mixture toward the enemy ships. For the next six centuries, the Byzantines used Greek Fire to thwart the Moslem and subsequent Russian sieges of Constantinople. Chinese

2-1

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manuscripts as early as 969 AD mention fire arrows, fire lances, and incendiary "rockets." But with the exception of Greek Fire, such weapons had little impact on warfare until World War I.

b. Smoke. While history tells us that screening smoke was employed in early conflicts, the results of these isolated incidents were always too uncertain to justify the adoption of smoke as a recognized agent of warfare. In fact, prior to World War I dense clouds of smoke generated by the black powder used in battle had become a definite nuisance. These clouds obscured the field of vision, interfered with aiming and firing, and hampered the movement of troops. More recently, these very same characteristics have been exploited tactically by the planned employment of screening smoke munitions.

2-3. Invention of Fireworks and Black Powder.

a. Fireworks. Fireworks are devices that produce displays of lights, noise, or smoke by the combustion of explosive compositions. Fireworks are managed under that group of ammunition designated as "pyrotechnics." Those who ply this art are called "artificers." Some historians credit the Chinese with being the first true artificers. In the reign of Haiao Tsung of Nan Subng (1169-1189 AD), true fireworks made their debut. They were similar to those used today. The first fireworks were made of incendiary materials with various powdered minerals added to color, or to increase the light or smoke effect. Not until the invention of black powder were the artificers able to generate the displays with which we have become familiar today, such as Roman candles, rockets, fire crackers, serpentines, whistles, and stars. The French, in particular, became very adept at civil pyrotechnics by the 17th and 18th centuries. Civil pyrotechnics are generally limited to fireworks used for public display, signalling, or rescuing.

b. Black Powder. Authorities differ upon the origin of black powder accrediting in turn the Chinese, Hindus, and Arabs. In 1249 AD Roger Bacon, an English monk, recorded a formula for black powder saltpeter (7 parts), charcoal (4 parts), and sulfur (4 parts). Although Bacon was not the inventor, his were probably the first truly scientific experiments with this explosive. Sulfur and charcoal had been used in incendiary compositions for many centuries. Saltpeter (potassium nitrate) appears in nature but requires refining to supply the proper amount of oxygen to ignite the black powder mixture. Bacon's knowledge of purified saltpeter probably came from the Arabs who obtained this information from the Chinese about 1225 AD. Bacon mentioned in his writings that the ingredients of black powder were used in firecrackers made in various countries of the world.

2-4. Introduction of Gunpowder in Europe.

a. Invention of Guns and Gunpowder. The age of gunpowder began early in the 14th century with the invention of the gun, which consisted of a metal tube from which a projectile was discharged by the explosive force of black powder. Guns and gunpowder provided a new means of propelling stone, iron, or lead balls with greater force than catapults or slings. The discovery of the usefulness of black powder for accomplishing mechanical work may be considered the real beginning of the history of explosives. When ignited by a torch, a loose charge of black powder above the borehole of a gun served as a priming composition. A train of black powder in the borehole advanced the ignition to set off the propellant charge of black powder in the gun tube. The Chinese and Europeans evidently became aware of this application of black powder about the same time. Because Chinese developments did not keep pace with those in Europe, the Europeans have been credited with inventing and developing guns and gunpowder. The earliest mention of black powder on military supply lists was in 1326 AD. Also at that time, a Latin manuscript called "On the Duties of Kings," written by Walter de Milemete, King Edward III's chaplain, included the first known illustration of a cannon.

b. Manufacture of Gunpowder. Roger Bacon's black powder recipe was not for gunpowder. Different proportions of saltpeter, charcoal, and sulfur were required to propel missiles from the early cannon and firearms. In the mid 12th century, John Arderne, an Englishman, gave the proportions of saltpeter, charcoal, and sulfur as 6:2:1, the same as recommended by Marcus Graecus around 1275 and by Albertus Magnus in 1300. The Germans, who some scholars claim invented gunpowder and guns around 1313 (i.e., the legendary Berchtold Schwarz), were using a mixture of 4:1:1 in 1350. The ingredients were ground, mixed, and used in a fine powder or meal. At first, the materials were mixed in a mortar using a pestle operated by hand and were later mixed by horse power. Later, improvements in machinery mixed gunpowder with rollers on a marble slab and with wooden stamps. Mixing black powder was considered a highly technical art and a dangerous one too. Sometimes the final mixing was done at the gun site to reduce the hazard of stores exploding. Nevertheless,

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the records of towns and armies during the early days of gunpowder contain many references to accidental explosions. Other mostly useless ingredients, such as amber, alcohol, camphor, wine, urine, arsenic, and sal armoniac, were added to the recipe to improve stability, reduce absorption of moisture, and to prevent crumbling. Depending on the weapon or the use, some countries varied the proportions of saltpeter, charcoal, and sulfur. For example, the French at one time made six different mixes - one strong and one weak each for pistols, muskets, and cannons. Different mixes have been used for blasting, mining, and sporting weapons. In 1895, most countries, including the USA, adopted the English standard 75:15:10 (saltpeter: charcoal: sulfur), which had been in effect since 1781. This standard is generally used for all arms, the only difference being in the size of the grains.

2-5. Developments Betwsen the 15th and 18th Century. The development of energetic materials from 1400 to 1800 were restricted mainly to improvements in the manufacture of black powder and related applications. By 1400, iron cannons, bound by iron hoops to keep them from bursting, and iron cannon balls were coming into use. At the end of the 14th century, a hand gun was invented that weighed 4.5 kilograms (10 lbs) and fired lead shot. One man carried the gun, which was mounted on a stand and aimed at the enemy. This weapon evolved into the arquebus or hargebus, a hand gun with a bent stock and a forked staff to support the barrel while firing. A lit match or fuse of serpentine black powder was used to ignite the propellant powder charge through a touch hole in the breech (closed end) of the gun barrel. Other important events or developments during this period are as follows:

a. 1425. Corning, a new process for making black powder into grains instead of the finer serpentine gunpowder, was invented. Corning consisted of wetting black powder to form a paste, which was then pounded into a cake. The cake was broken into small lumps by hand and sifted. The resulting pieces, which were called corned powder, absorbed less moisture and were more suitable for use in cannons than the serpentine powder. Flame from the priming powder was distributed more efficiently by the larger grains. This resulted in a more complete explosion and reduced fouling.

b. 1540. Standard gunpowder grain sizes for pistols, muskets, and cannons were adopted by the French. They discovered that less powder was needed to propel a projectile if the grain size was controlled. By using uniform, slow-burning grains they were able to control the pressure of the explosion in the gun, and thereby reduce the hazard of blowing up the gun. This discovery also led to improvements in gun design. c. 1560. Linen or paper bags containing gunpowder were used for charging cannons.

d. 1578. An instrument for testing gunpowder was devised by Bourne of England. Until then, the only test was to burn a small quantity to see how much residue would be left. The testing device consisted of a small metal cylinder with a heavy metal lid on a hinge. The lid was prevented from falling by a ratchet, and the angle to which the lid rose when powder was fired inside the cylinder measured the strength.

e. 1588. Explosive shells were used at the siege of Bergen op-Zoom and Wachtendonck, Holland by the Dutch. The shells were made from hollow iron balls filled with gunpowder. The gunpowder was ignited by a fuze consisting of a hollow tube filled with slow burning serpentine powder, and timed to burn 14 to 20 seconds, corresponding to ranges of 914 to 1830 meters (1000 to 2000 yards) for mortar fire. The knowledge for making this fuze was brought to the Dutch by an Italian deserter from Parma.

f. 1590. Cartridges with ball and powder combined were introduced for small arms.

g. 1602-1604. Fulminating gold, later used as a priming explosive, was invented by Johann Tholden, a Dutch chemist in the employ of the British Navy.

h. *1611-1632*. An improved paper cartridge was developed during the rule of Swedish King Gustavus Adolphus, thus increasing the rate of fire for firearms used in the Thirty Years' War.

i. 1613. Blasting powder is reported to have been used in German mines to blast rocks. Less saltpeter and more charcoal and sulfur were used in blasting powder than in gunpowder.

j. 1627. An improved instrument for testing black powder was devised by Curtenbach. This consisted of a heavy conical shot, which rested on the mouth of a small mortar and could travel vertically upwards along a stretched wire provided with a series of catches to stop the shot from falling.

k. 1627. Black powder was used to blast ore in the royal mines at Schemnitz, Hungary following experiments by a Hungarian engineer, Kaspar Weindl. Using black powder for this purpose was slow to be accepted because saltpeter was expensive, boring instruments were not available, and safety hazards from mine gases and cave-ins were increased.

I. 1628. Gold fulminate priming explosives for torpedos were invented by J. Thollen for the British Navy.

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m. 1647. Testing the strength of gunpowder, by firing a ball from a mortar and measuring the distance the ball travelled, was proposed by Master-Gunner Nye in his "Art of Gunnery." This mortar test was adopted by France and other countries soon afterward.

n. 1654. Ammonium nitrate was first prepared by J. R. Glauber, a German chemist.

o. *1679.* Blasting powder was used on a large scale in the construction of the Mal pas Tunnel, Canal de Midi, France.

p. 1684. Glazing process for gunpowder was introduced. Rough gunpowder corns were glazed by tumbling them in large wooden drums until the grain surfaces were smooth. Graphite was added to coat the grains. Glazed gunpowder was less hygroscopic and flowed more easily than the unglazed gunpowder.

q. 1735. Antimony sulfide and arsenic sulfide were used by Ruggieri of Italy in pyrotechnic mixtures for brilliant fireworks displays at Versailles.

r. 1738. The closed bomb for measuring the pressure generated by gunpowder fired in a closed vessel was designed by d'Antony of Italy.

s. 1742. The ballistic pendulum, which determined the velocity of a projectile's impact by measuring the recoil of a struck pendulum, was invented by Benjamin Robins, an English mathematician. Robins showed that air resistance on a moving projectile at high velocities is greater than the resistance at low velocities. Robins also developed the first practical chronograph, an instrument for measuring and recording short durations of time, and improved on a closed bomb for testing the power of an explosion.

t. 1771. Picric acid was first prepared by Pierre Woulfe, a French chemist, by treating silk with nitric acid. Picric acid is an aromatic nitro compound which was used as a yellow dye until its explosive properties were discovered in 1871.

u. 1784-1788. Potassium chlorate was prepared in its pure state by Claude L. Berthollet, a French chemist who discovered its detonating properties. His idea of using potassium chlorate instead of potassium nitrate in black powder was abandoned after a disastrous explosion during manufacture in 1788. Berthollet also prepared fulminating silver in 1788.

v. 1784-1789. Compact black powder grains were obtained by pressing the cakes with screw presses before corning at Faversham, England.

2-6. Nineteenth Century Development. Modern energetic materials technology began with the nineteenth century. New energetic materials began to

displace the black powder formulas that had been the choice for use in weapons, ammunition, and blasting for over 350 years. The discovery of new materials or the practical application of previously known materials (for example, picric acid) greatly influenced the design and performance of weapons and ammunition. In turn, the rapid development of weapons and ammunition, and the increased demands of new and expanding industries further accelerated the search for more effective, less expensive materials. During the nineteenth century, more powerful propellants (such as smokeless powder), better primers, various boosters or detonators, and new high explosives were introduced. There were significant advancements in the science and technology of weapons and ammunition, too. Among these were improved explosive (Congreve) rockets (later adapted for signaling and illumination), rifled arms, revolvers, magazirie-loading rifles, machine guns, revolving turrets, armored naval vessels, percussion caps (encapsulated primers), metallic cartridges, time fuzes and impact fuzes for artillery shells, rifled breech-loading field artillery, obturation devices, and spring and hydropneumatic recoil mechanisms for artillery. Modern mass production began when Samuel Colt, an American gunsmith, first manufactured standard rifle and revolver parts. Mass production of small arms ammunition began when G. Moore Peters used the first cartridge-loading machinery at his factory in Ohio. Nineteenth century developments of energetic materials follow.

a. 1800. Mercury fulminate was discovered by Edward Howard, an English chemist, who described its detonating properties in a paper before the Royal Society.

b. 1801. Fireworks formulas containing metal salts and ammonium chloride were published by C. F. Ruggieri, an Italian artificer. These salts produced brighter flames because volatile metal chlorides were formed during the combustion reaction.

c. *1807.* The principle of using mercury fulminate as a primer was patented by Rev. Alexander J. Forsyth of Aberdeenshire, Scotland.

d. 1823. Chlorates, discovered by C. F. Berthollet in 1786, were first used in fireworks by John Cutbush, an English artificer.

e. 1825. Benzene, creosote, and naphthalene were isolated from coal tar (obtained from bituminous coal) by Rev. Dr. Clayton in England. Most of his products were later nitrated to produce explosives, such as trinitrobenzene and nitronaphthalenes.

f. 1826. Aniline was first prepared by Unverdorben. Later, nitration of aniline resulted in the very powerful explosive called tetranitroaniline.

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g. 1831. Safety fuse for blasting was invented by William Bickford of Cornwall, England. The Bickford fuse consisted of a core of black powder tightly wrapped in textiles (mainly jute yarn). The timing, or burning time, for a given length of fuse was very accurate and consistent. This fuse soon replaced the less reliable fuses which were made of straws or quills filled with black powder, thus greatly reducing the hazard of accidental explosions in mining or construction. Later, the Bickford safety fuse was waterproofed by applying a coat of asphalt covered with either a textile or plastic.

h. 1832. Ammonium perchlorate was first prepared by E. Mitscherlich, a German chemist, who also nitrated benzene and toluene in 1833 or 1834.

i. 1833. Nitrostarch was discovered by Heriri Braconnot, a French chemist, while dissolving starch in concentrated nitric acid to form a flammable nitric acid ester of starch. This is considered to be the beginning of modern high explosive technology.

j. 1837-1838. Nitrated paper, soluble in ethyl alcohol, and nitrated cotton fibers, insoluble in ethyl alcohol, were prepared by Prof. Theophile Jules Pelouze, a French chemist. These products were highly combustible.

k. 1841. Ammonium picrate was first prepared by Marchand, and was used in 1869 by Brugere as a propellant.

I. 1843. Picric acid, discovered but not identified by Peter Woulfe in 1771, was rediscovered by A. Laurent who found that some of the salts were explosive.

m. 1845. Guncotton was prepared by Christian F. Schoenbein, a German chemist, while at the University of Basel, Switzerland. Upon nitrating cotton with mixed nitric acid and sulfuric acid, he demonstrated that the resulting nitrocellulose was up to four times as powerful as black powder for blasting. The guricotton burned without leaving an ash. Schoenbein also prepared the first nitrosugar, which deflagrated suddenly and violently when heated to a certain point. Schoenbein and R. Boetter of Frankfurt, Germany, who had discovered guncotton independently, obtained patents in 1846 and 1847 under the title: "Improvement in Preparation of Cottonwool and Other Substances as Substitutes for Gunpowder." Serious accidental explosions during early attempts to manufacture guncotton in 1847 delayed its acceptance as an explosive; however, guncotton eventually became accepted universally for use in blasting and for smokeless powder when mixed with nitroglycerin.

n. 1846-1847. Nitroglycerin, an ester of glycerin and nitric acid, was invented by Asconio Sobrero, an Italian chemist. Because nitroglycerin is very sensitive to slight shocks, commercial use was delayed until the invention of dynamite and blasting gelatin. Nitroglycerin was also used later to make smokeless powder.

o. 1847. Mannitol hexanitrate or hexanitromannitol was first prepared by A. Sobrero, but the explosive properties were not examined until 1878 when N. K. Sokoloff of Rüssia investigated these characteristics.

p. 1847. Cyanuric triazide was first prepared by Auguste A. T. Cahours, a French chemist.

q. 1850. A testing device for measuring explosive pressure in cannons was developed by Col. George Bomford of the US Ordnance Department. Bomford inserted pistol barrels in holes drilled along the gun tube and measured velocities of bullet blowout. Based on these data, the weight of guns could be reduced.

r. 1850. An improved testing device for measuring explosive pressures in cannons was designed by LTC Thomas J. Rodman of US Ordnance Department. Pistons with punch-type ends were installed at intervals on the cannon and were forced by the explosion of the propellant into copper blocks. Measuring the depth of the indentations indicated the relative pressures along the length of the gun tube. Rodman also developed a process of casting guns hollow and cooling them from within. The Rodman process put the metal surrounding the bore of the gun under a permanent compressive strain that greatly increased the gun's resistance to interior pressures.

s. 1853. Nitroglycerin absorbed in magnesia was developed by V. F. Petrushevskii, a Russian officer, for use in mining gold in Siberia. This was a precursor of dynamite.

t. 1857-1858. Sodium nitrate deposits found in Chile were originally converted to saltpeter (potassium nitrate) by reaction with potassium chloride, which was also in plentiful supply. Lammont du Pont, an American industrialist, introduced a new formula for black powder using sodium nitrate in lieu of potassium nitrate. Black powder containing potassium nitrate was called blasting powder A, and black powder contairing sodium nitrate was called blasting powder B. Blasting powder B was less expensive and more hygroscopic, which made it more suitable for blasting. Powder formulas were considered more suitable for firearms, safety fuses, and fireworks. u. 1858. Diazo compounds were discovered by Peter Griess, who also prepared dinol or diazodinitrophenol.

v. 1859. Ethylene oxide, ethylene glycol, and ethylene glycol ether were prepared by Charles A. Wurtz. A century later, ethylene oxide was used in fuelair explosives (FAX) developed by the US Armed Forces. Diethylene glycol was also developed simultaneously in 1859 by Wurtz and A. V. Laurenco.

A caseless propellant, consisting of w. 1860. cakes of compressed black powder cakes or grains with perforations, was developed by T. J. Rodman while working at Frankford Arsenal. Philadelphia. This led to the use of grains shaped into hexagonal prisms about 2.54 cm (1 inch) long and 2.54 cm (1 inch) across. Perforations and grooves in the grains channel the flame from the explosion. As the grains burn inward from the prism surfaces and outward from the perforations, the burning gases flow continuously, thereby permitting the explosive energy to build up gradually until the maximum power is exerted as the projectile leaves the muzzle of the gun. This acceleration imparts a more efficient thrust to the projectile and extends the range of the gun.

x. 1861. Guanidine was formed by the oxidation of guanine by Strecker. Guanine is a derivative of guano, which was formed from manure, especially that of birds and bats.

y. 1863. Trinitrotoluene (TNT) was prepared by J. Willibrand, German scientist. Although TNT was used for many years in the dye industry, TNT was not used as an explosive until 1904. Thereafter, TNT became one of the most used high explosives.

z. 1862-1866. Nitroglycerin production plants were designed for commercial applications by Alfred Bernard Nobel, a Swedish chemist, based on studies conducted with his father, Emmanuel, in 1859-61. In 1862, they built their first plant at Heleneborg, Sweden. Despite the tragic loss of his brother Emil in an explosion at that plant in 1864, Alfred erected two more plants in 1865 and another in 1866.

aa. 1865. Magnesium was first used for pyrotechnics.

bb. 1865. Nitrocellulose was purified by Sir Frederick A. Abel, an English chemist, who also successfully manufactured granulated nitrocotton. Abel pulped, washed, and compressed the nitrocellulose into blocks, sheets, discs, and cylinders, which were particularly useful for blasting.

cc. 1865. Smokeless powder, used as a sporting propellant, was invented by Schultze, a Prussian officer,

through nitrating wood, washing the wood with a dilute solution of sodium carbonate, and drying.

dd. 1866-1867. Dynamite was invented by A. Nobel by absorbing nitroglycerin (75) in kieselguhr (diatomaceous earth) (25). Kieselguhr, an inactive ingredient, stabilized the nitroglycerin, and made dynamite a much safer explosive to handle and use.

ee. 1867. The fulminate blasting cap, a device consisting of mercury fulminate in a copper tube used to detonate explosives, was invented by A. Nobel. This cap was crimped to one end of a safety fuse (e.g. Bickford fuse), and then inserted into the dynamite cartridge.

ff. 1867. Ammonium nitrate, pulverized and mixed with sawdust or charcoal, was proposed as an absorbant for nitroglycerin by J. H. Norribin and C. J. Ohlsson, Swedish inventors.

gg. 1868. Dry compressed guncotton was detonated with a mercury fulminate detonator by E. A. Brown, an English chemist, who also discovered that wet guncotton could be exploded by the initiation of a small quantity of dry guncotton. This important discovery, on the principle of a booster explosive, led to the use of large blocks of wet guncotton in naval mines with comparative safety.

hh. 1869. Dynamites with an active base were patented by A. Nobel. To create an active base dynamite, Nobel mixed nitroglycerin with combustibles (sawdust, charcoal, rosin, and starch), and oxidizers (sodium nitrate or potassium nitrate). This led to a more efficient explosive than guhr dynamite.

ii. 1870. Ohlsson and Norribin's patent for ammonium nitrate dynamite was purchased by A. Nobel, who subsequently began production of ammonium nitrate dynamite.

jj. 1871. Sprengel explosives, which consisted of mixing various combinations of oxidizing agents (chlorates, nitrates, and nitric acid) with combustibles (nitronaphthalene, benzene, and nitrobenzene), were patented by Hermann Sprengel, a German chemist. Oxidizing agents and liquid fuel were mixed on site before using.

kk. 1875. The "Explosives Act" was passed by the British Government after a disastrous explosion at Birmingham killed 53 persons. The Explosives Act established Inspectors of Explosives, who were given the power to inspect all magazines and factories to ensure that operations were carried out in a reasonably safe manner. As a result, the number of deaths in explosives factories was greatly reduced. The provisions of this act have been adopted by many other countries.

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II. 1875. Gelatinous dynamites and blasting gelatins were patented by A. Nobel.

mm. 1877. Nitroguanidine was first prepared by Jousselin, but was not used in propellants until 1900.

nn. 1879. Tetryl, a booster explosive, was first prepared by Michler and Meyer of Germany.

oo. 1879. Ammonium nitrate gelatins, known as ammongelatins, were patented by A. Nobel.

pp. 1882. Brown or cocoa gunpowder was made by the Germans using partially burned charcoal from rye straw. The grains were made in single, perforated hexagonal or octagonal prisms. Brown powder was of higher quality, but was more sensitive to friction than black powder. The United States used brown powder during the Spanish-American War.

qq. 1883. Tetryl was synthesized from picryl chloride and potassium methylnitramine by van Romburgh, a German chemist.

rr. 1883-1884. Colloided rifle powder was prepared by Max von Duttenhofer by nitrating brown charcoal before mixing the ingredients. This brown powder was adopted by the German Army in 1884.

ss. 1884. Smokeless powder, for military rifles, was invented by Paul Vieille of France. This powder was a completely colloided single-base nitrocellulose propellant. The French Army adopted Vieille's Poudre B. in 1866.

tt. 1884-1885. High-speed photographic cameras were used for ballistic studies by Eugene Mach and P. Salcher of Austria.

uu. 1885. Two flashless powders, ammoripulver and amidpulver, were patented and made by Gaens of Hamburg from ammonium nitrate, potassium nitrate, and charcoal.

vv. 1885. The Hell Gate blast in New York Harbor used 34,000 kg (75,000 lbs) of dynamite, and 11,000 kg (24,000 lbs) of potassium chlorate soaked in nitrobenzene (rack-a-rock) to remove Flood Rock, a menace to navigation. This was the largest amount of explosives used in a single blast until then.

ww. 1885-1888. Eugene Turpin, a French scientist, patented the process of melt-pouring picric acid into artillery shells as a high explosive filler. Sprengel had discovered that picric acid could be initiated by a powerful detonator, but had not exploited this knowledge. The French Government adopted a high explosive shell designed by Turpin using a picric acid filler. They designated the picric acid filler as melinite. In 1888, the British adopted picric acid, which they called lyddite as an high explosive filler. xx. 1888. The shaped charge effect was accidentally discovered by Charles E. Munroe, an American scientist, at the Naval Academy. Munroe discovered that a concave-shaped explosive charge pierces a steel plate.

yy. 1888. Cyclotrimethylene trinitrosamirie was discovered by Griess & Harrow and by Mayer, yet was not used until the Germans, who called it R-salz, used the composition in World War II.

zz. 1888. Ballistite, the first double-base smokeless propellant, was prepared by Alfred Nobel by replacing camphor with nitroglycerin. In 1889, Nobel prepared ballistite from collodion cotton and nitroglycerin using a solventless method.

aaa. 1888-1889. Cordite, the second successful double-base smokeless propellant, was prepared by Dr. W. Kellner in F. Abel's English laboratory. Sir James Dewar, British chemist and physicist, and Abel patented cordite for the British Government, which adopted cordite as a military propellant named Cordite Mark I or CSP (cordite smokeless powder).

bbb. 1890. Tetranitrocarbazole, used in igniter and pyrotechnic compositions, was first prepared by Karl Graebe, a German chemist. The current method of preparation was developed in 1912 by the Leopold Cassella Company in Frankfurt, Germany, a division of the Interessen Gemeinschaft (I. G.) Farben corporation.

ccc. 1889-1890. The development of explosive devices was greatly enhanced by the work of Theodor Curtius, German Nobel prize laureate, who discovered hydrazine in 1889 and hydrogen azide in 1890. He subsequently suggested to the German military the use of metal azides for primer application.

ddd. 1892. Tetranitrooxanilide was prepared by A. G. Perkin, an English scientist, and used as a comporient in black powder type explosives and pyrotechnic compositions.

eee. 1894. Butanetriol trinitrate, used a half century later as an explosive plasticizer for nitrocellulose, was first prepared by Wagner and Ginsberg.

fff. 1895. Liquid oxygen explosive (LOX), carbon black packed in porous bags and dipped in liquid oxygen, was introduced by Karl P. G. von Linde of Germany. LOX was widely used by Germany during World War I, and in the United States Midwest for strip-mining in the 1950's.

ggg. 1896. A layered smokeless propellant, which was prepared by glueing and compressing together several layers of different components, was paterited by A. B. Bofors, Nobelkrut of Sweden. The outer layers were slow-burning, while the burning speed increased progressively towards the inner layers.



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hhh. 1897-1898. Cheddite. an explosive for blasting consisting of potassium chlorate or perchlorate mixed with a nitro compound and castor oil, was invented in England by E. Street. Cheddite derives its name from Chedde, France, where it was made.

1899. Potassium dinitrobenzfuroxan, used in priming compositions, was first prepared by P. von Drost.

jji. 1899. Cyclonite (RDX) was first prepared by Henning of Germany. Henning used RDX, which he called Hexogen, for medical purposes. The first to recognize the value of RDX as an explosive was E. von Herz of Germany. The first to prepare RDX in quantity was G. C. Hale of Picatinny Arsenal, NJ, in 1925. However, it was not until World War II that the most important work in manufacturing processes and applications of RDX was done.

kkk. 1899. Aluminized explosives, containing aluminum to increase the performance of explosives, were first proposed by R. Escales of Germany and were patented by G. Roth. Ammonal, their first, contained ammonium nitrate, charcoal, and aluminum.

2-7. Twentieth Century Development through

World Warl (WWI). This period saw the use of cordite smokeless powder and repeating rifles by the British during the Boer War (1899-1902) in South Africa; large scale naval battles and full-scale use of machine guris in the Russo-Japanese War (1904-1905); and the introduction of submarine warfare, armored tanks, aerial bombing of civilians by dirigibles, and strafing and bombing by aircraft during World War I (1914-1918). World War I saw concentrated machine gun fire, artillery barrages, firing long ranges from railroad guns and from large guns on battleships, firing torpedoes, laying mines, using depth charges in anti-submarine warfare, and signaling and illuminating with flares. Soldiers were issued steel helmets and gas masks for individual protection.

a. 1900. Cordite smokeless powder, used by the British in the Boer War, caused excessive corrosion in gun barrels. As a result, the formula for cordite was changed to reduce the amount of nitroglycerin from 58% to 30% and to increase the amount of nitrocellulose to 65% with the amount of mineral jelly remaining at 5%.

b. 1900. Picric acid (British lyddite) shells were used in the Boer War but did not detonate completely. This was attributed to faulty construction of the detonators.

c. 1900. The Contact Process for manufacturing concentrated sulfuric acid and oleum was discovered by Badische Anilin-und Sodafabrik of Germany. This process was less expensive than the chamber method previously used. As such acid was required for mixed nitric-sulfuric acid to nitrate aromatic hydrocarbons to polysubstitution, trinitrobenzene and trinitrotoluene (TNT) could be inexpensively manufactured.

d. 1900. Chromatography, a physical method of separation in which the components are partitioned between two phases, was invented simultaneously and independently by American geologist D. T. Day and Russian botanist M. S. Tsvet. The qualitative method of separation of ingredients by adsorption was known for centuries.

e. 1900. Regular-delay electric blasting caps for rotational shooting (0.5 to 12 seconds) developed.

f. 1901-1904. A trinitrotoluene (TNT) manufacturing process consisting of three phases was developed by C. Haussermann of Germany. This method, which proved to be more economical than direct nitration of toluene to TNT, was used in the United States until World War II. The German industry adopted this process in 1902, when they adopted TNT as the filler for high explosive shells. They also used TNT for demolition purposes, replacing picric acid.

Detonating cord, developed in France, q. 1902. was improved, leading to adoption in the United States by the Ensign-Bickford Company in 1912.

1902. Antifreeze for dynamite was researched h. extensively in many countries following a disastrous explosion during defrosting dynamite in Greisnau, Germany. The problem of producing a satisfactory antifreeze remained unsolved until S. Nauckhoff of Sweden published his work in 1905, listing requirements for a satisfactory antifreeze, and compounds which met these requirements.

i. 1903. A muzzle-flash suppressor using vaseline with 1-2% sodium bicarbonate was proposed by Rottweil Fabrik of Germany. This was replaced in 1905 by soap or rosin.

j. 1904. The Obermueller Stability Test, which consisted of heating 1-2 grams of nitrocellulose in a small tube under vacuum at 135-140° and measuring the pressure of evolved gas by vacuum manometer, was introduced.

k. 1904-1905. Methyl picrate (2,4,6trinitroanisole) was patented for use in smokeless propellants. The powder consisted of an equal amount of methylpicrate and pyrocellulose.



2-8

I. 1905. Nitrostarch was produced in a stable form. Nitrostarch is similar to nitrocellulose but is lower in strength. Nitrostarch does not cause headaches from skin contact as do TNT, nitroglycerin, dynamite, and many other explosives.

m. 1906. Various substituted ureas, called centralites and akardites, were developed at the Central Laboratory for Scientific and Technical Research at Neubabelsberg, Germany, for chemical stabilizer application in smokeless powders.

n. 1906. Lead azide was proposed by Col. A. A. Solonina of Russia for use in compound detonators (initiating explosives) in lieu of mercuric fulminate.

o. 1906. Hexanitroazobenzene was prepared by E. Grandmougin and H. Lehmann of France, and recommended by Tenny L. Davis for use in boosters.

p. 1907. Diphenylamine, designated as poudre B, was approved as a stabilizer for French naval cannon propellants and other large caliber guns. This stabilizer replaced amyl alcohol after the disastrous explosion in 1907 of the battleship lena.

q. 1907. Mixed glycol esters, such as dinitroacetin with dinitroformin, were patented as dynamite antifreeze by Vezio Vender of Italy.

r. 1908. A detonating cord (cordeau detonant) containing TNT instead of blackpowder was patented in France. This detonating cord had a detonation velocity of 4,880 meters (16,000 feet) per second.

s. 1909. Ammonium picrate (Dunnite or Explosive D) was standardized in the United States as a bursting charge for armor-piercing (AP) shells. These AP projectiles could be fired through 12 inches of armor plate, and could be detonated on the far side by an insensitive primer.

t. 1909. Low-nitrated aromatic hydrocarbons, because of their stability and insensitivity to shock and to ignition, began to be used in coal mining explosives compositions.

u. 1909. Solventless powder (or propellant) was discovered by Brunswig and Thieme of Germany, although many others contributed to the development of such propellants.

v. 1910. Preparation of 2,3,4,6-tetranitroaniline, a powerful explosive, was patented by Flurscheim. This explosive was used during World War II by the Germans and Japanese.

w. 1910. Tetracene was first prepared by K. A. Hofmann in Germany. More extensive studies of the compound were conducted in 1931 by Rinkenbach and Burton.

x. 1910-1913. Laminated solventless propellants were prepared by Dr. C. Claessen, a German scientist. Making propellants into large solventless grains was less time consuming than making solvent propellants.

y. 1912. TNT was adopted as the standard bursting charge in high explosive shells for the field artillery of the US Army.

z. 1912. Nitroisobutylglycerol trinitrate or trimethylol nitromethane trinitrate, used as an explosive gelatinizer for nitrocellulose, was first prepared by Hofwimmer.

aa. 1912-1913. Tetranitroaniline (TNA) was patented by Dr. B. J. Flurscheim, an English scientist.

bb. 1914. Lead styphnate (trinitroresorcinol), an initiating explosive, was first prepared by E. von Herz of Germany. Col. A. A. Solonina of Russia was the first to propose using lead styphnate in compound detonators.

cc. World War I. The high-explosive technology of the contending powers greatly influenced the conduct of World War I. At the outbreak of war in the summer of 1914, the German General Staff had planned to fight a high-explosives war of great intensity. Their plan was to mount a sudden and overwhelming attack using vast stores of artillery ammunition accumulated over the preceding forty years. After the battle of the Marne in 1914, the Germans realized that explosives production must be expanded; and they turned to their dye industry for this expansion. When the war began, Germany's chemical industry was producing 85% of the world's dyes. The Germans were able to rapidly convert their plants to production of synthetic ammonia, nitric acid, and sulfuric acid, which were required for the manufacture of explosives and chemical warfare agents. When Germany's access to Chilean saltpeter was cut off by the Allied blockade, the key to the German war production of explosives was the Haber process for producing ammonia from atmospheric nitrogen. By expanding their nitrogen plants at Oppau and Merseburg, Germany was able to become independent of foreign countries for the supply of ammonia and nitric acid. Because these chemicals were so essential for the manufacture of explosives and fertilizer for food products, it is doubtful if Germany could have continued the war beyond 1916 without the amazing speed with which the I. G. Farben concern was able to convert their dye plants to explosives plants. For example, at Leverkuseri, a TNT plant producing 250 tons per month was put into operation in six weeks. The major powers began accelerating the search for substitutes or supplements to TNT. The most important were mixtures of high explosives, such as TNT, TNX, and TNN, with ammonium nitrate and aluminum. By 1914, the French had already begun



replacing picric acid (melanite) with TNT. In 1915, the British developed amatol (TNT plus ammonium nitrate) to extend the supply of TNT. In 1917, Austrian ammonal T (TNT, aluminum, and ammonium nitrate) was developed by R. Forg to be used in underwater explosives, such as torpedoes and depth charges. Lead azide was introduced as an initiator, and tetryl was used as a booster explosive for artillery shell charges. About 2,500,000 tons of high explosives were used by the contending powers during the war, resulting in an estimated 10 million casualties.

dd. World War I. High-explosive aerial bombs were first dropped from German Zeppelins during the 31 May 1915 raid on London. The Germans continued to use these dirigibles, practically unopposed, in their air raids on London and Paris until late in 1916. Then the British and French began to counter these attacks with anti-aircraft gunfire and fighter aircraft. Soon the Germans began using their large Gotha bombers, which they employed throughout 1917 and 1918. In retaliation, the Allies began producing fleets of larger bombers and various high-explosive bombs.

ee. World War I. Incendiary bombs were also first used during the German Zeppelin raid over London on 31 May 1915, when one dirigible dropped 90 incendiary bombs. The early incendiaries used by the Germans in their air raids over London and Paris were made from a mixture containing manganese dioxide and magnesium. Later, the French used sulfur-bound thermite, a mixture of iron oxide and powdered aluminum, in an incendiary drop bomb. The British were the first to develop incendiary bomb clusters, which could release either 144 or 272 bomblets. A De Haviland bomber could dispense up to 860 of these 6.5 oz incendiary bomblets, and a Handley-Page V bomber could dispense up to 16,000. By flying in formation, these bombers could cover a large area with a blanket of burning incendiary materials.

ff. World War I. Flamethrowers were first introduced by the Germans on the French front on 25 June 1915. Their weapon was a cylindrical steel vessel about 61 centimeters (2 feet) high and 38 centimeters (15 inches) in diameter, fitted with carrying straps. Internally, the cylinder was divided into a compression chamber and an air reservoir. A short hose carried the fuel to the nozzle where it was ignited. The propellant was nitrogen. The fiery spurt of burning oil, the roar of the flame, and the billowing clouds of black smoke had a terrifying effect on troops in trenches. Using this prototype of the modern portable flamethrower, the Germans drove back a British rifle brigade from trenches near Ypres, Belgium, in 1915. The Americans used a heavy viscous tar and a more fluid, flammable liquid such as crude benzene for their flame fuel mixture. A hydrogen pilot lamp at the flamethrower nozzle was used to ignite the flame fuel. The World War I flamethrowers had a range of about 30 meters. Although effective for assaulting fortifications, the flamethrower was also very hazardous for the operator because of its short range.

World War I. Smoke munitions were used aq. both on land and sea by the belligerent powers in World War I. In July 1915, the British were the first to use smoke pots, which were filled with pitch, tallow, black powder, and potassium nitrate. The first large-scale smoke operation occured on 20 September 1915, when the Canadians fired several thousand smoke shells from trench mortars during the attack against Messines Ridge. Although very successful against the Germans, the British and French tanks of World War I were capable of travelling only four miles per hour, which made them very vulnerable to artillery fire. The British Tank attack at Cambrai on 20 November 1917 was supported by intense artillery smoke shelling, which enabled 350 tanks to break through the German lines. On 15 June 1918, the Austrians used smoke to screen their crossing of the Piave River, from Vidor into San Giovanni, from Italian machine gun concentrations. The Allies generally used white phosphorus (WP) to fill their smoke shells; whereas the Germans, because of a shortage of phosphorus, used a mixture of sulfur trioxide in a chlorosulfonic acid solution. The Germans used this type of smoke (FS) to successfully screen their warships during the battle of Jutland in 1916. Later, the United States adopted FS smoke for use in spotting rounds, for liquid chemical agent shots, and in airplane smoke tanks. FS was reclassified obsolete in November 1975 because WP was considered better for marking targets and FS droplets from aerial spray destroyed the nylon fabric in parachutes. Titanium tetrachloride (FM) was also used as a filler for spotting rounds during both world wars, but was removed from the US inventory because of its high cost. In 1918, tanks carried containers filled with chemicals, which when injected into the vehicle exhaust system formed a cloud of screening smoke. Sulfuric acid. chlorosulfonic acid, oleum, and crude oil were used as the smoke screening agent in these early smoke generators. WP hand and rifle grenades were used by the infantry for screening movements. The main disadvantage was the danger of the user being exposed to falling particles of burning white phosphorus, which is also an incendiary. WP grenades were reclassified obsolete in November 1975 by the US Army.

hh. World War I. Incendiary artillery shells and rifle bullets were introduced in 1915 to set fire to buildings, supply dumps, and enemy observation balloons. The Germans used sodium in their 17.5 centimeter artillery shells. They also used thermite or an aluminum-thermite mixture in their other artillery rounds. The Allies used thermite most frequently. Thermite incendiary grenades were issued to raiding parties for hasty destruction of captured enemy weapons that could not be retrieved.

ii. World War I. Pyrotechnics for battlefield illumiriation were used extensively during World War I. The British alone used 10 million position light flares per month. The art of making illuminants had been neglected after the reign of Louis XIV until the twentieth century. In 1913, the German Krupp Works developed an illuminating projectile, which they called a searchlight shell and which later became known as the star shell. The first star shell contained six small tubes, called stars, loaded with an illuminating composition. The mixture used was similar to that in the white Bengal lights for fireworks displays; but ribbons of magnesium were substituted for antimony powder. A folded parachute was placed in the bottom of each tube. The projectile was fired from a cannon or mortar. When the projectile reached a height of 300 meters, a mechanical time fuze set off a small black powder charge releasing the tubes from the shell and igniting the pyrotechnic mixture. Springs were used to open the parachute instantly, and the tube with its burning star floated slowly to earth. The illuminating material burned very brightly for 45 seconds to several minutes depending upon the model. The French constructed a similar projectile containing eight cylinders, which was fired from their 155 millimeter howitzer. However, they preferred using burning-type fuses to set off the powder charge in their star shells. Later, the Germans replaced the star tubes with a six-sided prism, which was more compact and could be adapted for use with rifles, special pistols, and large caliber carbines. By using plates to retard the fall of the star, more space was made available in the star for storing the illuminating mixture; and a light of greater intensity or longer duration was obtained. The Italians used a hand-held, heavy pasteboard tube to discharge a sheet-iron star shell tube, which expelled its illuminating parachute flare. This flare burned about 40 seconds. Many different illuminating devices were developed and used by both sides, but perhaps the simplest and most useful for trench warfare was the illuminating grenade. Thus every soldier on night patrol had his own device for lighting his sector, and exposing the advancing enemy to aimed gunfire.

jj. World War I. During World War I, pyrotechnics for signaling included colored smoke cartridges, can-

dles, flares, streamers or trails, star signals, and night signals. Four general designs of firework devices were in constant use by the French and the British armies. These devices were Very-type signal pistols, rifle lights, rockets, and ground or position signals (e.g. candles). (The same type of devices were used for illumination.) The signal-pistol cartridges used by the French were fitted with delay fuzes, which effected the ignition when the projectile reached its maximum height. Some realization of the development in pyrotechnic construction due to the war may be had by considering the latest production of the French 35-millimeter signal cartridge, which included 14 varieties or combinations of signals. Upon entering the war, the United States adopted many of the French signals for Army use. This was mainly because the American forces were to operate in the French sector, which necessitated an identical system of signals. Generally, the fireworks and devices employed by the Germans were similiar to those of the French, but there was an important difference in the method of construction for the signal-pistol cartridge. The German cartridge was ignited just after emerging from the barrel of the pistol. Rockets mounted on sticks for stabilization during flight were employed by the Allies. The Germans followed Congreve's construction in the use of metal, but modified the design to eliminate the use of a stick. In the German rocket, the openings for escaping gas were in the base. Before the outbreak of the war, the art of pyrotechny had reached such a point that little difficulty was encountered in securing adequate mixtures for the various colors required in signaling. Different colored flares had been used for many years commercially. The railroad companies regularly employed pyrotechnic devices, such as red railroad fusee, while blue light pyrotechnics were used for signaling at sea. The colors used by the Allies included red, green, yellow, blue, black, various numbers of white stars, and changing colors. The Italians used a tri-color parachute flare, which emitted red, white, and green colors. The Italians also developed a hissing flare, which, when suspended from a parachute, burned with a hissing noise audible over an area of 3,000 meters (3,284 yards) in diameter. This was found particularly effective as a gas alarm. Some of the ingredients used in the WW I pyrotechnics were aluminum, potassium nitrate, sulfur, antimony sulfide, antimony metal, dextrine, meal powder, barium chlorate, potassium chlorate, fine charcoal, barium nitrate, red gum, paris green, shellac, sodium oxalate, magnesium carbonate, strontium carbonate, calomel, copper oxychloride, calcium carbonate, sawdust and grease mixture, sugar, lamp black, ultramarine blue, paranitraniline red, lactose, auramine, chrysoidin, synthetic indigo, phosphorus, paraffiri, and arsenic.



2-8. Developments after World War I through

World War II. The most complicated task confronting the US Army Ordnance Department at the end of World War I lay in the field of ammunition. Combat experience had shown the inadequacies of the ammunition used in 1917-1918, which were inaccuracies, failures, lack of safety features, and a host of needless complexities. But whereas the combat arms could specify exactly what the gun and vehicle requirements should be, their recommendations for the development of explosives, propellants, projectiles, and fuzes had to be couched in general terms. Here were basic research problems that ammunition experts had to define. Often they sought interim solutions, and waited until greater knowledge could supply better answers. Hence the ammunition designers had free reign within budgetary limits. Over the 20 years between the two world wars, the Army dedicated more money to the ammunition program than to any other development work. During these two decades, RDX, PETN, EDNA, DEGN, lead styphnate, and dextrinated lead azide were developed as military explosives. The development in the United States of processes for producing toluene from petroleum removed limitations on the availability of TNT, and permitted development of the powerful and castable explosives like composition B and pentolite. Flashless propellants were developed in the United States, and lowerosion DEGN propellants were developed in Germany and Italy. Diazodinitrophenol was developed as an initiator in the United States, and tetracene was developed in Germany as a new explosive ingredient of priming compositions. World War II (1939-1945) saw the development of rocket propellants based on nitrocellulose-nitroglycerin or nitrocellulose-DEGN mixtures, and the use of nitroguanidine in artillery propellants. New special-purpose binary explosives, such as tetrytol and picratol, were developed for use in demolitions, chemical bombs, and semi-armor-piercing bombs. A number of plastic explosives used for demolition work were developed in Great Britain and the United States, the most important being the C-3 composition based on RDX. The discovery and great value of the blast effect of explosives led to the development of tritonal, torpex, and minol, which contain powdered aluminum and have powerful blast effects. In the spring of 1943. EDNA or haleite was adopted for testing purposes after the DuPont Company, while under contract, overcame the problem of manufacturing ethylene urea, one of haleite's intermediates. But it was not until the end of the war that production of haleite could get started. Incendiaries were found to be even more effective than high-blast explosives in the destruction of cities. By using improved fire bombs filled with thickened or gelatinized incendiary oil or gasoline mixtures, and large clusters of incendiary bomblets filled with thermate (an improvement of the WW I thermite), the US air forces were able to literally set fire to cities like Dresden and Tokyo. Flamethrowers and smoke munitions were used extensively by both sides. Finally, the extensive use of armor during the war led to the development of anti-tank weapons, armor-piercing shells, and shapedcharge munitions. The application of the shaped-charge principle resulted in the use of special explosives of the pentolite type.

a. 1918-1939. Ammunition research in the first postwar years was inspired not only by new requirements, but also by the problems encountered in preserving ammunition, especially propellants, stored after the Armistice. Research proceeded in three areas: determining the stability of smokeless powder, studying the effects of long term storage on stability, and creating more efficient methods of drying. A good deal of valuable information on these substances was assembled at Picatinny Arsenal, NJ, before 1926, notably that on feasibility of the vapor method of drying, which reduced drying time from months or weeks to days. But a more permanent solution of some phases of the powder storage problem would be to develop new non-hygroscopic powders, which because of their chemical composition would not absorb enough moisture to affect their ballistics or chemical stability even when stored in a damp atmosphere. If, at the same time, flashless and smokeless qualities could be incorporated, the advantages would be even greater. Thus the search for flashless non-hygroscopic (FNH) powders was vigorously pushed. The DuPont Company, under a special agreement with the Ordnance Department, followed one route of investigation, while Picatinny Arsenal followed another. Each achieved considerable success. The peacetime development of complete single-base and double-base non-hygroscopic powders, flashless in many weapons, was one of the most useful accomplishments of the Ordnance Department before 1940. Traditionally, British propellants have been of the double-base type developed prior to World War II and designated as cordites. The cordites were made up of varying percentages of nitrocellulose, nitroglycerin, and mineral jelly. The mineral jelly (petroleum jelly or petrolatum) acted as a stabilizer. A sample of British MD cordite has been found to be of apparently unchanged stability after 30 years of temperature-climate storage.

The search for a compound that was both smokeless and flashless had its beginning in the requirement established by the US Army Ordnance's Westervelt Board in 1919. In the early 1920's, ordnance scientists offered the using arms samples of nitroguanidine, which to a degree unobtainable in any other known propellant, had both properties. But nitroguanidine gave off such noxious ammoniacal fumes in combustion that the Field Artillery vetoed its use. The Ordnance Department, with no customers in prospect, then abandoned all thought of building plants to make nitroguanidine. But ammunition specialists found no satisfactory substitutes. Adding potassium sulfate to propellants for antiaircraft fire, where flashlessness was all important, helped to solve that problem. However, it was no answer to the demand for a completely smokeless and flashless propellant for field artillery where smoke would obscure a gunner's vision and muzzle flash would reveal the tank or battery position.

b. 1918-1939. Between the two world wars very little was done in the United States to develop the art of rocketry and rocket propellants. A golden opportunity to assume leadership in this field was missed when just before the Armistice in 1918, Dr. Robert H. Goddard, Professor of Physics at Clark University, demonstrated a shoulder-fired "recoilless gun" or "rocket gun" at Aberdeen Proving Ground, MD. The results of Dr. Goddard's demonstration were summarized by Ordnance Department witnesses as proving the validity of his concept of modern rocketry. However, the lack of suitable powder and the need for further work on the electrical firing mechanism along with the Armistice led the Ordnance Department to shelve the project. Goddard died without receiving any acclaim for this pioneering work, although comparison of his rocket gun with the bazooka adopted 24 years later shows how closely the 1918 model resembles the later weapon. During the 1920's, metriol trinitrate or trimethylolethane trinitrate, used as an ingredient in rocket propellants in World War II, was prepared in Italy and Germany. In 1931, the US Army created a one-man rocket unit by assigning Captain Leslie A. Skinner to study the possible use of rockets. Skinner was handicapped by limited funds for research, and by the indifference of superiors. During the mid-thirties, the British began more intensive research on anti-aircraft rockets in anticipation of massive bomber air raids upon their cities. In the meantime, the Germans made great strides in the development of rockets and missiles and the attendant propellants. This was especially due to the work of Wernher von Braun in the late 1930's.

c. 1920. Cardox, a device for breaking coal in gaseous mines by the pressure produced on heating liquefied carbon dioxide, was developed. Similar devices were developed in the United States in 1930, and were improved upon in 1955 (Hydrox) and 1959 (Chemecol).

d. 1927. Diethyleneglycol dinitrate was thoroughly examined by W. H. Rinkenbach, and the current method of preparation was patented in 1928 by A. Hough.

e. 1930-1931. Dextrinated lead azide was adopted for use by the US Army, and began replacing mercuric fulminate in priming compositions.

f. 1931. 2,4-dinitrotoluene (2,4-DNT), obtained earlier as an impurity in crude TNT, was used in some explosive mixtures.

1935. From the 1920's onward, scientists at Picatinny Arsenal had been trying to find a compound that would have the high brisance of RDX without the sensitivity to friction and impact. Research on this problem, principally by Dr.George C. Hale, chief chemist, led to the discovery of ethylenedinitramine (EDNA or haleite) the first entirely American high explosive. More powerful than TNT, EDNA was slightly less powerful then RDX but was also less sensitive. EDNA's stability gave it an important advantage in considerations of manufacturing, loading, storage, transportation, and field use. Designated haleite, in honor of Dr. Hale, this new explosive could be press-loaded into small shells without a desensitizing agent, and its derivative, ednatol, a mixture containing 42 percent TNT, could be melt-loaded into large shells as easily as amatol. These advantages were offset in prewar days by the high manufacturing cost of one of its intermediates, ethylene urea. Delay in solving manufacturing problems prevented haleite from getting into combat in World War II.

h. 1936. Primacord, based on a French patent, was developed by the Ensign-Bickford Company, CT. Primacord consisted of PETN covered with textiles, waterproofing material, and plastics. This detonating cord had a velocity of 6,405 meters (21,000 feet) per second, and has been used extensively by the armed forces for demolition work.

i. 1937. Baratol, a mixture of barium nitrate and TNT, was developed by the British and used extensively in WW II.

j. World War II. High Explosive Bombs. When World War II began in September 1939, the standard United States filler for high explosive bombs was trinitrotoluene (TNT). On 5 June 1940, the United States released 8,000 metric tons (9,000 short toris) of TNT to the British under Lend Lease. This came out of a manufacturing surplus of only about 9,000 metric tons (10,000 short tons). Most of the war was fought by the United States with bombs standardized in 1941. The earliest departure from TNT for the fillings was RDX, an explosive known for its great power and brisance but generally considered too sensitive. The British had developed a method of using beeswax to desensitize the RDX, and used this filler with terrible effect in the 2-ton "blockbuster" bombs dropped on Berlin in April 1941. During the following summer, Air Marshall Arthur Harris had pressed for large-scale production of RDX in America. The United States Navy was also interested in the explosive because of its effectiveness under water, especially in a mixture with TNT and aluminum called torpex. But the United States Ordnance Department, while willing to start production for the British and the Navy, held back until May 1943 on the use of RDX in its AAF (Army Air Force) bombs, and then adopted only a less sensitive mixture with TNT known as RDX Compositon B. This first significant change in bomb-loading came about as a result of AAF insistence that the large fragmentation bombs developed in 1943 would need the greater power of RDX Composition B to burst their thick walls with the greatest effect. Henceforth, Composition B was used in only about 40 percent of the general pupose bombs. The reasons were twofold. First, the short supply caused by competition between RDX, and high octane gasoline, and synthetic rubber for production facilities and, second, the tendency of Composition B to detonate high-order without fuze action under the shock of impact. RDX was more prone than TNT to prematurely deflagrate (decompose rapidly without detonating) when employed in delayed-action bombs dropped from high altitudes. In the war-long argument over the relative merits of blast and fragmentation, the pendulum now began to swing back toward blast partly because by 1944 the AAF would have aircraft capable of delivering larger and heavier loads. After 1943, the new aluminized fillings were of far greater interest than either RDX Composition B or ednatol. Until WW II, the use of aluminum in explosives had not been extensive. Tests in 1941 in England had failed to indicate any significant difference between aluminized explosives and amatol or Composition B. Iri

1943, the discovery that German bombs containing aluminum were extremely effective spurred research. This led to the development of minol, a mixture of aluminum with amatol, and tritonal, a mixture of aluminum with TNT. For their 2-ton blockbuster bornb. the British favored Minol 2, a mixture of 20% aluminum, 40% TNT, and 40% ammonium nitrate; and they requested that Minol 2 be used in their blockbuster bombs being loaded in the US. The British, by using new methods of blast measurement and interpretation, had learned that Minol 2 produced an area of demolition approximately 30 percent greater than the area obtained with a TNT filler. US Army Ordnance technicians had independently arrived at a similarly high opinion of the blast effect contributed by aluminum. They arrived at this conclusion by comparing the performance of one- and two-ton blockbuster bombs loaded with minol, TNT, ednatol, and the RDX mixtures. In comparing minol and tritonal, they preferred tritonal, because it contained no ammonium nitrate. When even the slightest degree of moisture was present in the air, aluminum acted on ammonium nitrate and produced "spewing" (the evolution of hydrogen gas) and explosions. Tritonal was much safer, and the British were won over to it. The AAF adopted tritonal for large, light-case bombs for jungle warfare, and for all general purpose bombs. Other bombs were filled with explosives suitable to their particular purposes. For fragmentation bombs, RDX Composition B continued to be the preferred filling because it had more brisance than tritonal. The US one-ton semi-armor-piercing bombs developed in early 1944 were loaded with picratol, a mixture of TNT and ammonium picrate, or with Explosive D. Explosive D was the least sensitive to shock and friction, which made it the best explosive to mix with TNT in a bomb that had to withstand severe shock and stress before detonating.

k. World War II. Reverse Nitration of TNT. During 1941 and 1942 the inadequate supply of TNT for highexplosive bombs and shells was a major problem for Ordnance. Because the shortage had been foreseen, plans were made to use a substitute explosive called amatol (a mixture of TNT and ammonium nitrate) for shell or bomb loading until new TNT plants came into full production. Even so, a critical shortage of TNT developed despite these plans. But the shortage suddenly disappeared when a new process appeared on the scene almost by accident. During an inspection of a small Canadian TNT plant at Beloeil near Montreal in 1941, LTC John P. Harris of Ordnance discovered that the plant was "doing things backward" by putting toluene into the acid instead of putting acid into the toluene. Despite some resistance by US TNT producers, the new process was tried at the partly built Keystone Plant at Meadville, PA. The result was a trippling of TNT output. Lines designed to turn out 16 tons a day produced more than 50 tons a day. The need for TNT substitutes vanished, and the cost per unit was cut in half.

World War II. Toluene from Petroleum. I. Development of a new means of producing toluerie. the basic material from which TNT is made, was another highly significant technological advance of World War II. The importance of this chemical stems from the fact that nearly half of every unit of TNT (trinitrotoluene) must come from toluene. In World War I, toluene was derived from coal as a by-product of coke ovens, and some was extracted from natural gas. Yet the supply in 1917-18 was so limited that the Assistant Secretary of War, Benedict Crowell, later called this shortage "the greatest and most pressing of all the problems in regard to existing raw materials." In contrast, during World War II high-explosives production was never seriously hampered by lack of toluene. As early as 1927, Standard Oil of New Jersey had obtained patent rights from a German firm to use a process for producing toluene from petroleum. In 1939, a contract with Standard Oil was placed by Picatinny Arsenal to prepare toluene by this process at Baytown Ordnance Works, which was erected next to the Humble (a Standard Oil subsidiary) refinery in Baytown, TX. By October 1942 this plant was producing toluene at the rate of 246 million liters (65 million gallons) per year, which when compared with a total toluene production of less than 34 million liters (9 rnillion gallons) in the US during 1918 shows us the value of this process.

m. World War II. Artillery Propellants. The problem of obtaining artillery propellants that were both flashless and smokeless continued to plague the U.S. Army. Early in the war, the Navy seized upon nitroguanidine as the one feasible answer to novel conditions of combat. For the first time, American ships in the Pacific were preparing to fight in small harbors where maneuvering was all but impossible. Flash at night betrayed the vessel's position, and smoke by day made second rounds inaccurate. Negotiations with Canada in 1943 for the purchase of nitroguanidine, from the one plant upon which British and Canadian forces were also depending, succeeded in meeting Navy needs but left no surplus for the US Army. The Army Ground Forces were not convinced of the value of this propellant until

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shortly before D-Day. By then, urgent demand could not allocate facilities to produce nitroguanidine in large quaritities, and the Ordnance Department could only procure small lots for testing and experimental firing. Whatever the advantages of ritroguanidine, neither it nor any other composition was ideal for all purposes. Even in conventional artillery and small arms ammunition, where ballisticians understood propellant behavior better than in rockets and recoilless rifle ammunition. compromises were inescapable. The primary requiste for one weapon or one particular use tended to be different from every other weapon or use. In addition to these problems, World War II introduced the problem of climate extremes at which firing had to take place when Allied troops were fighting in arid deserts, damp jungle heat, or in the subzero winter weather of northern Europe and of the Aleutian Islands. Therefore, a series of propellants were needed to cover widely varying contingencies. Since basic research as well as prolonged applied research was necessary, many problems remained unsolved at the end of the war. But the field was explored more thoroughly than ever before in the United States, and lines of investigation were clarified for postwar development. In processing propellarits, industry and the Ordnance Department made considerable advances during the course of the war. One new method developed by the Hercules Powder Company for washing nitrocellulose in a continuous filter instead of in large tubs by the old "settle and decant" system. washed the nitrocellulose more thoroughly and thus improved the stability of nitrocellulose. The DuPont Company found that using preheated alcohol during the winter to dehydrate nitrocellulose reduced the hydration time cycle, improved the yield, and made for a more uniform product. This in turn produced a much better powder. The Radford Ordnance Works carried on extensive experiments to improve manufacturing and testing techniques as well as for finding better chemical compositions. Yet in the spring of 1945, reports from the Combined Intelligence Objectives Subcommittee, established to locate data in Europe on Axis research and manufacturing procedures, indicated that Germany had developed several processes more effective than those of the United States. The most novel German method was one of casting propellant grains by adding a paste of moist nitrocellulose and diethyleneglycol dinitrate (DEGN) to molten TNT and pouring the mixture into steel molds to cool. Grains as large as 1,000 millimeters were cast this way. After the war, complete sets of the German equipment deemed most useful and novel went to Picatinny Arsenal for study.

World War II. Wood Pulp and Cotton Linters. n Before the war, the standard practice for making smokeless powder called for the treatment of bleached cotton linters with a mixture of nitric and sulfuric acid. In the summer of 1941, it became apparent that even with a good cotton linters crop and capacity operation of bleacheries, the supply of linters for powder would fall short of requirements. Ordnance chemists, therefore. turned to the use of a special wood pulp that was available in quantity, was suitable for most kinds of powder, and was cheaper than cotton linters. The Hercules Powder Company had made smokeless powder from wood pulp for a number of years, and Ordnance found the product completely acceptable. Use of wood pulp as a supplement of, but not a replacement for, cotton linters was approved promptly except for rifle powder and certain other uses. Soon most plants had one or two lines for nitrating cotton, an equal number of lines for nitrating wood pulp, and several "swing lines", which were adaptable for use of either materials. From January 1942 to the end of the war, Ordnance plants used roughly equal quantities of cotton linters and wood pulp. There was never a concurrent shortage of both materials, although there were times when the supply of one ran low or was expected to run low. At such times, Ordnance drew upon its inventories while converting the swing lines to meet the situation. The use of wood pulp doubled the existing supply of cellulose for powder, and eliminated a serious potential bottleneck in ammunition production.

o. World War II. Rocket Propellants. Difficult though the US program was for improving propellants for conventional weapons, the question of developing suitable rocket propulsion was still harder to answer. From the very beginning everyone concerned with rocket research agreed that single-base powders would lack the necessary energy and that double-base powders, that is nitrocellulose and nitroglycerin combined, must be used. Double-base powders, made by the solvent process, had been manufactured in the United States for a number of years for use in intermediate and large caliber artillery. The method used a solvent of acetone and alcohol to make a colloid, from which grains or flakes could then be formed. About 1939, the Hercules Powder Company found a way of producing a solventless double-base propellant, which was plasticized by heat and pressure and then rolled out into sheets for mortar increments. But neither was adaptable for rockets where a solid stick or grain, not sheet propellant, was needed, and where the essential quality of uniform burning precluded using a grain without so

much as a hair crack or fissure. Even a tiny crack in a burning grain of powder would create pressure peaks at particular spots of the encasing rocket mortar tube and thus either burst the tube or cause erratic populsion. Consequently, to get a safe usable rocket propellant made by the solvent process meant using grains of small cross-section (in technical phraseology, thinwebbed powder) in which malformations occuring in drving would be few and inspection could be exacting. A method of manufacturing solventless double-base propellant by a dry extrusion process had been developed in the late 1930's by the British. This produced much thicker-webbed, and therefore longerburning, grains, but required enormously heavy presses to extrude or compact, and force out the propellant into the desired shape.

World War II High Explosive Artillery Projectiles. р. Considerable power combined with sensitivity, which made for easy loading, stability, and safety in handling and transport, made TNT and amatol the preferred highexplosive fillings for most high-explosive artillery shells at the outset of World War II. This was largely due to their availability in large quantities. As the war progressed and ammunition became more complex in design and more specialized in function, demand arose for improved explosives. This demand could not be met to any extent because the explosives developed between wars did not get into large-scale production in time. Nevertheless, thoughout the war the US Army Ordnance Department sought ways of using more powerful new explosives, and ways to adapt old ones to special purposes. There were at hand several explosives of higher shattering effect, or brisance, than TNT. The most important were, first, cyclotrimethylene trinitramine, which the Americans called cyclonite and the British called RDX ("Research Department Explosive"); second, pentaerythritol tetranitrate or PETN; and third, EDNA (later called haleite). RDX and PETN were too sensitive to be used in the pure state in a shell. Therefore, to form usable compositions it was necessary to combine them with oils or waxes or with other explosives. The British had managed to desensitize RDX by adding nine percent beeswax to form Composition A for press-loading into shells; with 39.5 percent TNT and one percent beeswax to form Composition B, chiefly for bomb loading; and with 11.7 percent of a plasticizing oil to form Composition C, for demolition work. These formulas were provided by the British to the US in 1940, and development work was undertaken by the DuPont Company under contract of the Ordnance Department.

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The most sensitive of all high explosives was PETN, which was even more readily detonated than RDX. PETN was desensitized by mixing with TNT to form a composition named pentolite, which has been extensively used in detonators, bazooka rockets, rifle grenades, boosting devices, and in the shaped charges of antitank shells. Because of production difficulties, haleite, the most promising of the new high explosives, never saw much use in World War II except in the form of ednatol in mixtures with other explosives.

q. World War II Armor-Piercing and Antitank Projectiles. Much of the work of improving high-explosive compositions was directed toward finding the most efficient filling for anti-tank shells. For armor-piercing projectiles, relatively insensitive ammonium picrate, "Explosive D," had long been preferred. As it was not likely to detonate on impact, the shell could penetrate the armor plate before exploding. But experience with heavy German tanks in North Africa showed that something more was needed in the way of power and fragment action coupled with greater incendiary effect within the tank. Chemists at Picatinny Arsenal accordingly tried several expedients. In armor-piercing shell, addition of a small amount of powdered aluminum to cyclotol (a mixture of RDX and TNT), to ednatol, or to TNT produced more brisance than Explosive D and increased sensitivity to impact. In high-explosive antitank shell fillings, conversely, the difficulty was the exact opposite. The high sensitivity of pentolite made it liable to detonation on target impact so that the problem was to desensitize it to the proper degree. Several possibilities considered were the addition of wax to the pentolite, the reduction of the PETN content, and the substitution of ednatol or Composition B. None was entirely satisfactory. The search for an explosive composition of the greatest possible power and brisance took a new turn after analysis of foreign explosives at Picatinny Arsenal during 1943. Hitherto, research had been concentrated on binary explosive compositions such as pentolite, Composition B, or ednatol. The examination of a Soviet 76mm high-explosive armorpiercing round suggested the possibility of employing ternary mixtures. Tests revealed that castable ternary explosive mixtures, such as RDX-TetryI-TNT and Haleite-PETN-RDX, offered promise not only for armor-piercing projectiles but as fragmentation ammunition for weapons designed to produce blast, and for demolition charges. Further study showed that haleite ternaries were unstable. The best combination seemed to be a mixture of PETN-RDX-TNT designated PTX-2 (Picatinny Ternary Explosive). More brisant than any of

the binary compositions, PTX-2 was more stable than 50/50 pentolite and less sensitive to impact. Preliminary firings at Picatinny indicated that PTX-2 would be particularly adaptable to shaped-charged ammunition; but PTX-2 was still in the testing stage at V-J Day.

r. World War II. Shaped Charges. If no new explosive for artillery shell came into use during the war, a new way of employing explosives nevertheless did. The effect of a hollow-charge or shaped-charge projectile against armored targets was first successfully demonstrated by the bazooka and the rifle grenade. The intense forward jet of the charge, serving to focus part of the energy of the explosion in a limited area, gave to the light-weight, low-velocity rocket the armor-piercing advantages hitherto possessed only by high-velocity artillery. The antitank rifle grenade, containing only 113 grams (4 oz) of pentolite, would penetrate up to 102mm (4 inches) of homogeneous armor plate at a normal angle of impact. The first rifle grenade to use this principle was designed by a Swiss inventor. Henri Mohaupt. whose claims of inventing a "new explosive" had interested the British in 1939. However, the price Mohaupt quoted for his discovery was considered too high and the British showed no further interest in his invention. Mohaupt then offered to show the United States particulars of the construction of his device for a fee of \$25,000 paid in advance. Caution on the American part further delayed acquiring the rights until a demonstration by Mohaupt at Aberdeen Proving Ground, MD, was permitted in 1940, doubtlessly because Mohaupt provided 200 grenades for the demonstration. Army and Navy representatives who witnessed the test firings were convinced that this was indeed an important "new form of weapon." A similar proposal by Nevil M. Hopkins, an American inventor, for a shaped-charge bomb had been rejected earlier by the United States Ordnance Department as not being a new concept. By citing a 1911 British patent by Egon Neuman of the "Munroe-Neuman" principle, the Ordnance Patent Section thereupon showed Mohaupt's "secret" to be no secret. Thus the Ordnance was able to conclude a more reasonable contract with Mohaupt's company than the Swiss had originally demanded. An adaption of Mohaupt's design later formed the basis for the M9A1 antitank rifle grenade, and the 2.6-inch antitank "bazooka" rocket. Application of the shaped-charge principle to artillery naturally proceeded. The choice of howitzers was logical because their low velocity made conventional types of armor-piercing projectiles ineffective, whereas for a shaped-charge explosive low velocity was an advantage. Before Pearl Harbor, in an

atmosphere of great secrecy, work began on a shaped-charge shell, specifically the "HEAT" (highexplosive antitank) round, for the 76mm howitzer. The designers, paying careful attention to the length of the ogive, the filler of 50/50 pentolite, and the striking velocity, came up with a round of the same length as the corresponding high-explosive round. The HEAT round. at a muzzle velocity of approximately 305 meters per second, would penetrate 76 millimeters (3 inches) of homogenous armor plate. A similar shell for the 105 millimeter howitzer appeared simultaneously. Standarized in late 1941, HEAT shells were produced in time to take part in the North African tank battles early in 1943. The Ordnance Department had high hopes that the HEAT rounds would succeed in penetrating the heavy German armor plate that had defeated solid armor-piercing ammunition. Although sometimes successful, the performance of shaped charges was not dependable enough. In an effort to find out why, the Ordnance Department, with the help of the National Defense Research Committee (NDRC) and the Navy, intensified its research. In some cases, observers in the field had blamed faulty manufacture, but investigators proceeded on the assumption that design of the round and the principle of operation needed improvement. Because of the difference in behavior of the nonrotating rocket and the rotated shell, the effect of the spin was carefully studied as well as the method of fuzing. One of the most important discoveries was that an increase in plate penetration was directly proportional to an increase, up to approximately three calibers, in "standoff" distance, that is, the distance from the base of the cone to the target at the moment of detonation. Yet this finding was only a beginning, and the solution to the puzzling behavior of hollow charge projectilles was not found during World War II.

s. World War II Smoke Screening Munitions. In the spring of 1940, the Germans demonstrated the value of smoke to screen their advance when they blitzed the Low Countries. Basic developments in smoke employment during World War II were its use to screen river crossings, beach landings, paratrooper assaults, and rear area targets from artillery fire and aircraft observation and attacks. Prewar versions of the HC smoke pots were enlarged, and floating smoke pots were developed for amphibious operations. Aircraft smoke tanks were developed for spraying liquid smoke mixtures. Smoke generators were developed for screening large areas by vaporizing fog oil. White phosphorous (WP) was the choice filler for most projectiles, but also had the undesirable disadvantage of sometimes becoming an incendiary. Another disadvantage was that WP tended to melt in hot climates, which affected the stability of the round in flight. Storage in hot climates also resulted in expansion of the WP and subsequent leakage. Despite these shortcomings. WP was very effective for building up smoke screens as particularly demonstrated by the 4.2-inch mortar battalions in Europe and the Pacific. Smoke bombs filled with WP and PWP were used extensively for spotting targets and for screening parachute drops. Plasticized WP or PWP was developed to reduce the pillaring effect of the exploding munition found with pure WP. PWP is obtained by mixing WP with a very viscous solution of synthetic rubber to form a homogenous mass. For loading into munitions where a longer lasting smoke screen is desired, HC (hexachloroethane mixture) was preferred, e.g., smoke pots and base ejection shells. WP was used in rifle grenades. HC was used in hand grenades. US tanks in North Africa were outfitted with smoke grenade launchers to screen the tanks from antitank fire.

t. World War II. Pyrotechnics for Illumination. In 1944, the Army Air Forces (AAF) made an important change in doctrine that affected munition development requirements when they initiated 24-hour bombing operations. Night bombing, always favored by the Royal Air Force but hitherto opposed by the United States, gave new importance to pyrotechnics. Aircraft flares came close to the usual bomb design. The AN-M26 aircraft parachute flare, designed to provide illumination for night bombardment, contained its illuminant mixture in a round-nosed, finned-tail cylinder and developed 800,000 candlepower for about three minutes. The most important development concerned high-altitude night photography, and markers to identify targets at night. The prewar M46 photoflash bomb gave only 500 million candlepower. Picatinny Arsenal experimented with different combinations of case, filler, and initiating system. The result was a photoflash bomb that produced approximately three times as much light as the M46. Target identification bombs grew out of a technique evolved by the British to improve the accuracy of their night bombing. Their "Pathfinder Force" equipped with special navigational aids flew over a target in advance of the attacking force and dropped various kinds of candles and flares, some to illuminate the general area and others to mark the special target with color. One muni-



tion designed specifically for this work was a stabilized bomb that ejected sixty-one pyrotechnic candles at a predetermined altitude. In the United States, the earliest research on target identification markers produced five bombs of this type. All were modifications of the 250-lb general purpose bomb and differed one from the other in the type of candle they contained. The candles were small flares that burned with either red, green, or yellow light for about three minutes. Each target identification bomb released its load of these signal candles, which together made a pattern of colored light approximately 100 meters in diameter around or on the target. These signal candles were designed to be visible from altitudes as high as 35,000 feet. To keep the candles from being disturbed while they were on the ground, one type of candle had an explosive charge that would detonate at the end of the burning time of the candle, the time being from one to two minutes. As the AAF extended its night operations, especially low-level bombing and strafing of illuminated targets by fighters and light attack bombers, need arose for ground burning flares that would produce a minimum amount of smoke and thus leave the targets as clear as possible. For this purpose, the Ordnance Department developed flare bombs loaded with smokeless units. At the end of the war Army and Navy experts agreed that future developments must be aimed at greatly increasing the candlepower, burning time, and visibility of all pyotechnics, especially the photoflash bornb.

u. World War II. Pyrotechnics for Signaling. With the use of massive bombing air raids and close ground support by the Army Air Forces came the need for better signaling devices. Especially important were hand signals for downed fliers. Survival kits were developed which included colored smoke and flare distress signals for the aviators to carry. A substantial improvement in the ground signals used by the Armed Forces was made when the US Army Chemical Warfare Service (CWS), now the Chemical Corps, made a change in the method of consolidating the colored smoke mixtures in the grenades used for this purpose. The prewar M1 colored smoke grenades used a slow-burning mixture that burned about two minutes. In 1942, the Army Ground Forces established a requirement for a colored smoke grenade that would form a smoke visible at a slant range of 3,050 meters (10,000 feet) and last about one minute. By devising a method of consolidating the pyrotechnic smoke mixture with heavy presses, CWS engineers were able to provide a grenade meeting the Army

Ground Forces' requirements. After limited testing, the new grenade was type classified as the M18 smoke grenade and was issued in four colors: green, red, violet, and yellow. The M18 grenade remains the most widely used signaling device for ground troops today, which is a remarkable achievement considering that the M18 was adopted for Army use within six weeks of the statement of the requirement. This same loading technique was later applied to artillery base ejection canisters for marking boundaries.

World War II. Flame and Incendiary Munitions. V. In the intervening years from World War I to World War II, the development of flame weapons was studied by most nations except the United States. During the Ethiopian War in 1935 and 1936, the Italians employed the first armored vehicle-mounted flamethrowers. The Germans employed a flame tank during the Spanish Civil War and in 1939 used portable flamethrowers in Poland. These instances proved to the United States that the development of flame weapons could no longer be denied. In 1940, the US Army took steps toward developing a flamethrower and a flamethrower tank. These flamethrowers served an important role in the war in the Pacific, particularly in dislodging the determined Japanese soldiers from caves and fortifications. On Okinawa alone, flamethrowers are credited with the capture or death of 20,000 Japanese soldiers who were holed up in the caves while less than 100 American flamethrower operators were killed in the operations. The development of napalm ("nap" for the napthenic acids and "palm" for the coconut fatty acids which made up the first type of this thickner) by the United States in 1941 made possible the greater use of gasoline for use in flame weapons. This gelled mixture made it possible for aircraft to deliver fire bombs over hard-to-get pinpointed areas and for flamethrowers to project a flame rod over a greater distance than was previously obtainable. By August 1944 the United States AAF Board had come to the conclusion that "where there is vulnerability to fire, the damage by fire is greater than by demolition,' a conclusion, to be sure, that observers had reached during the London blitz of 1940 but which had not been acted upon. The decision of the Board in 1944 was to increase the incendiary bomb program to the highest priority. The United States Army CWS provided the Army Air Force with about 48 million incendiary bombs, which were effectively used, especially on the large cities of Japan. Most of these bombs were clustered bomblets containing thermate (TH3 and TH4), a new

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incendiary mixture, which replaced the original thermite mixture. When ignited, thermate burns intensely at 2,200°C. Molten iron from burning thermate will melt metal, burn through steel plate, and ignite flammable materials. Oil and metal incendiary mixtures, such as PT1 and PTV, were also used as fillings in large thincased bombs. PT1 is a complex mixture based on "goop." a paste comprised of magnesium dust, magnesium oxide, and carbon, with a sufficient amount of petroleum distillate and asphalt to form the paste. PTV is an improved oil and metal incendiary mixture of polybutadiene, gasoline, magnesium, sodium nitrate, and p-aminophenol. However, napalm proved to be one of the most effective aerial incendiary agents in the war. On the evening of 9 March 1945, more than 300 superforts (B29 bombers) swarmed over Tokvo dropping about 2.000 tons of incendiaries, mostly clusters of M69 six-pound bomblets. The M69 bomblet was a tube which contained a black powder propellant charge that ignited and projected the napalm filling from the tube. Aerial photos indicated 16 square miles had been burned out. Tokyo police records, examined after the war, showed that more than 250,000 buildings were destroved about one fourth of Tokyo - in this one raid. More than 100,000 tons of incendiaries were dropped on the cities of Japan during World War II. Most of these were M69 bomb clusters. For destroying materiel to prevent enemy use, the CWS developed a thermate grenade, which was standardized as the AN-M14 TH3 incendiary grenade for use by the Army and Navy. Harvard University also developed a napalm fire starter (MI), for use by troops to ignite fires in wet climates. The armament of the American heavy bombers was usually the .50 caliber machine gun. During World War II, enemy fighter aircraft did not have armor plating capable of deflecting a .50 caliber bullet, although, bullet penetration of the plane's armor did not necessarily knock out aircraft. The enemies use of self-sealing fuel tanks necessitated the development of effective incendiary ammunition. Most urgently needed was an effective .50 caliber incendiary round. The first acceptable design was the work of the Remington Arms Company whose staff already had considerable experience in working on Swiss patents for incendiary ammunition. The Remington development was based upon the British .303 B Mark VI Z, and was adopted in September 1941. The bullet was a flatbase type with lead base closure and steel body, and was charged with 35 grains of a incendiary mixture consisting of 50 magnesium alloy and 50 percent barium nitrate. An improved design was developed

shortly thereafter by Frankford Arsenal and was standardized for United States use.

2-9. Post-World War II Developments. The nuclear bombs that ended World War II did not end requirements for conventional explosives and ammunition. As was shown by the Korean War (1950-1953) and the Vietnam War (1964-1973), the need for the United States to develop even more effective munitions and more powerful explosives or energetic materials became more apparent than ever. In spite of intensive effort, chemists at the Army's laboratories and arsenals failed during World War II to develop a new explosive composition for shell loading that was both satisfactory and readily available in quantity. The obstacles were often disheartening. The characteristics of an explosive might be considerably affected by impurities that existed in the raw material or which were admitted during manufacture. For example, the instability of PETN was probably due to impurities in the raw material, pentaerythritol. Other variables that had to be taken into account were the different methods of testing compositions and the differences in interpreting results. Assuming a composition had been found that promised to combine greater brisance with less sensitivity, there was still the question of whether it could be economically manufactured, safely handled, and made unchanging in character in temperatures ranging from arctic cold to tropical heat. In the search for explosives with special properties, much work had been done in the field of aluminized explosives, but, although aluminized TNT (tritonal) was used in bombs, much remained to be done. At the end of the war the Ordnance Department felt that deeper study of the fundamental properties of all high explosives was essential to effective developments in the future. Some of the problems of finding suitable high explosives and propellants have been resolved in the decades following World War II. Other problems have cropped up as the expanding techniques of modern warfare lead to more and more specialized requirements for explosives and propellants. Future developments may be expected to take the direction chiefly of mixtures of currently known explosives and other materials. But in some cases, the requirements can be satisfied only by new and more powerful explosives which are presently being sought. As seen by the experience of the two world wars, scientists engaged in the field of energetic materials must keep abreast of foreign technology and be prepared to exploit technical intelligence. The everchanging and rapid advance of

technology makes it necessary to shorten the lead time from research and development to deployment of new ammunition and explosives. But research and development is only the tip of the iceberg; the biggest expenditures for materiel in the Army go to the procurement and management of ammunition. An Army cannot fight for long without the right kinds of ammunition being available in the necessary mix and quantities needed to perform its mission. A responsive, flexible, viable production base and balanced inventories must be maintained to assure a strong readiness posture. With continuing budget restraints, all those in the armaments research and development community must consider these restrictions and exercise close control of the limited resources allocated to them for this purpose. Therefore, scientists and technicians working in this field must direct their priorities for research and development to those projects with the best prospects of being beneficial to armed forces materiel readiness, and avoid projects that may have only marginal applications to wars of the future.

a. 1945. PLX (Picatinny Liquid Explosive), consisting of 95 percent nitromethane and five percent ethylenedinitramine, was developed at Picatinny Arsenal by L. H. Eriksen and J. W. Rowan for use in mine clearing. The Germans had used similar liquid explosives during World War II under the name Myrol.

b. 1945. Tripentaerythritol octanitrate was patented by J. A. Wyler of Trojan Powder Company, PA, for use as a high explosive and possible gelatinizer for nitrocellulose.

c. 1946-1949. Composition C-4, known as Harrisite, was developed by K. G. Ottoson at Picatinny Arsenal as a replacement for Composition C-1, C-2, and C-3. Composition C-1, C-2, and C-3 were the United States standard plastic RDX demolition explosives, and were originally derived from Britian's Composition C, which was developed during World War II.

d. 1946-1949. Benite, a black powder substitute, was developed at Picatinny Arsenal for use in igniter compositions of artillery primers, or in base igniter bags for separate-loading ammunition. Benite is in the form of extruded strands consisting of ingredients of black powder in a matrix of nitrocellulose. e. 1946-1949. Composition D-2, which is not an explosive but serves as an emulsifier and desensitizer of explosives like HBX-1, was developed. Composition D-2 consists of 84 percent wax, two percent lecithin, and 14 percent nitrocellulose.

1950-1953. When World War II ended, the United States had a tremendous inventory of ammunition on hand, but unfortunately it was not a balanced stock. There were enormous quantities of some types of ammunition, and only small amounts of others. The hasty mobilization of manpower for the Korean conflict stripped the Ordnance Department of the military and civilian personnel that might have properly assessed and cared for the huge inventories of ammunition in its custody. During the years preceding the Korean War, powder packed in cotton bags and fuzes made of substitute metals deteriorated. The Army drew too freely upon the large ammunition stockpile for training purposes, yet made no real effort to replace consumption or balance the items in stock. The lack of postwar orders sent the ammunition industry into an eclipse. When the United States entered the Korean struggle so suddenly in 1950, ammunition facilities and plants were at a low ebb, and businessmen were reluctant to reconvert their factories to wartime effort. Another element that restrained a shift to the immediate production of ammunition was the prevalent belief that the Korean War would be short, and did not warrant a sizeable dislocation of the United States industrial effort. Even after this fallacy was shattered by the entry of the Chinese into the war in late 1950, the policy of butter and guns continued, and no large scale mobilization of industry took place. Compounding the situation of unbalanced stocks, the lack of industrial mobilization that normally follows the outbreak of war led to further setbacks in the battle for ammunition production. By the time funds budgeted in 1951 were translated to production in 1953, the war was practically over. In the meantime, the answer to the shortages in Korea was for the Army to reduce the authorized ammunition required supply rates in the belief that the combat units were wasting their ammunition. The net result was a war in which American firepower could not be used to its best advantage. The lesson learned from this is that a need for better industrial mobilization planning, and for closer contact with industry in the development and maintenance of a viable production base exists.



g. 1950-1973. During the Korean conflict. both portable and mechanized flamethrowers were used and found to be very effective. Flame mines, using incendiary bursters to set off 55-gallon drums of napalm, were used in a defensive role. The large batches of napalm required for these operations were mixed in truckmounted service units. M1 fuel thickening compound was used to gel the gasoline for flamethrowers and landmines. An undesirable feature of M1 thickener is that it absorbed moisture rapidly from the air, which degraded the gelling properties so that the gel became unstable. Army chemists at Edgewood Arsenal, MD, began work on a nonhygroscopic thickener, which was standardized later as M4 flame fuel thickening compound. The M4 flame fuel thickening compound is a di-acid aluminum soap of isooctanoic acids derived from isooctyl alcohol or isooctyl aldehyde, which are obtained from the oxidization of petroleum. Because of the large World War II surplus inventory of M1 thickener, M4 thickener was not produced in quantity until the Vietnam War. The Air Force used tremendous quantities of fire bombs. These bombs were essentially large fuel tanks filled with napalm, which were ignited by pyrophoric igniters (WP or sodium) upon impact. Continuous process mechanical mixers were developed for use at Air Force bases to mix and fill the fire bombs on the spot. M1 thickener could be mixed only in batches, so a new thickener, M2, was developed and fielded. M2 flame fuel thickening compound is an intimate mixture of 95 percent M1 thickener and five percent devolatilized silica aerogel or other approved antiagglomerant. M2 thickener was an improvement of the M1 thickener for use in fire bombs. This is because of the free-flowing and fast-setting characteristics, which allow its use in continuous mechanical mixers. M2 thickener was not suitable for use in flamethrowers, which require an aged gel obtained in the batch process. Napalm B, a special fire bomb fuel formulation, was developed by the Air Force to replace M2 thickener. Napalm B currently consists of 46 percent polystyrene, 21 percent benzene, and 33 percent gasoline by weight. Napalm B withstands high velocity impact dissemination more effectively than M2 thickened gasoline gels, resulting in less fuel burned enroute and more fuel delivered on target.

h. 1950. MOX (metal oxidizer explosives) were developed by National Northern Technical Division of the National Fireworks Ordnance Corporation, West Hanover, Mass, for use mostly in small caliber antiaircraft shells. i. 1952. Military medium velocity dynamite was developed by W. R. Baldwin, Jr. at Hercules Powder Company Laboratory.

j. 1952. PB-RDX (plastic-bonded RDX) was developed by the Los Alamos Scientific Laboratory of the University of California for use as a mechanical strength explosive. PB-RDX consisted of 90 percent RDX, 8.5 percent polystyrene, and 1.5 percent dioctylphthalate.

k. 1957. Military low velocity dynamite was developed at Picatinny Arsenal by H. W. Voigt.

I. 1958. HTA-3 (high temperature explosive) consisting of 49 percent RDX, 29 percent TNT, and 22 percent aluminum was prepared at Picatinny Arsenal.

m. 1958. Octols 70/30 and 75/25, mixtures of HMX and TNT, were developed at Northern Corporation as fillers for bombs and shells. Octols are standard high explosive fillers, which have been adopted for Army use.

n. 1958. Slurry explosives were developed by M. A. Cook and H. E. Farnham by adding water to ammonium nitrate to form slurries of the oxidizer salt, ammonium nitrate and sodium nitrate, and a solid fuel sensitizer. Slurry explosives provide three to six times the detonation force of ammonium nitrate-fuel oil (ANFO) explosives.

o. 1960. Detaclad process or explosive cladding, which is also called explosive bonding, was developed by the DuPont Company.

p. 1960. Detacord, detaflex flexible cord explosive, and detasheet flexible sheet explosives were developed by the DuPont Company.

g. 1964-1973. The war in Southeast Asia (SEA) (Vietnam) was characterized by an imbalance of ammunition supplies to meet the peculiar requirements of a longer, different type of war than had been anticipated. In the beginning, much of the war had to be fought with the ammunition surpluses from World War II and Korea. Critical shortages developed on those ammunition items which were best suited for the type of war being fought. Ammunition supply rates had to be adjusted constantly because production problems at home delayed filling vital requirements. The expanded use of the helicopter in this war and the fielding of rapid firing armament, such as the "Gatling" 40mm automatic cannon raised the supply rates far beyond the planners' expectations. The demand for signaling devices, such as the M18 colored smoke grenades, doubled, tripled,

and continued to rise until the ammunition supply rates for the grenades were as much as 100 times the World War II and Korea rates. Due to ammunition shortages, terrain, climate, and guerrilla warfare, the United States troops were often forced to rely upon field expedients during their missions. A new development program called ENSURE (Expedited Non-Standard Urgent Requirement), whose function was to meet troop demands for special items needed to support SEA operations, was established by the Defense Department. Many of the ENSURE items fielded under this program were ammunition related and are now standard items for Army use. For example, although flamethrowers were used extensively in SEA, a stand-off capability to project flame was needed to reduce the vulnerability of the operator to enemy fire. From this ENSURE requirement, a 66mm multishot flame rocket launcher (M202 and M202A1) was developed. The resulting M74 incendiary TPA incendiary 66mm rocket was fielded and is now a standard item. The rocket is filled with TPA (thickened pyrophoric agent), which consists of triethyl aluminum (TEA) thickened with polyisobutylene (PIB). Other significant ENSURE developments were a broad range of various 40mm cartridges and signaling devices, improved mines, and pyrotechnics for battlefield illumination.

r. 1973. The problem of managing a rapidly increasing number of conventional ammunition items in the Army inventory was addressed at the conclusion of the war in Vietnam. Although many items developed as a result of the ENSURE program had justified their existence in combat, others were, by their very nature "field expedients" or were advance prototypes from ongoing development programs.¹ In addition, many of the items in the inventory were obsolescent - left over from Korea, World War II, and even pre-World War II assets. Accordingly, the Deputy Chief of Staff for Logistics (DCSLOG), Department of the Army, established an

Ammunition Proliferation Study Committee staffed with representatives from the developing arsenals (Picatinny, Frankford, and Edgewood), the National Inventory Control Point, and the United States Army Training and Doctrine Command (TRADOC). This committee. chalred by DCSLOG, was assigned to review every conventional ammunition item with a stock number or every ammunition item in development, and recommend deletion of all items considered not essential to the mission of the Army. Hundreds of obsolescent and non-essential items of ammunition and explosives were eliminated. Among these were FS smoke and M1 thickener. Ammunition supply rates were considered. For example, because of a low usage factor, the AN-M14 TH3 incendiary grenade was considered for elimination until it was established that the incendiary grenade was used only when necessary to destroy equipment to prevent enemy use; therefore, ammunition supply rates are not applicable to this item. Retention of the M18 violet smoke grenade was justified because violet was the second most used color for signaling in Vietnam; and more colors, not less, were needed to prevent the enemy from guessing the purpose of the signal.

s. 1973-1976. To protect tanks, the United States Army devoted considerable attention to the problem of rapidly screening tanks from enemy antitank rounds and missiles. A DARCOM Project Manager for Smokes and Obscurants was appointed to manage a program of developing and fielding countermeasures. One of the first items adopted for Army use was a British smoke grenade launcher, which fires salvos of red phosphorous (RP) UK L8A1 smoke screening grenades from armored vehicles. After launch, these grenades detonate in the air to form an immediate, dense white smoke cloud that obscures the tank from enemy view. Smoke grenade launchers have been developed for use in many of the armored vehicles in use or development today, including the M1 tank.



CHAPTER 3 GENERAL CHARACTERISTICS AND CLASSIFICATION OF ENERGETIC MATERIALS

3-1. Types of Energetic Materials. Energetic materials are chemical compounds, or mixtures of chemical compounds, that are divided into three classes according to use: explosives, propellants, and pyrotechnics. Explosives and propellants that have been properly initiated evolve large volumes of hot gas in a short time. The difference between explosives and propellants is the rate at which the reaction proceeds. In explosives, a fast reaction produces a very high pressure shock in the surrounding medium. This shock is capable of shattering objects. In propellants, a slower reaction produces lower pressure over a longer period of time. This lower, sustained pressure is used to propel objects. Pyrotechnics evolve large amounts of heat but much less gas than propellants or explosives.

3-2. Characteristics of Burning and Detonation.

Burning and detonation of energetic materials are exothermic redox reactions. The reaction is selfsustaining after an initial activating energy has been applied. On the basis of mass, the amount of energy released by propellants and explosives is comparable. However, this energy is considerably less than is produced by common fuels such as carbon burning in air. Propellant burning, or deflagration, is the very rapid burning that results from having a fuel and an oxidant in very close contact. In some propellants such as nitrocellulose, the fuel (which consists mainly of hydrogen and carbon) and oxygen are parts of the same chemical compound. In other propellants, finely divided discreet fuels and oxidents are mixed. The fuel may be a hydrocarbon or other readily oxidizable material such as aluminum. The oxidizer is usually an inorganic compound such as ammonium perchlorate or ammonium nitrate which contain oxygen in excess of the amount required for their own oxidation. Deflagration of propellants proceeds the same as normal burning. Combustion takes place on the surface and proceeds into the grain. The rate determining factors in the reaction are the rate of heat transfer into the propellant grain from the burning surface and the rate of decomposition of the propellant formulation. The rate of heat transfer depends on the pressure of the combustion products. The burning rate is defined as the rate at which the burning surface consumes a propellant grain in a direction normal to the grain surface. Detonation of explosives is a completely different process than deflagration. A shock wave moving at supersonic speed proceeds through the explosive causing decomposition of the explosive material. The reaction rate is determined by the velocity of the shock wave, not by the rate of heat transfer. The velocity of the shock wave depends on the physical characteristics of the individual explosive material. The range of velocities is from about 2,000 meters per second to about 9,000 meters per second. The factors that affect the velocity include density, degree of confinement, and geometric configuration of the charge.

3-3. General Behavior of Pyrotechnic Compositions. Pyrotechnics is the technology of utilizing exothermic chemical reactions that, generally speaking, are non-explosive, relatively slow, self-sustaining, and self-contained. Pyrotechnic compositions are generally finely divided fuels such as metals, alloys, and hydrocarbons mixed with oxidizers.

3-4. Classification of Energetic Materials. There is considerable variation among the properties of the compounds that constitute each of the three major classifications of energetic materials.

The variation in the properties of explosives is a. put to practical use in armaments by an arrangement called an explosive train (figure 3-1). An explosive train consists of elements arranged according to decreasing sensitivity and increasing potency. The first element, the initiator, consists of a small quantity of highly sensitive material. The highly sensitive material consists of a primary explosive and other ingredients. Primary explosives are easily detonated by heat, spark, impact, or friction. In large quantities these materials are extremely hazardous because of their great sensitivity. The other ingredients in the priming composition increase the sensitivity of the mixture to the desired property, such as percussion or heat. The second element, the booster, contains a larger quantity of less sensitive but more powerful material called a secondary or high explosive. The booster is used either as an intermediate stage to detonate material that is too irisensitive to be detonated by the relatively weak initiator or to ensure complete detonation of the main charge. The main or bursting

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charge, also a secondary explosive, is the least sensitive material but comprises the bulk of the explosive charge. Secondary explosives differ from primary explosives in three major ways. Small, unconfined charges (one to two grams) of secondary explosives. even though ignited, do not transfer easily from a burning or deflagration reaction to a detonation. Except in the case of dust clouds, ignition by electrostatic spark is difficult. The shock required for ignition is much greater for a secondary explosive than for a primary explosive. In some cases, two other elements, a delay and a relay, may be added to the explosive train between the initiator and booster. The delay is calibrated to prevent detonation of the booster for a specified length of time. A delay is considered a pyrotechnic device. A relay may be required to strengthen the relatively weak output of the delay to detonate the booster.



Figure 3-1. Explosive train.

b. An ignition train, which is used to ignite propellant charges, is shown in figure 3-2. The primer contains a priming composition which consists of a mixture of fuels and oxidants that are sensitive to stimuli such as impact, heat, or spark. Application of the appropriate stimulus causes ignition. The primer ignites the igniter which in turn ignites the propellant charge. The igniter is considered a pyrotechnic device.

c. Propellants are divided into four classes: single-base, double-base, triple-base, and composite. Division of the propellants into these classes is on the basis of composition, not use. Single-base compositions are used in cannons, small arms, and grenades; double-base compositions are used in cannons, small arms, mortars, rockets, and jet propulsion units; and triple-base compositions are used in cannon units. Composite compositions are used primarily in rocket assemblies and jet propulsion units. The choice of a propellant for a specific use is determined by ballistic and physical requirements rather than on the basis of composition. A given propellant composition may be suitable for use in several applications.



Figure 3-2. Ignition train.

(1) Single-base. These compositions contain nitrocellulose as their chief ingredient. In addition to a stabilizer, they may contain inorganic nitrates, nitrocompounds, and nonexplosive materials, such as metallic salts, metals, carbohydrates, and dyes.

(2) Double-base. This term has been applied generally to compositions containing both nitrocellulose and nitroglycerin. However, since other gelatinizers such as DEGN are used by other countries, a better definition of a double-base composition is one containing nitrocellulose and a liquid organic nitrate which will gelatinize nitrocellulose. Like single-base propellants, double-base propellants frequently contain additives in addition to a stabilizer.

(3) Triple-base. This term is applied to propellants containing three explosive ingredients with nitroguanidine as the major ingredient. The other two explosive ingredients are usually nitroglycerine and nitrocellulose. As in the double-base propellant, other gelatinizers may be substituted for the nitroglycerine. The nitroguanidine in the formulation produces a lower flame temperature and a greater amount of gaseous combustion products. The lower flame temperature considerably reduces erosion of gun barrels and the greater amounts of gas produce a greater force on the projectile. Triple-base propellants also contain additives in addition to a stabilizer.

(4) Mixed ritrate esters. Two propellant compositions were developed in the United States to replace the triple-base formulation due to the shortage of nitroguanidine. The XM35 composition contains nitrocellulose, TMETN, TEGDN and DEGDN. The higher force XM34 formulation contains nitrocellulose, BTTN, TMETN and TEGDN. The combination of mixed nitrate esters give higher gas volumes and lower flame temperatures than nitroglycerin alone.

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3-2

(5) Composite. Most composite propellants contain neither nitrocellulose nor an organic nitrate. They generally consist of a physical mixture of a fuel such as metallic aluminum, a binder which is normally an organic polymer (generally a synthetic rubber which is also a fuel), and an inorganic oxidizing agent such as ammonium perchlorate. These are heterogeneous physical structures.

d. Pyrotechnic compositions are divided into the following categories according to use.

(1) Flares and signals. Flares burn to produce intense light that is used for illumination. Signals produce colored flames that are used as semaphores.

(2) Colored and white smoke. Colored smoke is used for signaling while white smoke is used for screening.

(3) Tracers and fumers. Tracers and fumers are small, smoke producing charges that are placed in projectiles. During the flight of the projectile, the charge burns. In a tracer, the smoke is used to track the flight of the projectile. A fumer produces smoke at the proper rate to fill the partial vacuum that movement through the air creates behind the projectile. This cuts drag and increases range.

(4) Incendiaries. Incendiaries produce large amounts of heat that cause fires.

(5) Delays and fuses. A delay is an element that consists of an initiator, a delay column, and an output charge or relay in a specially designed inert housing. The delay column burns for a predetermined amount of time. Delays are used to provide an interval between initiation and functioning of a device. A fuse is a cord of combustible material commonly used in demolition.

(6) Photoflash composition. Photoflash powders are loose mixtures of oxidizers with metallic fuels. When ignited, these mixtures burn with explosive violence in a very short time. The mixtures are used to provide light for military aerial photography, and in simulator devices.

(7) Igniters and initiators. These devices are used to ignite propellant charges and initiate detonation in explosive charges.

3-5. Chemical Nature of Energetic Materials.

Chemical properties of individual energetic materials are discussed in the appropriate chapters of this manual. The properties discussed for these materials include the following:

a. Heat of Fusion. The heat of fusion is the amount of heat necessary to transform (melt or fuse) a unit of solid into a liquid at the same temperature and standard pressure. This quantity is usually expressed in terms of calories per gram.

b. Heat of Vaporization. The heat of vaporization is the amount of heat necessary to convert a unit of liquid to vapor at the same temperature. This quantity is usually expressed in terms of calories per gram.

c. Heat of Sublimation. The heat of sublimation is the amount of heat necessary to convert a weight of solid directly into vapor in a constant temperature process. This quantity is usually expressed in calories per gram.

d. Heat of Detonation. Two quantities are usually given for the heat of detonation, one with liquid water in the reaction products and one with gaseous water in the reaction products. The test used to determine these quantities uses a standard calorimeter. When the water is allowed to condense to liquid, the total heat produced by the detonation reaction is measured. The heat of detonation with gaseous water more accurately reflects the process of detonation in a non-laboratory setting. However, the results are less reproducible.

e. *Heat of Combustion.* The heat of combustion is the amount of heat produced when a material is burned. This differs from the heat of detonation because the products formed are different. Generally, the products formed in combustion are at a lower energy level than the products formed during detonation. For example, carbon monoxide and carbon dioxide may be products of both detonation and combustion for a particular explosive. However, the detonation process might produce more carbon monoxide, while combustion might produce more carbon dioxide.

f. Sensitivity. Various external stimuli can cause release of the energy contained in energetic materials. Knowing the response of individual energetic materials to specific stimuli is important from the point of view of safety and in determining the suitability of a material for a specific application.

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(1) The response to a blow is called impact sensitivity. Traditionally, explosives have been subjected to falling weights to measure impact sensitivity. The results are then reported as the distance a given weight must fall to produce detonation 50 percent of the time. The physical significance of this type of test has recently been questioned. The results are more qualitative than quantitative. For example, there is no question that lead azide is much more impact sensitive than TNT and that TNT is much safer to handle than lead azide. But the quantitative meaning of "much more impact sensitive" is ill-defined. The results of this test should be considered for general comparisons among explosive compounds. These same remarks are also valid for sensitivity to friction. Tests which are more applicable to specific hazards and applications such as the SUSAN test and 40-foot drop test are discussed in Chapter 5.

(2) Sensitivity of an explosive to shock is a very reproducible quantity. Shocks generated by a donor explosive can cause detonation in another explosive material. The strength of the shock wave required is a relative measure of the sensitivity of the material under test. In practice, a strong shock is produced and attenuated in an inert medium. The width of the medium that will allow detonation in 50 percent of the trials is reported as the test result. These tests are called gap tests. Gap test results are much more reliable data than impact test results, although there is some dependence on the geometry of the test apparatus. Gap test procedures are covered in detail in Chapter 5.

(3) Electrostatic sensitivity is an important quantity because of safety. Some explosives can be detonated from the shock of a person charged with static electricity. The test procedure used to determine electrostatic sensitivity is covered in Chapter 5.

(4) Thermal sensitivity is an important quantity which needs to be determined in considering explosives for applications. In some cases, such as in the warhead of a high speed intercepting missile, the heat generated during flight can cause detonation of explosive charges that are not highly resistant to heat.

g. Brisance. Brisance is the shattering capability of an explosive. Several tests are commonly used to determine brisance. In the sand test 0.400 grams of the explosive are placed in 200 grams of sand and detonated. The amount of sand crushed by the explosive is a measure of brisance. The plate dent test, in which a sample of the explosive is detonated in close proximity to a metal plate, is also used to measure brisance. The size of the dent is proportional to the brisance. Another method of measurement involves detonating a sample of explosive on top of a cylinder made of copper and measuring the contraction in length of the cylinder. The number, size distribution, and velocity of fragments produced by an explosive in a projectile is also related to the brisance of the explosive.

h. Detonation Velocity. The detonation velocity is simply the rate at which the detonation reaction proceeds through an explosive. This quantity is closely related to the brisance. With a limited number of exceptions, increased detonation velocity increases brisance.

i. Power. The power of an explosive is the total energy available to do work. This is a different quantity than brisance, even though on the surface they appear rather similar. Consider two explosives, ammonium nitrate and RDX. If a charge of each is placed beneath a boulder, the ammonium nitrate might hurl the boulder many meters but the RDX might pulverize the boulder into many fragments. The former quality is power whereas the latter quality is brisance. Power is measured by the Trauzl lead block test in which a sample of the explosive is detonated in a cavity in a lead block. The expansion of the cavity is a measure of the power of the explosive. The ballistic pendulum and ballistic mortar tests are also used to measure power. A heavy weight is accelerated by the detonation of an explosive. The swing of the pendulum or movement of the mortar's weight is a measure of the power of the explosive. The oxygen balance of the explosive is closely related to the power. The oxygen balance is the ratio of oxygen contained in the explosive material to the amount of oxvoen required for complete oxidation of the explosive material. Explosive compositions with better oxygen balances are more powerful.

j. Stability. Stability is the ability of energetic materials to retain, unaltered, such properties as detonation velocity and sensitivity after long periods of storage under adverse conditions. All energetic materials are unstable to some extent. The degree of instability varies greatly. TNT can be stored for 20 years with no change in stability while other explosives, which are not used by the military or commercially, decompose and/or detonate in a matter of days or minutes. Several tests are used to measure stability of explosives. In the heat tests, a sample of the explosive is subjected to a specified temperature for a given amount of time. The

sample is then weighed and any loss of weight above the evaporation of moisture indicates volatility or decomposition. The heat tests are usually carried out at 75°C or 100°C. In the 75°C test a ten gram sample is heated for 48 hours then cooled and weighed. In the 100°C heat test two samples of the explosive weighing O.60 grams each are heated to 100°C. One of the samples is withdrawn after 48 hours, cooled, weighed, and replaced in the oven. This sample is then withdrawn after an additional 48 hours of heating, cooled and weighed again. The second sample is left in the oven for 100 hours and any detonation or ignition is reported. The 100°C heat test is a more accurate predictor of stability than the 75°C test. The currently preferred test of this type, however, is Thermal Gravimetric Analysis (TGA). A TGA can be run in two ways. The temperature can be held constant and the weight is monitored continuously. The data is then plotted as weight or percentage of weight change versus time. The other method commonly employed is to vary the temperature at a specified rate and plot the weight or percentage of weight change versus temperature. The results reported in this manual use a sample size of approximately 10 milligrams and a heating rate of 10°C per minute. The vacuum stability test is used extensively to measure stability. In this test a sample of an explosive is subjected to both elevated temperatures and vacuum. The amount of gas evolved after a specified time is recorded as the test result. The test may be run at any temperature but between 100°C and 150°C is the most common temperature range. In Chapter 5 the test procedure is given in detail. A test that is sometimes performed is the KI (potassium iodide) test. In this test a strip of potassium iodide - starch test paper - is suspended in a test tube with the material under test. The top of the strip is saturated with a 50 percent water 50 percent glycerin solution. The sample is heated. As the heating continues, moisture condenses on the test tube up to a certain point. The position of the test paper is moved up so the line of demarcation between the dry and glycerin-water soaked portions is kept level with the ring of condensation. The appearance of discoloration of the upper half of the test paper indicates the test is

finished. The results are reported as the amount of time from the start of heating to the end of the test. A blank is run at the same time to ensure the test results are greater than the time required for the blank to indicate. This test is of limited applicability. The discoloration is caused by acidity, so the major application is testing nitrocellulose at 65.5°C and nitroglycerin at 82.2°C for purity. A test that is performed on explosives to determine stability is the LLNL reactivity test. In this test a sample of explosive is heated at 120°C for 22 hours. A two stage chromatography unit is used to measure the individual volumes of N2, NO, CO, NO2, and CO2. The result is the sum of the volumes of these gasses per 0.25 gram of sample. A test that yields a great deal of useful information is the Differential Thermal Analysis (DTA). Detailed testing procedures for explosives are given in Chapter 5. In the usual DTA analysis, identical containers are set up. The sample under test is placed in one of the containers and a reference substance is placed in the other. The containers are placed in identical thermal geometries with temperature sensors arranged to give both the temperature of each container and the difference in temperatures between containers. The data are displayed as DTA thermograms; the temperature difference is plotted against the temperature of the sample. The standard reference material chosen is one with thermal behavior that does not change rapidly. Such a plot is nearly a straight line if the sample under test also has no rapidly changing thermal behavior. A straight line is also produced if the test sample has thermal characteristics similar to the reference substance. Excursions above and below a background line result from endothermic or exothermic changes. The DTA analyses permit interpretation for phase changes, decomposition and kinetic information, melting points, and thermal stability. Another very useful test is pyrolysis. A sample is placed in a pyrolysis chamber that is then flushed with helium. When the air has been swept out, the temperature of the chamber is raised at a constant rate. Gas evolution is measured as a function of temperature by a bridge formed by two thermal conductivity cells. The pyrolysis test results are plotted with the DTA results for each explosive.



CHAPTER 4 CHEMISTRY AND PHYSICS OF ENERGETIC MATERIALS

4-1. Introduction. This chapter contains a discussion of the physical processes involved in the detonation and deflagration of energetic materials. The initiation phenomenon, blast effects in surrounding media, and shaped charge principles are also discussed.

4-2. The lanition-initiation Process. Direct ignition or initiation of explosives by an external stimulus is caused by the thermal decomposition of the explosive involved. Impact, friction, electrostatic discharge, gap, and other sensitivity tests produce hot spots in the material under test. A hot spot is a localized region of higher than average temperature. Existence of the hot spots is confirmed by the lag time between the application of the stimulus and the detonation or ignition. For example, if a two kilogram weight falls 30 centimeters on a 20 milligram sample of RDX, ignition occurs within several hundred microseconds. Assuming that the impact energy heated the sample uniformly and that no heat loss occurred, the temperature of the RDX would be about 250°C. At that temperature, the ignition lag for RDX is about one second. In solid explosives, energy is transferred out of the hot spot in the form of shock and rarefication waves. The shock wave heats the surrounding explosive. Some hot spots fail to detonate the surrounding material. Whether or not an explosion occurs depends upon the initial strength of the shock wave and how rapidly the shock decreases at the hot spot interface. Several modes of hot spot generation which have been proposed include:

a. Adlabatic heating due to compression of gas spaces can operate in impact and friction initiation of pressed solid and liquid explosives.

b. Frictional heating on a confining surface or on a grit particle can cause a hot spot. This mode of initiation can operate in impact and friction initiation of pressed solid and liquid explosives.

c. Hot spots can be caused by the intercrystalline friction of the energetic material. This mode of initiation can operate in impact and friction initiation of pressed solid explosives.

d. Viscous heating at high rates of shear can create hot spots. This mode of initiation is operative only at strong shock inputs. This is the main mode of initiation and propagation in homogeneous liquid explosives or defect-free single crystals.

e. Heating by plastic deformation at a sharp point can cause hot spots. This mode is operative in the shock initiation of solid explosive compacts and explosive liquids containing inhomogeneities.

f. Hot spots can be formed by the mutual reinforcement of relatively weak shock waves at inhomogeneities in the shocked medium. This mode is operative in the shock initiation of solid explosive compacts and explosive liquids containing inhomogeneities.

g. Particles which are spalled off crystallite by an incoming shock wave can form hot spots by impact on the opposite wall of a void. This mode is operative in the shock initiation of solid explosive components or liquid explosives containing inhomogeneities.

h. Micro shaped charged jets which are formed by shock waves acting on concave walls of bubbles, cavities, or voids can cause hot spots. This mode is operative in the shock initiation of solid explosive compacts or liquid explosives containing inhomogeneities.

4-3. The Deflagration Process. Deflagration of a propellant proceeds in a direction normal to the surface of the propellant grain. Material is consumed in parallel lavers, so the geometry of the grain does not change as the burning takes place. Propellant is volatized by heat transfer from the flame zone which is in the gas phase above the propellant surface. An increase in the ambient pressure causes the flame zone to move closer to the propellant surface. This increases the rate of heat transfer. The more rapid heat transfer causes an increase in the rate of voiatilization of the propellant which correspondingly increases the rate of defiagration. If the flow pattern of the hot combustion gases is perturbed and penetrates the fiame zone, an increase in the rate of heat transfer may occur. An increase in the flame temperature also causes an increase in the rate of heat transfer. The flame temperature is a function of the propellant composition. Propellants tend to burn more smoothly at high pressure than at low pressure.



4-4. Deflagration to Detonation Transfer (DDT).

In some energetic materials deflagration can build to detonation. In a DDT, local ignition forms a convective flame front. A convective flame front is an ignition wave which is propagated by the passage of hot combustion gases through the pores of the charge. The hot gases are forced into the pores of the charge by the pressure built up as a result of charge confinement. The hot gases heat the pore walls and are consequently cooled. A continuous flow of gases is required to raise the temperature of the pore walls to the point of ignition. Ignition of the pores causes the convective flame front to advance and as the convective flame front advances, the pressure increases linearly with time. The pressure increase causes compaction of most porous charges. Formation of a post convective or compressive wave marks the beginning of accelerated pressure buildup. Subsequent coalescence of the compressive waves into a shock wave completes the DDT. The degree of compaction of the explosive determines how much material is consumed before the DDT occurs. The runup distance is defined as the length of material which will deflagrate before detonation occurs. The following subparagraphs describe the physical phenomenon involved in the variation of runup distance with density of the explosive material.

a. At crystal density and in cast charges there is no porosity and the explosive is impermeable. A convective flame front cannot form. A DDT can occur only if the explosive is relatively sensitive and there is a rapid pressure rise in the ignition region that produces a sufficiently strong shock wave. Some high explosives when unconfined at this density will burn without detonation. Under sufficient confinement, however, these explosives will detonate. Other more sensitive explosives will explode even without confinement.

b. The introduction of porosity into a charge does not mean that the charge will be permeable since the pores may or may not be interconnected. If the pores are not connected, permeability is very low and essentially negligible. The criteria for DDT in this case will be the same as for cast charges. The runup distance will be smaller, however, because the porosity will increase the exposed surface area of the explosive. This will cause the rate of change of the pressure with respect to time to be slightly higher than for the cast material. If an explosive does not undergo DDT at crystal density, then there would probably not be a DDT at this density.

c. As the porosity increases, the fraction of pores which are interconnected increases rapidly. However, the permeability of the charge should remain small. Under these conditions a convective flame front can be established. Establishment of the front will depend on the permeability of the charge, the adiabatic flame temperature of the explosive, ignition characteristics of the explosive, and the ability of the confinement to allow a critical driving pressure to be established. The onset of convective burning indicates that nonnegligible amounts of energy can be transported by gas flow beyond the ignition region. However, only very small quantities of gas can flow out of the ignition area over a time period as long as 100 microseconds. The runup distance for DDT in this case would be less than for charges with either lesser or greater porosity.

d. As more porosity is introduced into the charge, the gas flow can no longer be described as choked. Enough pores are connected to permit flow which may be described as steady state. The increased permeability for this case leads to smaller rates of pressure increase near the ignition point. Burning for a longer period of time is required before the rate of pressure increase begins to accelerate. DDT occurs only after the acceleration occurs. A sharp rate of pressure increase is required to produce compressive waves which can coalesce into shock waves. The runup distance is correspondingly increased.

e. For very permeable charges, the runup distance increases with increasing porosity. Energy losses from the burning region can be great enough to prevent a rapid enough rate of pressure rise to cause DDT. In this case, the pressure builds relatively slowly (in one to two hundred microseconds) to a high level. The high pressure crushes the porous material immediately around the ignition region. The greater density crushed material, upon combustion, may then produce a rapid enough pressure rise to cause DDT. The runup distance for this case is the longest of any of the cases discussed.

4-5. The Detonation Process.

a. Detonation is caused by a self-sustaining shock wave which passes through an explosive material. The velocity of the shock wave is also called the velocity of detonation. A shock wave is a very rapid, almost discontinuous change in pressure. Beyond the range of the pressures involved in transmission of sound through a medium, the propagation velocity of a pressure wave increases as the pressure increases. Shock waves are formed by a pressure pulse of sufficient amplitude. The high pressure region of the pressure pulse moves faster than the low pressure region and so catches up as shown in figure 4-1. The shock wave will continue to have the sharp pressure rise shown in figure 4-1c until the wave is dampered out. The dimension of the x-axis can be either distance or time. Five variables relate the state of the region in front of the shock wave and the region behind the shock wave. The variables are illustrated in figure 4-2. The shock velocity is the velocity at which the shock wave moves through the material. The shock velocity is greater than the sound velocity of the material at a given density. The particle velocity is the velocity attained by the material as a result of the acceleration of the shock wave. Particle velocity is in the same direction as shock velocity. Pressure, density, internal energy, and temperature increase as a result of the passage of the shock wave.

b. To derive relationships between the variables that specify shocked and unshocked material, refer to figure 4-3. We assume the shock front is stationary and the material is moving at the shock velocity through the shock front. Application of the laws of conservation of mass, momentum, and energy yields the following relationships among the variables.

(1) In a given amount of time, t, mass moves from one side of the shock front to the other side. By definition, mass, m, is given as a function of density, p, and volume, V, by the equation:

$$m = \rho V$$
 (4-1)

The volume, V, carl be expressed in terms of area, A, and length, L, by the equation:

The length, L, is the distance a particle travels in our assumed time interval, t, times the velocity, v:

$$L = tv \tag{4-3}$$

By figure 4-3 the velocity can be seen to equal:

$$v_0 = (v - u_0)$$
 (4-4)

and

$$v_1 = (v - u_1)$$
 (4-5)

By equations 4-1 through 4-5 the mass entering the shock front is:

$$m_0 = p_0 V_0$$

$$m_0 = p_0 AL$$

$$m_0 = p_0 At(v - u_0)$$

Similarly, the mass leaving the shock front is:

$$m_1 = p_1 v_1$$

 $m_1 = p_1 A L_1$
 $m_1 = p_1 A t (v - u_1)$

Invoking the principle of conservation of mass:

$$m_{0} = m_{1}$$

$$p_{0}At(v - u_{0}) = p_{1}At(v - u_{1})$$

$$p_{0}(v - u_{0}) = p_{1}(v - u_{1})$$
(4-6)

(2) In our system the force produced is the pressure difference across the shock acting on the cross-sectional area:

$$F = (P_1 - P_0)A$$

The rate of increase in momentum of the system is the final momentum less the initial momentum per unit time or:

momentum change/t =
$$(mu_1 - mu_0)/t$$

By equations 4-1 through 4-5:

momentum change/t = $\begin{bmatrix} p_1 Atu_1(v - u_1) - p_0 Atu_0(v - u_0) \end{bmatrix} / t$

Setting the force equal to the rate of momentum increase per unit time:

$$(P_1 - P_0)A = \left[\rho_1 A t u_1 (v - u_1) - \rho_0 A t u_0 (v - u_0)\right]/t$$

Cancelling and rearranging yields:

$$P_1 - \rho_1 u_1 (v - u_1) = P_0 - \rho_0 u_0 (v - u_0)$$
 (4-7)

(3) The rate of work being done on the system, w, per unit time, t, is given by the equation:

$$w/t = p_1 A u_1 - p_1 A u_0$$





4_4

	BEHIND	AHEAD	
PARTICLE VELOCITY PRESSURE DENSITY INTERNAL ENERGY TEMPERATURE	U P P E T	Uo=0 Po Po Eo To	(P → P₀) (T → T₀)
PLANE SHOCK FRONT			

DIRECTION OF SHOCK WAVE PROPAGATION

Figure 4-2. Steady plane shock front.



Figure 4-3. Control volume or mass passing through a shock front.



The rate of increase of energy per unit time is the difference between the rate of change of the sum of the internal and kinetic energies in the initial and final state:

increase energy/t =
$$[(p_1AL_1e_1 + 0.5p_1AL_1u_1^2) - (p_0AL_0e_0 + 0.5p_0AL_0u_0^2)]/t$$

Using equations 4-1 through 4-5 the increased energy can be expressed as:

$$\left[Atp_{1}(e_{1}+0.5u_{1}^{2})(v-u_{1})-Atp_{0}(e_{0}+0.5u_{0}^{2})(V-u_{0}^{2})\right]/t$$

Equating the work done on the system with the rate of energy increase and cancelling the t's:

$$p_1u_1A - p_0u_0A = Ap_1(v - u_1)(e_1 + 0.5u_1^2) - Ap_0(v - u_0)(e_0 + 0.5u_0^2)$$

Cancelling the A's yields:

 $p_1u_1 - p_0u_0 = p_1(v - u_1)(e_1 + 0.5u_1^2) - p_0(v - u_0)(e_0 + 0.5u_0^2)$

Rearranging terms yields:

 $p_1u_1 - p_1(v - u_1)(e_1 + 0.5u_1^2) =$ $p_0u_0 - p_0(v - u_0)(e_0 + 0.5u_0^2)$ (4-8) (4) Equations 4-6, 4-7, and 4-8 are called jump equations because the state variables jump from one value to another very rapidly across the shock. To these, another relationship tying together any of two state variables (P, v, u, e, t, p) which is specific for a given material is needed. An equation of state, which completely describes the material is more than is needed. A simpler relationship called the Hugoniot equation suffices. The Hugoniot is determined experimentally. The relationship can be obtained by measuring shock pressure and velocities at various shock states, or shock velocity and particle velocity, or any two of the state variables simultaneously. The Hugoniot which describes the relationship between the shock velocity, v, and particle velocity, u, has been found to be:

$$v = c_0 + su \tag{4-9}$$

i

where c_0 is the sound velocity in the medium and s is a constant that is related to the specific heat and thermal expansivity of the material. This relationship is not a path along which the variables change, but is actually a locus of solutions or discreet shock states. Table 4-1 lists the values of c_0 and s for several explosives in the unreacted state.

Explosive	Density in grams per cubic centimeter	Temperature °C	Co in millimeters per microsecond	S	Range of <i>u</i> (by experiment) in millimeters per microsecond
Ammonium nitrate	0.86	25	0.84	1.42	0.81 - 2.32
Composition B	1.70	25	3.0±0.04	1.73	0.0 - 1.5
Composition B	1.68	25	2.71 ±0.05	1.86±0.07	0.0 - 0.9
DATB	1.78	25	2.45±0.04	1.89±0.06	0.0 - 1.2
H-6	1.76	25	2.83±0.07	1.70±0.08	0.0 - 1.1
H-6	1.76	25	2.65	1.98	0.0 - 2.0
HBX-1	1.75	25	2.93±0.08	1.65±0.10	0.0 - 1.0
HBX-3	1.85	25	3.13±0.02	1.61 ±0.02	0.0 - 1.0
HNS	1.38	25	0.61 ±0.21	2.77±1.09	0.0 - 0.5
HNS	1.57	25	1.00±0.05	3.21 ±0.10	0.0 - 0.7
75/25 Octol	1.80	25	3.01 ±0.4	1.72	0.0 - 1.2

Table 4-1.	Unreacted	Hugoniot	Data
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4-6

Explosive	Density in grams per cubic centimeter	Temperature °C	Co in millimeters per microsecond	ş	Range of <i>u</i> (by experiment) in millimeters per microsecond
50/50 Pentolite	1.67	25	2.83±0.4	1.91	0.0 - 1.2
PETN	0.82	25	0.47	1.73	0.76 - 3.50
PETN	1.0	25	0.76	0.66	0.28 - 0.42
PETN	1.59	25	1.33 ±0.08	2.18±0.27	0.03 - 0.37
PETN	1.60	25	1.32	2.58	0.2 - 0.4
PETN	1.72	25	1.83	3.45	0.2 - 0.6
PETN	1.55	110	-0.6 ± 0.5	8.7±1.7	0.24 - 0.29
RDX	1.0	25	0.40	2.00	0.44 - 2.60
RDX	1.54	25	0.7	3.2	0.25 - 0.6
RDX	1.58	180	0.71 ±0.24	4.22±0.42	0.25 - 0.32
RDX	1.64	25	0.70±0.18	4.11±0.37	0.35 - 0.47
RDX	1.80	25	2.87	1.61	0.75 - 1.6
RDX	1.64	25	1.93±0.05	0.666±0.168	0.11 - 0.35
ТАТВ	1.85	25	2.34±0.07	2.32±0.08	0.3 - 1.4
TNT	1.62	25	2.93	1.61	0.75 - 1.6
TNT	1.63	25	2.57	1.88	0.0 - 1.25
TNT	1.62	25	2.27±0.30	2.65	0.0 - 0.6
TNT	1.62	25	2.99	1.36	1.0 - 1.5
TNT	1.61	25	2.39±0.03	2.05±0.03	0.0 - 1.4
TNT	1.64	25	2.08±0.13	2.3	0.2 - 1.4
TNT	1.64	25	2.4	2.1	0.1 - 0.5
TNT (liq)	1.47	92	2.14	1.57	0.8 - 1.7

Table 4-1. Unreacted Hugoniot Data - Continued

By substituting terms from equations 4-6, 4-7, and 4-8 into equation 4-9 and solving, we can obtain more forms of the Hugoniot, for example:

$$P = p_0(c_0 u + s u^2)$$
 (4-10)

(5) Three planes or two dimensional plots are used to describe the shock properties and shock histories of materials. They are the distance-time (x-t) plane, the pressure-particle velocity plane (P-u) described by equation 4-10, and the pressure-specific volume (P-v₉) curve.

(a) The x-t plane is used to display the positions of shocks, material surfaces, and rarefications (the opposite of a shock) in time and distance. Figure 4-4 shows a simple collision of two materials. (1) is the surface of the target and (2) is the front surface of a flyer plate which is a small mass that impacts the target at a very high velocity. The slope of (2) is the plate velocity, (3) is the impact point when the two materials meet, (4) is the forward going shock in the target, (5) is the interface of the plate and target moving slowly to the right, (6) is the left going shock driven back into the flyer, and (7) is the back surface of the flyer. All slopes on this plot are velocities. As the shocks reflect and rarefications fan out and the surfaces move, the x-t plot is used to keep track of the variables.





(b) The P-u plane is where the Hugoniots are normally plotted. An example is shown in figure 4-5. This plot is used to perform graphical solutions to impact problems (uniaxial). Intersections of Hugoniots represent simultaneous solutions of two Hugoniot equations. Chords drawn from initial to final states on this plot have slopes proportional to the shock velocities of the final state in that particular material. Figure 4-5 shows the solution of an impact problem where a flyer, material N at a velocity of u₀ impacts a stationary target, material M. The final pressure and particle velocity after the impact are the same in both flyer and target and are P1 and u1, respectively. (1) is the chord drawn from the initial state to the final state of the flyer. The slope is equal to $-P_0v_1$, the initial density times the shock velocity in the flyer. (2) is the chord drawn from the initial state to the final state of the target, the slope of the chord is Povr, the initial density of the target times the shock velocity in the target. The negative slope of - Povr indicates the shock in the fiver is traveling toward the left. The lines N and M are the P-u Hugoniots of two individual materials. The P-u Hugoniot is not fixed on the plane. The position of the plot relative to the P and u axis is not unique. The physical explanation for that is, a material specimen can exist at any pressure state regardless of bulk or particle velocity. The shape of the Hugoniot and the relation of slope to the axis is unique.





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(c) The specific volume Vs is defined as the reciprocal of the density. Plots in the P-Vs plane, as shown in figure 4-6, are useful in describing the thermodynamics of the shock because areas on this plane represent work or energy per unit mass:

$$PV_{s} = \frac{Force}{Area} \times \frac{Volume}{Mass} = \frac{Force \times distance}{mass}$$

The Hugoniot position on this plane is unique.



Figure 4-6. Shock properties in the P-V_s plane.

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c. A detonation shock wave is self-sustaining because the energy added by the chemical reaction taking place behind the wave balances the losses due to normal attenuation. Figure 4-7 shows the pressure distribution of a detonation wave that is moving through explosive material. Chapman and Jouquet (CJ) developed the theory of shock wave propagation through explosive materials. The CJ conditions for each explosive are unique for that explosive at some unique or specified density. If we change the initial density, we will change the CJ conditions. The theory is based on these assumptions: that pressure is constant from the shock wave to the CJ point, that the pressure decays in a Taylor wave beyond the CJ point, that the reaction is complete and the products are in equilibrium at the CJ point, and that the energy in the Von Neuman spike is negligible in comparison to the energy in the reaction zone and so can be ignored. Figure 4-8 shows a representative plot of the Hugoniots of unreacted explosive and decomposition products under detonation conditions. The Rayleigh line connects the initial unshocked state, Vso, with the final shocked state, VF. Table 4-2 lists the reaction zone length (i.e., the length of the zone between the shock wave and the CJ point) for various explosives. Table 4-3 lists the detonation pressure in the reacting zone for various explosives. The pressure of the Von Neuman spike can be explained by referring to figure 4-8. The point that the Rayleigh line crosses the unreacted explosive Hugoniot, VF, corresponds to the high pressure in the Von Neuman spike. This is obviously at a higher pressure than the CJ point.



Figure 4-7. Detonation wave.



Figure 4-8. P-V_S plot during detonation.

Explosive	Density, in grams per cubic centimeter	Approximate length, in millimeters
Amatol 80/20	1.67	4
Composition B	1.67	0.13
HBX-1	1.60	0.19
Nitroglycerin		0.21
RDX		0.826
(microporous)	1.30	1.82
(single crystal)	1.80	2.90
TNT		0.36
	1.00	0.32
	1.55	0.18
		0.13
		0.21
	1.59	0.70
(pressed)	1.63	0.3
(cast)	1.615	0.42 at 291°K
	1.70	0.55 at 77.4°K
	1.71	0.62 at 20.4°K
(liquid)		0.9 at 100°C
		1.1 at 100°C
TNT/RDX 50/50	1.67	0.12

d. Several computer programs are available that predict the detonation characteristics of a compound from basic chemical and physical properties. One such program is based on the Becker-Kistiakowsky-Wilson (BKW) equation of state. The BKW program requires information about the initial state of the explosive and about the state of the detonation products. The information required for the initial explosive is elemental composition, heat of formation, density, and formula weight. The information required for the detonation products is elemental composition, heats of formation, co-volumes (the effective size of the molecules), and fits of each products ideal gas entropy as a function of temperature. If any solid detonation products are present, the density, molecular weight, and an equation of state are required. From this information the BKW program computes the equilibrium composition of the detonation products at specified temperatures and pressures, the Hugoniot curve, the CJ pressure, the CJ temperature, the CJ density, the detonation velocity, and the isentrope of the detonation products through the CJ point. The values of pressures and temperatures obtained from the program agree to within 20 percent of the values observed experimentally and the detonation velocity agrees to within 10 percent. This margin of error is caused by the assumption of the BKW equation that detonation is steady state. To perform time-dependent flow calculations of the detonation process, other programs are used. These include SIN, EIC, 2DL, and 2DE. These programs require an equation of state of the detonation products (such as BKW), an equation of state for the unreacted explosive, an equation of state for mixtures of unreacted and totally decomposed explosive, and an equation of state that describes the rate at which the explosive decomposes into detonation products.



	Density in	Pressure in kilobars		
Explosive	grams per cubic centimeter	Measured	Calculated	
Composition B, grade A	1.717	295	-	
Composition B-3	1.715	287	-	
Composition C-4	1.59	-	257	
Cyclotol 77/23	1.752	316		
DATB	1.78	259	250	
HBX-1	1.712	220.4		
НМХ	1.89	390	394	
HNAB	1.60	205	-	
HNS	1.60	-	200	
LX-14	1.833	370	-	
Nitrocellulose (12.0% N)	1.58	-	200	
Nitrocellulose (13.35% N)	1.58	-	210	
Nitroglycerin	1.59	253	251	
Octol 77.6/22.4	1.821	342	-	
Pentolite 50/50	1.70	-	255	
PETN	1.77	335	332	
PETN	1.67	300	280	
PETN	0.99	87	100	
RDX	1.767	338	348	
ТАТВ	1.88	-	291	
Tetryl	1.71		260	
TNT	1.63	210	223	

Table 4-3. Detonation Pressures

4-6. Blast Effects. When a high explosive is detonated, the solid charge is rapidly converted to gaseous products. This process, which occurs in about 0.001 second, develops very high temperatures and pressures. Of the total energy available, as much as half may be used to expand the bomb casing and the remainder is used to compress the surrounding environment.

a. Blast Effects in Air.

(1) When an explosive charge is detonated in air, the gaseous products expand rapidly and compress the surrounding air. The air moves outward with high velocity, thus initiating a shock wave. This layer of compressed air is bounded by an extremely sharp front called the shock front in which the pressure rises abruptly. The shock front moves outward with an initial velocity much greater than that of sound but, after a short distance, the velocity decreases rapidly. The gaseous products of detoriation move as a strong wind behind the shock front and are prevented by their own inertia from decreasing in velocity as rapidly as the pressure at the point of detonation decreases. As a result, a rarefaction effect is produced at this point and the pressure decreases. This condition of reduced pressure also moves outward, trailing the shock front. When the pressure becomes less than atmospheric, the wind reverses in direction and blows backward toward the point of detonation. Any light object, such as a leaf, when struck by the shock front, is rapidly carried away from the point of detonation and then is blown back almost to the original position when the wind reverses. The shock front, the high pressure area behind it, and the following rarefaction form a complete wave to which the terms blast and shock wave, generally, are applied (figure 4-9).

(2) While the duration of the positive pressure portion of the blast wave is about one-fourth that of the portion at less than atmospheric pressure, the amplitude of the pressure at the shock front is much greater than the amplitude of the decrease in pressure below atmospheric. The duration of the positive phase varies with the explosive charge and distance from the point of origin. In one case, the duration of the positive phase is of the order of 0.006 second at a distance of 15.5 meters from the bomb. A wall struck by such a blast wave is first pushed forward by the short, sharp, hammer-like blow of the positive pressure phase and then pulled backward by the much longer negative phase. Whether the wall falls forward or backward depends upon circumstances.

(3) Blast effect is measured by two criteria, peak pressure and impulse. Peak pressure is the pressure increase at the shock front or the highest pressure in the shock wave minus atmospheric pressure. Impulse is mathematically equal to the area under the timepressure curve for the duration of the positive phase (figure 4-9). This is approximately half the peak pressure multiplied by the duration of the positive phase. Peak pressure represents a measure of the maximum force exerted against a surface by a blast wave, since force is equal to the product of pressure and area. Impulse represents a measure of the force multiplied by the duration. (4) As the shock front moves outward, the peak pressure decreases and the duration of the positive pressure phase increases. The rates of these changes vary with the magnitude of the peak pressure, but the net effect is decrease in impulse. With increase in distance from the bomb, impulse decreases approximately as the reciprocal of the radius.

(5) In general, two criteria must be satisfied in order to demolish any structure. Both peak pressure and impulse must exceed certain minimum values which depend upon the type of structure. Window glass requires a moderately high peak pressure but only a low impulse value since the positive pressure need not last long to cause fracture. On the other hand, a brick wall withstands only a small peak pressure, but the pressure must be of relatively long duration and therefore the impulse value must be high. The blast from almost any charge that develops sufficient peak pressure will have sufficient impulse to break glass. Most bomb charges that develop sufficient impulse to demolish a brick wall also develop sufficient peak pressure to do so. A general rule is that structures that are strong and light in weight, with respect to the area presented to the shock front, require high peak pressure but no great impulse for demolition. Heavy but relatively weak structures require considerable impulse but not such a high peak pressure.



Figure 4-9. Typical pressure-time record for the blast from a bomb.

(6) Blast waves are reflected from solid surfaces but not in the same manner as sound and light waves are reflected. When the incident and reflected waves intersect on the ground, they do not make equal angles with the ground as do sound waves. Refer to figure 4-10. At small angles of incidence (the angle between the normal to the blast front and the normal to the reflecting surface), the angle of reflection is smaller than the angle of incidence, and the pressure behind the reflected wave is greater than behind the incident wave. Such reflection of a blast wave from a bomb that has detonated above the ground gives rise to an increased pressure wave at ground level. When the angle of inciderice (a) is greater than an extreme angle (a_e) (40 degrees for strong to a value approaching 90 degrees for very weak shocks), the incident and reflected waves do not intersect on the ground. This is known as irregular or Mach reflection. Reflection that occurs when the angle of incidence occurs at the extreme angle is known as the extreme regular reflection, whereas, reflection occurring where the angle of incidence is smaller than the extreme is known as regular reflection. When the incident angle exceeds the extreme angle, the reflected and incident waves intersect at some point above the ground. The lower portion of the reflected and the incident waves fuse into one wave which is known as the Mach stem (M. figure 4-10), the point of intersection being known as the triple point (TP, figure 4-10). The resulting existence of three waves, termed the Mach reflection, causes a density discontinuity and a region of high pressure termed the Mach region is formed. The pressure behind the front of the Mach region is approximately twice that of the incident wave. The top of this high-pressure region, the triple point, travels away from the reflecting surface. As pressure and impulse appear to have their maximum values just above and below the triple point, respectively, the region of maximum blast effect is approximately that of the triple point. The region of maximum blast effect is determined by the height above the ground at which the blast occurs. At distances that are large compared to the height of the burst, the incident and reflected waves have fused and proceed outward as a single shock. After the point of complete fusion of the waves, the shock wave is the same as one produced by a double charge detonated on the ground. As the distance from point of the blast increases, the Mach stem becomes normal to the ground.

(7) Blast effects are enhanced by confinement due to the reflection of blast waves by the confining surfaces. A blast wave traveling through a tunnel, corridor, trench, or even a street decreases in intensity much more slowly than in the open. If a bomb detonates within a building, there is considerable reflection of the blast wave from the walls, even if they are demolished. The rapid reflection of the wave from various walls, in such a case, results in a multiple punch effect on ariother wall. The overall effect of confinement is increased in the vulnerable radius of demolition of the bomb charge. The analogous vulnerable radius of visible damage (as detected by aerial observation) is also used to evaluate the effects of bombing.

b. Blast Effects Underground. An explosive charge, if detonated while buried, exerts pressure on the surrounding earth and causes movement effects over a distance known as radius of rupture. If the depth of burial is less than the radius of rupture, the explosion products blow through the surface of the ground and form a roughly circular depression known as a crater. An explosion on the surface of the ground makes a shallow crater which may be a greater diameter than that produced when the explosive is buried. This is due to the scouring action of gases projected downward from the explosive charge. Important factors in crater formation are the type of earth cratered and the type of explosive used. Explosives of a moderate charge in swampy ground make a relatively huge crater, while in a rock formation only a small crater will be formed. An explosive of low detonation rate that produces a large volume of gases, may form a larger crater than TNT if the charge is well below the surface and the ground is not too hard or rocky. If the charge is on the surface, a low-rate explosion makes a smaller crater than TNT because of the weaker scouring action of the lower velocity gases. If an explosive is buried at a depth exceeding the radius of rupture, the compression effect downward and horizontally and the lifting with subsequent subsidence cause a depression on the surface known as a camouflet.

Blast Effects Under Water. The detonation of C high explosive under water results in shock waves of extremely high pressure which decay rapidly with distance from the charge. Since the total damage is due to both the shock wave and the subsequent bubble pulses. these effects must be separately evaluated. One measurement to make is that of the periods of oscillation of the bubble, that is, the time intervals between successive minima in the bubble radius. The length of the bubble period is related to the energy left after passage of the shock wave. In general, the longer the bubble period the greater the energy. A second measure of the energy may be obtained from a study of the maximum and minimum radii of the bubble. By a combination of radius and period measurements, energy calculations can be made.



Figure 4-10. Mach reflection of blast wave.

4-7. Shaped Charge Effect. A shaped charge (figure 4-11) is a cylindrical explosive charge with a lined conical cavity in one end. The explosive is generally pressed or cast. The higher the detonation velocity and CJ pressure the more effective the shaped charge is.

Very little effect is produced by explosives having rates of detonation less than 5,000 meters per second. The liner focuses the energy of detonation, thus enabling penetration of very thick and very hard targets such as armor.



a. As the charge explodes, the detonation wave passes over the liner. The liner material is accelerated somewhat normal to the explosive-liner interface (figure 4-12). Nearer the apex of the cone, the liner mass to charge ratio is lower so the velocity the liner material attains is higher. Also, nearer the apex of the cone, the metal liner does not have to distort as much as further down. This also causes the velocity to be higher toward the apex. When the liner material converges at the center line, or axis, of the charge, the surface material is squeezed out at high velocity. This material forms the jet. Since the material closest to the apex is at a higher velocity, the portion of the jet which comes from that area is also highest in velocity. Therefore, the jet has a velocity gradient. The material in the leading tip is moving faster than the material toward the rear. The remaining material, which is the bulk of the liner, forms a heavy slug which follows the jet at a much lower velocity. After traveling a distance of about five or six diameters of the original charge, the jet begins to break up because of the velocity gradient and inhomogenieties in the charge and liner. Inhomogenieties in the charge and liner cause the jet particles to have slightly different directions of flight.

b. The pressure applied by a shaped charge to a target is to the order of several megabars. This is well into the plastic range for almost all materials. Figure 4-13 illustrates the response of the target material to a

shaped charge jet. Penetration occurs as the target material flows out of the hole. The material dislodged in the deeper parts of the hole flows out along the walls. Penetration is affected greatly by the distance of the base of the shaped charge to the target. This is called stand-off and is usually expressed in charge diameters. There is an optimum stand-off distance for maximum penetration. At closer distances, the jet has not fully formed and at further distances the jet is breaking up, causing the particles to hit off center such that they do not contribute to penetration. Generally the optimum stand-off is between two and six charge diameters. Penetration is normally around four to six diameters but could go as high as 11 to 12 diameters. The optimum liner thickness is about three percent of the charge diameter for soft copper. If a different material is used, the thickness should be determined by measuring the weight of soft copper that would be used for the particular charge diameter. This amount of material is then used. Liners made of less dense material will be thicker than the copper counterpart and liners made of more dense material will be thinner. Materials which are commonly used include copper, steel, glass, and aluminum. The angle of the cone apex varies from 42 degrees to 60 degrees in American ammunition and 18 degrees to 90 degrees in foreign ammunition. Forty-two degrees is the optimum arigle for maximum penetration.





A. LINER IS ACCELERATED NORMAL TO EXPLOSIVE-LINER INTERFACE



B. MATERIAL IS SQUEEZED OUT TO FORM THE JET

"SLUG"

"JET"

0.5 TO 2

0.5 TO 2 MILLIMETERS/ MICROSECOND

BACK 1-5 MILLIMETERS/ MICROSECOND TIP 6-10 MILLIMETERS/ MICROSECOND

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C. SHAPED CHARGE JET





Figure 4-13. Shaped charge penetration.



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c. When used in projectiles that rotate, shaped charge penetration is considerably reduced. Projectiles that have conical liners may lose as much as 50 percent of their effectiveness due to rotation. In general, penetration is reduced as spin increases from about zero to 200 revolutions per second, after which further increases have little effect. Rotating shaped charges produces holes of greater diameter than static charges, but rotation does not affect the volume of the hole produced. Changing the apex angle of the cone does not eliminate the reduction in penetration caused by rotation of the charge. d. The United States uses one other geometry of shaped charge liner, hemispherical. A hemispherical liner produces comparable jet energies to a coneshaped liner. However, the velocity and mass distribution in the jet are different. Hemispherical liners turn inside out with almost all of the material projected in the jet. As much as 70 to 80 percent of the material in conical liner stays behind to form the slug. In hemispherical shaped charges, however, jet velocity is only about half of that obtained in a conical shaped charge. Hemispherical shaped charges are less sensitive to rotation than conical shaped charges.



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