

Chapter 10

COMBUSTION PRODUCTS OF PROPELLANTS AND AMMUNITION

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INTRODUCTION

HISTORY OF PROPELLANTS

COMPOSITION OF PROPELLANTS

- Primers and Igniters
- Gun Propellants
- Rocket Propellants

COMBUSTION PRODUCTS OF PROPELLANTS

- Primers and Igniters
- Gun Propellants
- Rocket Propellants

CONTAMINANTS FROM AMMUNITION

IDENTIFICATION OF HAZARDS

- Conditions of Exposure
- Assessing Toxic Hazards
- Studies That Predict Toxic Exposures
- Toxicological Assessment of Combustion Products

HEALTH EFFECTS OF EXPOSURE TO AIRBORNE PRODUCTS OF PROPELLANT COMBUSTION

- Tissue Asphyxiants
- Irritant Gases
- Inhalable Metal Particulates

CURRENT MEASURES TO CONTROL EXPOSURE

SUMMARY

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INTRODUCTION

Soldiers and civilians whose work includes firing weapons, launching rockets, and demilitarizing ammunition, or who work around conflagrations that involve ammunition (or tactical vehicles that contain ammunition) encounter potentially hazardous exposures to combustion products. These exposures are related to the combustion of propellants and other chemicals that provide the energy for firing a projectile or rocket, the materials that are contained within the projectile, the interaction between the projectile and the firing tube or barrel, and numerous other chemical and physical events that occur during firing.

Propellants are chemicals that rapidly liberate large volumes of gases under high pressure and temperature. Military personnel probably have been exposed to the combustion products of propellants for more than 1,000 years.¹ These *energetic* gases (their reaction is exothermic) propel a projectile through and out of a gun tube or power the reaction motor when a rocket is launched. Propellants differ from other energetic materials such as fuels in their method of combustion: fuels require ambient oxygen to burn, whereas the oxidant is a chemical constituent of a propellant. The combustion of most propellants cannot be quenched once it has begun.

This chapter primarily considers the risks of exposure via inhalation, the skin, and the eyes to the major combustion products of commonly used solid propellants—carbon monoxide, ammonia, hydrogen chloride, oxides of nitrogen and sulfur, and lead—in army weapons systems. (Exposures to carbon monoxide and lead are such significant hazards to military personnel that they are considered in separate chapters of this textbook.) Potentially hazardous substances contained in projectiles (such as depleted uranium [DU], zinc, and lead) are also addressed. The U.S. Army has not used liquid propellants to any great extent, mainly because solid propellants have met operational requirements and were less expensive. Liquid propellants are considered to be potentially hazardous: they may contain chemicals that (a) are toxic (strong acids) and (b) could burn rapidly if the components come into contact with each other. The Lance missile system uses liquid propellants and has had an extremely good safety record despite both the theoretical hazards and considerable operational movement—including airdrops.² One system that currently uses liquid propellants has had operational problems: the Scud missiles that the Iraqi army used against Israel and the allied forces during Operation Desert Storm

were charged with liquid propellants; the Scuds, fueled in the field, took longer than 1 hour to charge, and could only be charged one at a time.²

Conventional weapons of immense destructive power have been developed during the 20th century: effective rapid-fire weapons; recoilless weapons, rockets, and missiles, all of which liberate large amounts of combustion products per unit of time; weapons that are operated in confined spaces and in various urban locales; and tightly enclosed vehicles that can be used as weapons platforms for operations in chemically contaminated environments. A side effect of utilizing these weapons is that the soldiers who operate them are exposed to the combustion products of propellants.

Casualties of inhalational exposures to these combustion products have definitely occurred, but published case reports are not readily available in the medical literature of any language.^{3,4} Several factors have minimized the number of reports documenting the adverse effects of these exposures. During weapons firing, the exposure settings are characterized by short-lived clouds of contaminants, with high peaks of pollution that rapidly dissipate. Exposures like these are very difficult to measure, particularly under field conditions. Sporadic, episodic weapons firing during training and battle operations deprives medical observers of a steady-state experience, such as would be found in an industrial setting where the same or similar operations are performed in the same location day after day. The scant information derived from field observations is often secluded in classified documents, or documents with limited accessibility, and often with little or no verification by the civilian or even the military medical communities.

One documented instance of carbon monoxide intoxication occurred at Fort Hood, Texas, in February 1984. It involved an M1E1 Abrams tank undergoing operational testing. This rare report of carbon monoxide intoxication is discussed in Chapter 11, Carbon Monoxide. Anecdotal evidence is not so rare; tank design was implicated as an important factor contributing to inhalational exposure, and poor crew conditions inside Soviet-made tanks that were captured by the Israeli Defense Forces during the Six-Day War (1967) have been described:

One of the main drawbacks of the original Soviet [T-55] design was the total disregard of human engineering for crew members. The Soviets pick the smallest of their recruits to serve in tank units, but even these

midgents did not feel too happy in the confines of their tank turret and driver's compartment. Bad ventilation in the cramped interior caused fatigue and exhaustion, reducing combat efficiency and endurance. In fact, Arab tank crews, overcome by deadly fumes and heat stress under severe climatic conditions, often abandoned their tanks, which were picked up perfectly intact.^{5(p18)}

The U-STS (2A20) 115-mm smoothbore gun, at first, seems a very efficient tank gun, [but] its combat effectiveness leaves much to be desired. The firing sequences present most of the drawbacks. The gun's exhaust fumes are overwhelming and the fighting compartment soon fills with carbon monoxide, despite the bore evacuator designed to remove fumes. Poor ventilation causes combat fatigue, and crews have been known to abandon their mounts totally exhausted, choking from the poisonous fumes.^{5(p17)}

By bringing the potential risks and problems related to the use of various weapons to the attention of medical personnel, those who care for soldiers will be prepared to recognize, treat, report, and, ideally, eventually minimize the adverse effects. Military physi-

cians must take the time to describe and report the clinical details and exposure events surrounding workplace-related injuries and illnesses so that our ability to prevent morbidity and mortality can be improved. U.S. Army Medical Department (AMEDD) officers are required to report actual overexposures or any suspected clustering of symptoms in soldiers regardless of whether these occur in garrison or in the field. In these situations, the Special Telegraphic Report of Selected Condition. (RCS MED-16[R4]—Requirement Control Symbol, Medical), which is required by army regulations, must be used.^{6,7} This report is essential; it enables occupational health personnel to assess the effectiveness of previously established engineering, administrative, or personal protective controls and to identify areas where the need for controls was overlooked. Eventually, these reports will be used by design engineers to eliminate or reduce hazardous exposures in military ordnance, vehicles, and equipment that are being developed for future use. The ultimate objective is the primary prevention of morbidity and mortality and the elimination or reduction of exposures that diminish soldier performance.

HISTORY OF PROPELLANTS

Perhaps the first recorded uses of propellants were by the Byzantine defenders of Constantinople against the Saracen fleet in AD 673 and 717.¹ The Byzantines used *Greek Fire*, a flaming propellant that was itself a chemical weapon, generating acrid smoke. Greek Fire was probably made of a powdered mixture of sulfur, naphtha, and quicklime. By the 13th century, Mediterranean Muslims launched small stone balls that were propelled by *black powder*, a mixture of sulfur, charcoal, and saltpeter (potassium nitrate), through tubes.¹ The origin of black powder remains a mystery, but many believe the Chinese were the first to use it, probably in fireworks and signals.⁸ By the 14th century, Europeans reportedly imported black powder from China. Black powder has been used for nearly two millennia, and is still used (in approximate proportions: potassium nitrate, 75%; charcoal, 15%; and sulfur, 10%) to a limited degree in modern munitions such as low-velocity guns, rockets, and as an igniter of larger propellants.⁹

Many renowned scientists contributed to the fields of propellants and the related discipline of ballistics. scribed a variety of weaponry—including grenades, flame throwers, and portable projectile hurlers (the forerunners of contemporary small-caliber arms)—in his 15th-century book, *The Pirotechnia of Vannoccio Biringuccio*.¹⁰ Biringuccio analyzed the mechanical

process of propellant combustion and also described the deleterious effects of inhaling combustion products.

By the early 17th century, King Gustavus Adolphus of Sweden established the first true field artillery, which consisted of heavy, iron, firing tubes on wheels; propellant in the form of black powder; and ball projectiles. He established artillery (and therefore propellants) as an important component of the battlefield armamentarium, and he laid the foundation for a flourishing Swedish arms industry (Figures 10-1 and 10-2).^{1,11}

Dramatic improvements in propellants evolved during the 19th century:

Modern propellants date from 1845, when a German chemist, Christian Schoenbein, discovered nitrocellulose, which burns completely leaving no solid residues. Gunpowder [black powder] by comparison produces over half its weight as solid residue. A satisfactory propellant in the form of cakes was first produced in 1884 by a French physicist, Paul Vieille, by gelatinizing nitrocellulose with an ether-alcohol mixture. This was used by the French army under the name of Poudre B. Alfred Nobel produced a similar propellant by using nitroglycerine instead of ether alcohol. Abel in Britain gelatinized nitrocellulose ... using a mixture of nitroglycerine and vaseline [petro-



Fig. 10-1. Gustavus II Adolphus, called Gustavus Adolphus, was King of Sweden from 1611 to 1632. He reorganized tactical military units and effectively integrated artillery to achieve increased firepower and mobility. He also revolutionized the manufacture and use of artillery including standardizing components used in the manufacture of artillery pieces; increasing the mobility of artillery by shortening barrels; and increasing the rate of fire through the use of premeasured powder charges in bags. He established Swedish artillery as the best in the world. Source: Holmquist BM, Gripstad B. *Swedish Weaponry Since 1630*. The Defence Matériel Administration of Sweden. The Royal Army Museum. Arlöv, Sweden: Berlings; 1982.



Fig. 10-2. By the middle of the 17th century, Sweden had developed a diversified and extremely productive arms industry that produced cannons, muskets, pistols, and many other items for its own army and for export. The two 17th-century weapons shown to the left were attempts during the black-powder era to develop rapid-fire guns. The *skottbalk* (organ-gun), (a), had twenty 20-mm barrels and was used as a defensive weapon. To fire the weapon, powder was placed in grooves in the crosspiece and butt and ignited with a match, thereby igniting the propellant charge in each barrel in rapid succession. This weapon fired bullets weighing 36.5 g each. The gun itself weighed 30 kg. The *pusikan* (fire-lance), (b), is an assault gun. It also has twenty barrels of 20-mm caliber. Powder and a fuse were put into the center core, which had a communicating opening into each barrel. This gun was mounted on the end of a lance, and after the fuse was ignited the lance would be pointed or thrown toward the enemy. Source: Holmquist BM, Gripstad B. *Swedish Weaponry Since 1630*. The Defence Matériel Administration of Sweden. The Royal Army Museum. Arlöv, Sweden: Berlings; 1982: 16.



leum jelly]. It was known as *cordite* due to its shape and was adopted by the British army in 1891 and is still used.^{12(p5)}

Despite the European propellant discoveries, black powder was used almost exclusively as the propellant in military guns in the United States throughout the 1800s. At least one European innovation, a nitrated cotton called guncotton (a form of nitrocellulose) that was invented in Switzerland, was tried as a replacement propellant but was rejected because it was too costly to produce and its strong gases corroded gun barrels. Black powder was initially produced in small cottage industries. Later, powder mills were constructed but there were few production innovations. This situation changed in 1866 when Alfred Nobel perfected dynamite from nitroglycerin, black powder, charcoal, brick dust, and wood dust. Dynamite was a successful commercial explosive for mining and excavating but was not militarily significant. However, the flourishing dynamite industry of the latter 19th century demonstrated that a relatively safe ener-

getic chemical mixture could be produced at reasonable cost and that the chemical constituents could be modified to achieve different explosive characteristics. These events signaled the development of a large, greatly improved military explosive and propellant industry.⁸

From the beginning of the American Civil War to the beginning of World War I (1861–1914), major improvements occurred in both the military propellant industry and the development of military ordnance such as cannon and guns (Figure 10-3). As a result, the Spanish-American War (1898) was the last major conflict in which black powder was used in large quantities. World War I was fought with new chemicals that propelled projectiles from modern artillery and with innovative smaller weapons like machine guns.^{3,8,13}

During World War I, two new kinds of weapons systems significantly increased soldiers' exposure to the toxic products of propellant combustion: the battlefield tank with a breechloading gun, and the rapid-firing machine gun. The battlefield tank essentially



Fig. 10-3. An innovation that significantly increased the possibility that soldiers would be exposed to propellant combustion products was the rear- or breech-loaded cannon. The breech-loaded cannon was conceived at least as early as the Middle Ages but manufacturers could not produce a tight seal that would prevent leakage of propulsion pressure. A simple mechanism that was found to be effective was the “sliding breech block,” which was used in this 19th-century Swedish cannon. After the breech door was closed, the piston on the right (the breech block) was moved to the left to complete the breech seal. Another 19th-century innovation was the brass cartridge case, which was forced tightly against the inside of the barrel. Other devices used to seal the breech include the interrupted screw breech block (sections of thread are cut away, allowing the breech block to be locked with only a turn of a few degrees) and the soft obturator ring. The obturator ring, located directly in front of the interrupted screw breech block, is forced against the breech block by the propellant explosion, forming a tight seal. Sources: (1) Holmquist BM, Gripstad B. *Swedish Weaponry Since 1630*. The Defence Matériel Administration of Sweden. The Royal Army Museum. Arlöv, Sweden: Berlings; 1982: 66. (2) Harding D, ed. *Weapons: An International Encyclopedia from 5000 BC to AD 2000*. Leicester, England: Galley Press (WH Smith and Son Limited); 1984.

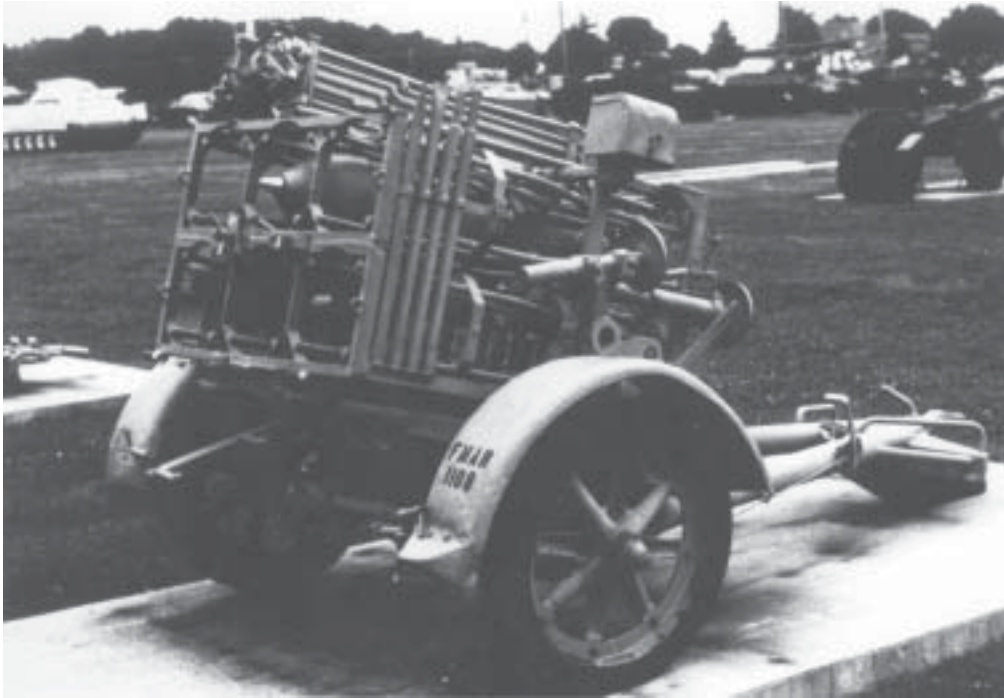


Fig. 10-4. This German *Nebelwerfer* (smoke thrower) 42, or mobile rocket launcher, was towed; it fired a rocket that achieved a range of 4,976 yards. Each rocket contained seven tubular sticks of propellant composed of nitrocellulose and diglycol dinitrate. An electrical firing mechanism was used. These devices were originally used for chemical or smoke barrages, which gave rise to the name. However, high-explosive, antipersonnel rockets were added. Sources: (1) US Army Office of the Chief of Ordnance. *Catalogue of Enemy Ordnance Materiel*. Vol 1, German (R). Washington, DC: Office of the Chief of Ordnance. 1 May 1945: 350,354,375. (2) US Army Ordnance Museum. Aberdeen Proving Ground, Md. Accession File ORD-FMAR-1108. (3) US Army Ordnance Museum. Aberdeen Proving Ground, Md. Accession File ORD-FMAR-588.

enclosed the space around its gun breech. Because ventilation was often inadequate, air inside the tank quickly became oppressive, and it was painful for the crew to breathe.¹⁴ When under enemy fire, the crew could close all the tank hatches and be relatively protected from the outside threat, but then they were at greater risk from their own gun's combustion products inside the tank. Chemical warfare forced soldiers to protect themselves in the field by sealing themselves inside their fortifications. Rapid-firing machine guns produced dangerous levels of carbon monoxide from incomplete propellant combustion inside these enclosed fortifications; for the first time, the gas produced by the combustion of propellants was itself reported to be the cause of casualties.³

The earliest reported use of rockets in warfare was during the siege of Kaifeng, China, in AD 1200; rocket experimentation, development, and use in warfare continued sporadically through World War I. (Rockets were fired by British troops at the siege of Fort

McHenry in the Baltimore, Maryland, harbor during the War of 1812, an event that inspired Francis Scott Key to include the words "the rocket's red glare" in the song that became the United States' national anthem.) However, rifles and cannons were generally more popular than rockets, and rockets were unsafe and had to be hand made. As late as World War I, the only rocket propellant used, black powder, had to be tightly packed into the rocket by hand to achieve a high degree of compression when burned. The tightly packed propellant had a tendency to become brittle, crack, and explode. These rockets were considered unsafe and unsuitable for use in front lines.¹⁵

Between 1936 and 1940, Great Britain, Germany, and the United States initiated the development of improved rocket propellants. Safe and reliable charges that did not have to be compressed allowed for the mass production of rocket tubes and other rocket parts. The British propelling charge consisted of nitroglycerin (50%), nitrocellulose (41%), and



Fig. 10-5. The V-2 was the second “Vengeance” or “V” weapon developed by the Germans for use against England and Belgium in reprisal for the allied bombings of German cities. The V-1 or “buzz bomb” was a pilotless aircraft, whereas the V-2 was the first inertially guided ballistic missile and traveled at 3,600 mph. From Peenemunde on the Baltic Sea, about 1,500 were fired at England; over 2,100 were directed at Antwerp; and about 650 malfunctioned after firing and never reached their targets. The V-2 was 45 ft 10 in. long and 5 ft 5 in. in diameter. It was powered by liquid propellant (4 tons of alcohol and 4 tons of liquid oxygen), which were pumped into the motor at a rate of 9 tons per minute. The rocket’s total weight was 14 tons: 8 tons of fuel and 1 ton of explosive. It reached an altitude of 75 miles and had a range of 200 miles. After World War II, about 180 scientists from Peenemunde and 300 freight cars full of V-2 parts were captured by US Army Ordnance experts and taken to New Mexico, where the V-2 rockets were assembled and test-fired as the first step in the development of the United States’s ballistic missile and space programs. Sources: (1) *German Explosive Ordnance (Bombs, Fuzes, Rockets, Land Mines, Grenades and Igniters)* TM 9-1985-2/ TO 39B-1A-9. Washington, DC: US GPO; 1953: 209–215, 346. (2) US Army Ordnance Museum. Aberdeen Proving Ground, Md. Accession File ORD-AMMO-919.

carbamite (9%). Carbamite (diethyldiphenyl urea) was a gelatinizer and stabilizer. The United States formulation was nitrocellulose (approximately 60%) and nitroglycerin (approximately 40%). Diphenylamine was used as a stabilizer, but apparently in very small quantities.¹⁵

During World War II, the antitank rocket and tube (bazooka), the 4.5-in rocket launcher, the German 300-mm Nebelwerfer 42 (which fired single rockets or multiple rocket barrages) and free-flight rockets (such as the German-made, liquid-propellant system V-2) were developed (Figures 10-4 and 10-5).¹ These three types of rockets generated larger amounts of combustion products per unit time, resulting in a greater potential for exposure to the soldiers who operated these weapons.

Since World War II, technological advances in rocketry and other weaponry and the need for sealed vehicles that are capable of surviving a chemically

contaminated environment have markedly increased the risk that soldiers will be exposed to the toxic products of propellant combustion. Since the 1970s, increasing concern about chemical carcinogenicity and mutagenicity has created a broader perspective for examining the toxicity of propellant combustion products, extending beyond the acute effects.¹⁶ As they did in World War I, gun breeches on armored vehicles still open into crew compartments; firing-tube exhaust and vehicle ventilation systems are still necessary to evacuate combustion gases. Additionally, the development of improved military armor that was very difficult to penetrate triggered a search for projectiles of greater density and strength. This led to the inclusion of DU in 25-, 105-, and 120-mm caliber projectiles and gave rise to a new potential exposure of concern for the soldiers who fired the projectiles or who would be exposed to projectile fragments.¹⁷

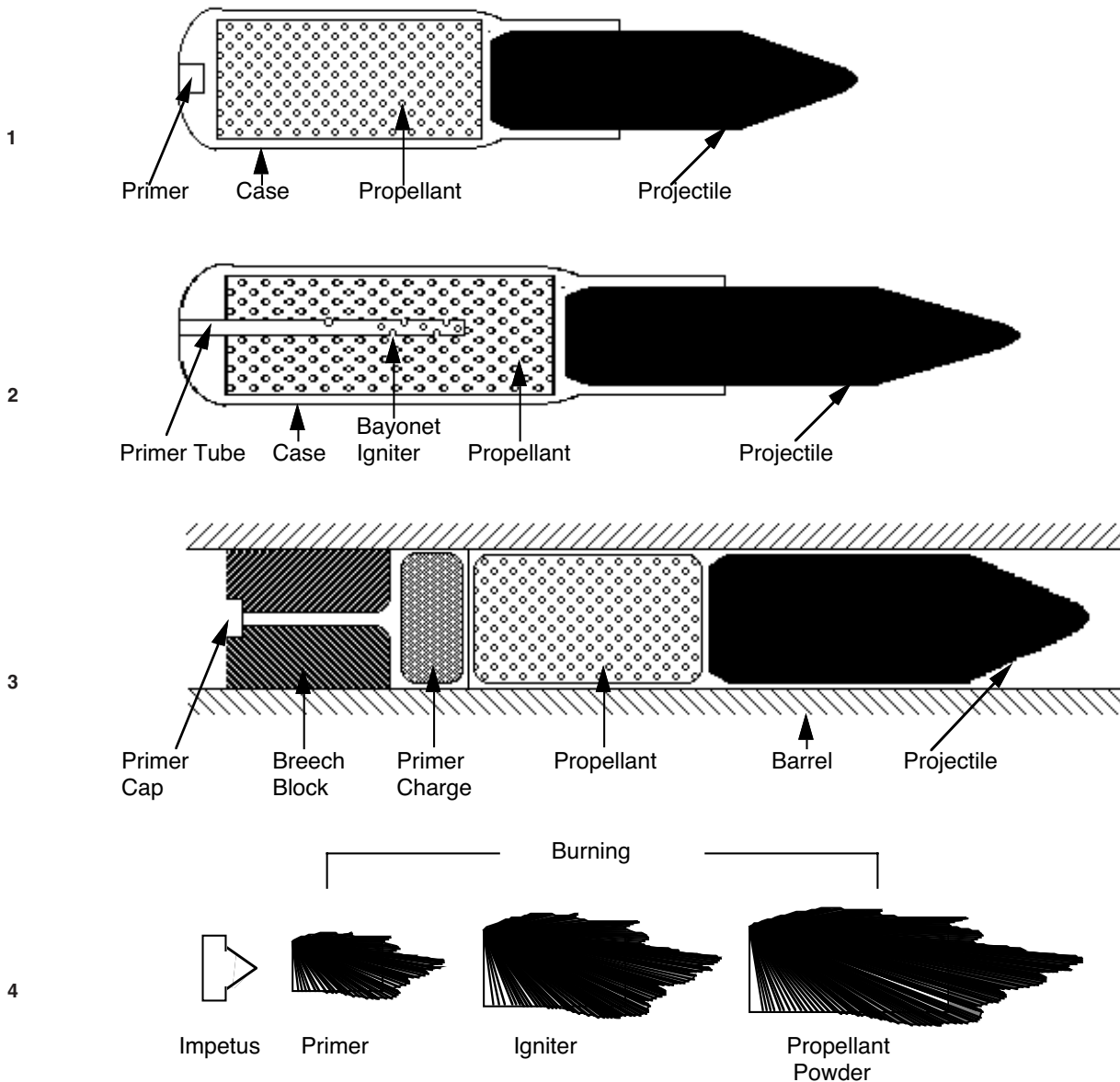


Fig. 10-6. Drawings 1, 2, and 3 show the general configurations of primer, igniter, and propellant mixes in typical ammunition. Drawing 4 is a schematic representation of the firing sequence in typical ammunition, usually referred to as the “explosive train” or the “ignition train.” A small electrical and/or mechanical (percussion) stimulating impetus is intensified through a succession of intermediate charges to obtain optimum firing of the main charge, the propellant. The “ignition train” typically consists of four steps: stimulating impetus, primer burning, igniter burning (shown only in drawings 2 and 4) and propellant burning. Igniters are not generally placed in small-caliber ammunition (drawing 1) but are found in the bayonet igniter of tank gun rounds (drawing 2) and in close association with the propellant in artillery rounds (drawing 3). Igniter mixes are generally not used in rocket propulsion motors. Propellants are “low explosives” in that they burn relatively slowly (400 m/sec or slower) at a sustained rate. In contrast, “high explosives” like dynamite detonate at 1,000 to 10,000 m/sec producing a sudden, powerful shock wave. Sources: (1) Farrar CL, Leeming DW. *Military ballistics—A basic manual*. In: *Battlefield Weapons Systems and Technology Series*. Vol 10. Oxford, England: Brassey’s Pub Ltd; 1983. (2) US Department of the Army. *Military Explosives*. Picatinny Arsenal, NJ: AMCCOM; 1984. Technical Manual 9-1300-214. (3) Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1. (4) Ciccone TQ. Primers. In: Kaye SM, ed. *Encyclopedia of Explosives and Related Items*. Vol 8. Dover, NJ: US Armament Research and Development Command; 1978: 372–387.

COMPOSITION OF PROPELLANTS

In most military weapon propellant systems, the initiation of an impetus (usually a percussion force or an electrical stimulus) causes a number of different energetic chemicals to burn in series (Figure 10-6). The composition of these energetic materials varies among primers, igniters, and propellants; and the three different chemical mixes used vary with the weapon system. In small-caliber ammunition, as measured by the diameter of the projectile (generally considered to be less than 40 mm, like that used in the 5.56-mm M16 rifle and the 7.62-mm machine gun), the primer usually ignites the propellant charge. In larger-caliber ammunition (such as that used in 155-mm and 8-in howitzers and 105- and 120-mm tank guns), a booster charge, known as an igniter, acts between the primer and the propellant. These various mixes or charges (which are sometimes referred to collectively and incorrectly as "the propellant") are designed and developed by chemists and ballisticians to (a) achieve the desired projectile motion inside and outside the firing tube and (b) deliver the projectile payload accurately over a specified distance. Other considerations in the chemical design and development of charges include the potential toxicity to humans from component chemical ingredients and combustion products; the physical safety of manufacturing workers and soldiers who will use the propellants and ammunition; the storage life of the propellant; and the preservation and extended life of the weapon system used to fire the ammunition, especially the firing tube.

AMEDD personnel who evaluate potential or actual toxic exposures related to energetic chemicals in the ignition train often have difficulty locating anything more than imprecise qualitative and quantitative descriptions of the chemical mixes. Additionally, toxicity studies of combustion products are also difficult to obtain. There are at least two reasons for this: first, the compositions are militarily important and may be classified, or at least controlled in their release; and second, personnel who work in the research and development of energetic materials often focus on a limited area of interest and are not knowledgeable about the broad, general topic of human health effects. As a result, AMEDD physicians and scientists involved in a toxicity assessment of a military propellant may not be able to easily locate toxicity data, or even the detailed chemical composition, of a propellant of interest. The toxicity data may not exist and the propellant formulation may be classified for reasons of national security. Additionally, several propellant scientists may need to be interviewed before a reason-

ably complete database, one that will support a health hazard assessment (see Chapter 6, Health Hazard Assessments), can be assembled.

Primers and Igniters

Pyrotechnic devices (which we call fireworks or signal flares today) are alleged to have been used over 1,000 years ago. However, before the 19th century, little if anything was recorded about the manner in which the burning of the energetic chemicals in these devices was started. The first modern primer, which contained potassium chlorate, charcoal, and sulfur, was probably invented by Forsyth in 1807 (Table 10-1).^{9,18} The first high explosive (HE) chemical (nitroglycerin [NG]), which was developed by Sobrero in

TABLE 10-1
COMPOSITION OF PRIMERS AND IGNITER

Primers	Ingredient	% by Weight
First modern primer	Potassium chlorate	70.6
	Charcoal	11.8
	Sulfur	17.6
FA70	Potassium chlorate	53
	Antimony sulfide	17
	Lead thiocyanate	25
TNT		5
FA956	Lead styphnate	37 ± 5
	Tetracene	4 ± 1
	Barium nitrate	32 ± 5
	Antimony sulfide	15 ± 2
	Aluminum powder	7 ± 1
	PETN	5 ± 1
Igniter *	Gum arabic	< 1
	Black powder:	
	Potassium nitrate	76 ± 2
	Charcoal	14 ± 2
	Sulfur	11 ± 1

* Also may contain nitrocellulose, mealed gunpowder, finely divided smokeless powders, and/or other substances
Sources: (1) Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1. (2) Ciccone TQ. Primers. In: Kaye SM, ed. *Encyclopedia of Explosives and Related Items*. Vol 8. Dover, NJ: US Armament Research and Development Command; 1978: 372-387.

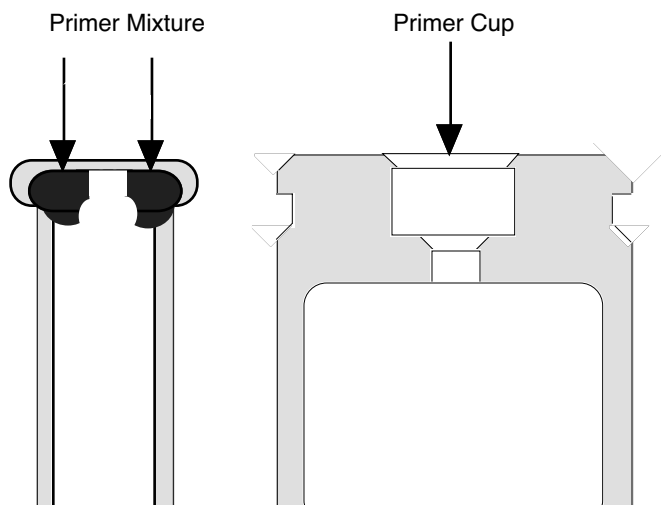


Fig. 10-7. Percussion primers in military ammunition may be either rimfire (left) or centerfire (right). In the rimfire model, the primer energetic material is placed around the rim of the base of the shell casing. The firing pin strikes the rim of the metal casing and the percussion force starts the burning of the primer. Rimfire primers are generally restricted to 0.22-mm caliber ammunition, which is extensively used in commercial sporting ammunition, and is also used by the military to a limited degree for training purposes. In centerfire ammunition, the box or cup containing the primer is located in the center of the base of the shell. The figure above is a representative centerfire box, but there are many varieties of centerfire percussion-box configurations. The metal used to make the cup may be a brass alloy (70% copper and 30% zinc) or some other metal or alloy that will provide the desired sensitivity to the applied percussion force. Adapted from Ciccone TQ. Primers. In: Kaye SM, ed. *Encyclopedia of Explosives and Related Items*. Vol 8. Dover, NJ: US Armament Research and Development Command; 1978: P372–P387.

1846, and other significant improvements in energetic materials in the latter 19th century, stimulated interest and innovations in the physical and chemical means used to activate explosive and propellant charges. Within the scope of most of the discussion in this chapter, the impetus that begins the explosive or ignition train can be considered to be either a percussive or an electrical force. (Other means to initiate energetic materials, such as friction, have been used to a lesser degree.) In ammunition, the percussion force is applied to either the rim (rimfire) or the center (centerfire) of the end of the shell casing (Figure 10-7).¹⁸

During the early 1900s, a primer with a mercury fulminate base (which is believed to have originated in Austria) was widely used in the U.S. Army. Around 1917, the army switched to a nonmercuric formula, called FA70, which contained potassium chlorate, antimony sulfide, lead thiocyanate, and trinitrotoluene (TNT). A variant (FA90), which contained antimony sulfide and pentaerythritol tetranitrate (PETN, which replaced TNT), was used in caliber 0.50 ammunition. Potassium chlorate decomposed on firing to form potassium chloride. The potassium chloride was deposited in the gun barrel and quickly caused extensive rusting. In 1948, lead styphnate was chosen from among several candidates as the replacement

compound and was incorporated into a standard primer mix called FA956.¹⁸

Priming mixtures are developed to (a) fire when the impetus of the ignition train is initiated, (b) propagate the ignition train once they are fired, and (c) reliably perform the first two functions under various conditions. For example, environmental temperatures may vary considerably and the pressures applied to shell casings that house percussion primers will differ with different weapon systems. (Potassium chlorate is still occasionally used in primers intended for use in very hot environments.) Additionally, the percussion force applied to the energetic primer mixture could be high or low, depending on the design requirements of the system. As the amount of applied energy is decreased, the sensitivity of the primer must be increased. Increased sensitivity is accomplished by using thinner metals and softer alloys to contain the primer mixture and by modifying the composition of the mixture itself.

The ignition train in rockets usually consists of an impetus, the primer, and the propellant. The impetus is an electrical impulse that travels along a bridging wire or squib to the primer, which usually contains KBNO_4 . The current emphasis in the development of energetic materials for army rockets is to minimize the production of any substance produced during firing

that could reveal the firer's position (provide a battle-field "signature"). Substances of concern are those that could be detected by infrared sensors or that are visible to the naked eye (such as smoke or muzzle flash). While KBNO_4 is not entirely smokeless, it is considered an acceptable primer.²

Routinely used igniter mixtures are reported to include black powder (potassium nitrate, charcoal, and sulfur), nitrocellulose, mealed gunpowder, finely divided smokeless powders, and /or other substances.⁹

Gun Propellants

All solid propellants other than black powder are known as smokeless powders, although they are neither powders nor completely smokeless.¹² The basic types among these include the single-base, which are prepared by dissolving nitrocellulose in ether and alcohol; the double-base, which are prepared by dissolving nitrocellulose in nitroglycerin; and the triple-base, which are prepared by dissolving nitrocellulose in nitroglycerin with nitroguanidine added to reduce the temperature of the combustion-produced gas.¹²

Nitro-based propellant charges typically contain one to three nitro compounds and a wide variety of other added chemicals that are introduced to produce a particular, desired effect (Tables 10-2 and 10-3).

Double-base propellants are more powerful than single-base propellants, however they suffer from high propellant-gas temperatures [that] can cause excessive barrel erosion and muzzle flash. Triple-base propellants are similarly powerful, but the addition of cool-burning nitroguanidine reduces the temperature of the gas to near that of the single-base propellants. Other ingredients added to smokeless propellants are used primarily to control [the] burning rate and [to] suppress decomposition during storage.^{12(p14)}

Recently, compounds such as the nitramine propellant RDX (*research department explosive*, which is also called cyclonite; see Chapter 9, Explosives and Propellants), which have traditionally been considered explosives, have been used as propellants. An RDX-based propellant is now included in the M900 round for the 105-mm tank gun. The combustion products from this propellant are expected to be dif-

TABLE 10-2

TYPICAL COMPONENTS OF NITROCELLULOSE-BASED PROPELLANTS AND THEIR FUNCTIONS

Component	Application
Nitrocellulose	Energetic polymeric binder
Nitroglycerin, metriol trinitrate, diethylene glycol dinitrate, triethylene glycol	Plasticizers: energetic dinitrate, dinitrotoluene
Dimethyl, diethyl or dibutyl phthalates, triacetin	Plasticizers: fuels
Diphenylamine, diethyl centralite, 2-nitrodiphenylamine, magnesium oxide	Stabilizers
Organic and inorganic salts of lead (lead stannate, lead stearate, lead salicylate)	Ballistic modifiers
Carbon black	Opacifier
Lead stearate, graphite, wax	Lubricants
Potassium sulfate, potassium nitrate, cryolite (potassium aluminum fluoride)	Flash reducers
Ammonium perchlorate, ammonium nitrate	Oxidizers: inorganic
RDX, HMX, nitroguanidine, and other nitramines	Oxidizers: organic
Aluminum	Metallic fuels, cross-linking catalysts
Lead carbonate, tin	Defouling agents
Vaseline, centralite	Inert materials to decrease erosion
Graphite	Recarbonate steel barrels

RDX: *research department explosive*; HMX: *high melting explosive*

Adapted with permission from Lindner V. Explosives and propellants. In: Kirk RE, Othmer PF, eds. *Encyclopedia of Chemical Technology*. Vol 9, 3rd ed. New York: John Wiley;1980: 622. Additional source: Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1.

TABLE 10-3
COMPOSITION AND SELECTED COMBUSTION PRODUCTS OF CHARACTERISTIC GUN PROPELLANTS

	Propellants					
	M1	M5	M8	M10	M15	M17
Composition, wt %^{1,2}						
Nitrocellulose	85.0	82.0	52.2	98.0	20.0	22.0
(nitrogen, %)	(13.15)	(13.25)	(13.25)	(13.15)	(13.5)	(13.15)
Nitroglycerin	—	15.0	43.0	—	19.0	21.5
Nitroguanidine	—	—	—	—	54.7	54.7
Ethyl centralite	—	0.6	0.6	—	6.0	1.5
Diphenylamine	1.0*	—	—	1.0	—	—
Dinitrotoluene	10.0	—	—	—	—	—
Dibutyl phthalate	5.0	—	3.0	—	—	—
Potassium nitrate	—	0.7	1.2	—	—	—
Barium nitrate	—	1.4	—	—	—	—
Potassium sulfate	1.0*	—	—	1.0	—	—
Lead carbonate	1.0*	—	—	—	—	—
Cryolite	—	—	—	—	—	0.3
Graphite	—	0.3	—	0.10*	—	0.15*
Combustion Products, mol/g x 10^{2+1,2}						
CO	2.33	1.61	1.28	1.81	1.45	1.15
CO ₂	0.19	0.48	0.66	0.40	0.14	0.25
H ₂	0.88	0.34	0.19	0.44	0.92	0.57
H ₂ O	0.64	1.08	0.11	0.99	0.83	1.07
N ₂	0.44	0.48	0.54	0.46	1.29	1.30

* Added if required

† At loading density of 0.2 g/cm³

Adapted with permission from Lindner V. Explosives and propellants. In: Kirk RE, Othmer PF, eds. *Encyclopedia of Chemical Technology*. Vol 9, 3rd ed. New York: John Wiley; 1980: 627.

¹Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1.

²Roth J, Carpenter EL. Propellants, Solid. In: Kaye SM, ed. *Encyclopedia of Explosives and Related Items*. Vol 8. Dover, NJ: US Army Armament Research and Development Command; 1978: 402–473.

ferent from nitrocellulose-based propellants in that much more hydrogen cyanide and nitrous oxide (which is relatively nontoxic compared to the other oxides of nitrogen) are produced.¹⁹

Rocket Propellants

In some respects, propellants used in rockets such as the soldier-held Stinger (shown in Figure 6-4, Chap-

ter 6, Health Hazard Assessments), the Patriot air defense system, and the Multiple Launch Rocket System (MLRS), are different from those used in rifles, pistols, and artillery pieces. Successful rocket flight depends on the solid fuel's burning so that the gases produced forcefully exit rearward, thereby generating the pressure required to thrust the rocket forward.¹⁵

One variable that is important in propulsion is related to the total surface area of the propellant mixture that

is being burned at any time. For example, consider a rocket propellant charge filling the entire circumference of the rocket (wall-to-wall) and running down the long axis of the rocket. If the burning is initiated in a simple longitudinal hole that runs the length of the propellant charge, then the largest burning surface (and the concomitant greatest release of gas) would occur at the last instant of burning. To produce a more even burn, the center hole can be made in a star shape. In some rockets with wall-to-wall propellants, a center hole is not used; the propellant is ignited across the

surface of one end and burns lengthwise to the other end (as a cigarette burns). Depending on the burn method desired, the primer compound is placed in a center hole or on the surface at one end of the rocket.^{2,15} The double-base propellants of World War II-era rockets usually burned unrestricted. Since World War II, however, the burn of solid rocket propellants has been controlled by selecting both the chemical composition of the propellant and the method of burning.¹⁵

Double- and triple-base nitrocellulose propellants are used in rockets (Table 10-4). Based on their ballistic and thermochemical-thermodynamic properties, propellant A is classified as low energy and propellants B and C are classified as high energy.^{9,20}

In 1942, work began on the development of composite rocket propellants, which usually do not contain nitrocellulose or an organic nitrate. However, they normally contain a fuel such as metallic aluminum; an organic polymer binder such as a synthetic rubber, which is also a fuel; and an inorganic oxidizing agent such as ammonium perchlorate (Table 10-5).^{20,21}

The Stinger missile is a shoulder-fired rocket that provides air-defense protection. It has an infrared homing device that identifies the heat emitted by its target, such as aircraft. The Stinger has two rocket motors. When the soldier fires the missile from its launch tube, the small launch motor carries the missile a safe distance away; then the flight motor ignites the composite propellant, which propels the rocket to its target (Table 10-6). The combustion product of primary medical concern in the Stinger missile system is hydrogen chloride, which is equivalent to hydrochloric acid when in contact with water vapor.²²

Research and development efforts are underway to improve the composition of currently fielded rocket propellants. These efforts are directed toward reducing cost, improving safety, decreasing the firer's battlefield signature, and/or reducing the possibility of adverse health effects from propellant combustion product toxicity.^{2,22} For example, currently available composites containing ammonium perchlorate are unacceptable because (a) the hydrogen chloride produced as a combustion product of ammonium perchlorate forms a white cloud of gas that reveals the firer's position and (b) the gas can produce adverse health effects in humans. One consideration is to replace ammonium perchlorate with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) or HMX (high-melting explosive; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). These two high-energy explosives would increase the sensitivity of the propellant (making the propellant more susceptible to explosion) and would require further modification of the chemical composition to reduce that sensitivity.²

TABLE 10-4

COMPOSITION AND MAJOR COMBUSTION PRODUCTS OF TYPICAL NITROCELLULOSE-BASED CAST ROCKET PROPELLANTS

	Low Energy	High Energy	
	Prop A	Prop B	Prop C
Composition of Propellants, wt %			
Nitrocellulose (12.6% N)	59.0	20.0	22.0
Nitroglycerin	24.0	30.0	30.0
Triacetin	9.0	6.0	5.0
Dioctyl phthalate	3.0	—	—
Aluminum	—	20.0	21.0
HMX	—	11.0	—
Stabilizer	2.0	2.0	2.0
Ammonium perchlorate	—	11.0	20.0
Lead stearate	3.0	—	—
Combustion Products Composition, mol/100 g			
C	2.12	—	—
CO ₂	0.31	0.05	0.07
CO	2.12	1.30	1.15
H ₂	1.06	0.75	0.66
H ₂ O	0.66	0.27	0.33
N ₂	0.43	0.49	0.38
Pb	0.004	—	—
Al ₂ O ₃	—	0.35	0.37
H	—	0.20	0.23
OH	—	0.05	—
Other	—	0.15	—
HCl	—	—	0.10

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TABLE 10-5
TYPICAL COMPONENTS AND CHARACTERISTICS OF COMPOSITE ROCKET PROPELLANTS*

Components	Characteristics
Binders	
Polysulfides	Reactive group, mercaptyl (–SH), is cured [†] by oxidation reactions; low solids loading capacity [‡] and relatively low performance; now mostly replaced by other binders
Polyurethanes polyethers polyesters	Reactive group, hydroxyl (–OH), is cured with isocyanates; intermediate solids loading capacity and performance
Polybutadienes copolymer, butadiene and acrylic acid	Reactive group, carboxyl (–COOH) or hydroxyl (–OH), is cured with difunctional epoxides or aziridines
Terpolymers of butadiene, acrylic acid and acrylonitrile	Superior physical properties and storage stability
Carboxy-terminated polybutadiene	Cured with difunctional epoxides or aziridines; have very good solids loading capacity, high performance, and good physical properties
Hydroxy-terminated polybutadiene	Cured with diisocyanates; have very good solids loading and performance characteristics and good physical properties and storage ability
Oxidizers	
Ammonium perchlorate	Most commonly used oxidizer; has a high density, permits a range of burning rates, but produces smoke in cold or humid atmosphere
Ammonium nitrate	Used in special cases only; hygroscopic and undergoes phase changes, has a low burning rate, forms smokeless combustion products
High-energy explosives (RDX and HMX)	Have high energy and density, produce smokeless products, limited ranges of low burning rates
Fuels	
Aluminum	Most commonly used; high density; produces an increase in specific impulse and smoky and erosive products of combustion
Metal hydrides	Provide very high impulse but generally inadequate stability, smoky products, low density
Ballistic Modifiers	
Metal oxides	Iron oxide most commonly used
Ferrocene derivatives	Permit significant increase in burning rate
Others	Coolants for low burning rate and various special types of ballistic modifiers
Modifiers for Physical Characteristics	
Plasticizers	Improve physical properties at low temperatures and processability; may vaporize or migrate; can increase energy if nitrated
Bonding agents	Improve adhesion of binder to solids

*In 1942, at the Guggenheim Aeronautical Laboratory of the California Institute of Technology, work began on the development of cast composite propellants for rockets. The initial formulation contained approximately 25% asphalt and 75% potassium perchlorate.

[†]Cured: the conversion of a raw product to a finished and useful condition by application of heat and / or, as in this table, chemicals, which induce physicochemical changes. Source for this definition: *Condensed Chemical Dictionary*. 10th ed. New York: Van Nostrand Reinhold; 1981.

[‡]Solids loading capacity: the ability of a binder to allow more solids (eg, oxidizers) to be added to a propellant mixture. A binder with a higher solids loading capacity allows more oxidizer to be added and is therefore more energetic. Source for this definition: Chew B. Propulsions Directorate, Redstone Arsenal, Huntsville, Ala. Personal communication; 21 October 1992.

RDX: *research department explosive*

HMX: *high melting explosive*

Reprinted with permission from Lindner V. Explosives and propellants. In: Kirk RE, Othmer PF, eds. *Encyclopedia of Chemical Technology*. Vol 9, 3rd ed. New York: John Wiley; 1980: 624.

TABLE 10-6

COMPOSITION OF PROPELLANT AND COMBUSTION PRODUCTS OF STINGER ROCKET MOTORS

Propellant Ingredients*		Propellant Combustion Products (mol/100 g of propellant)		
Launch Motor	Flight Motor*	Combustion Product	Launch Motor	Flight Motor†
Ammonium perchlorate	Polymer, carboxy terminated	CO	0.551	0.944
		CO ₂	0.539	0.045
Polyvinyl chloride	Resin	Cl	—	0.003
Di(2-ethylhexyl)adipate	Epoxy resin	H	0.869	0.009
Copper chromite	Chromium octoate	HCl	0.800	0.575
Aluminum powder	Di(2-ethylhexyl)adipate	H ₂	—	1.297
Carbon black	Lecithin	H ₂ O	0.925	0.315
Stabilizer	Ferric oxide	N ₂	0.308	0.290
Sodium dioctyl sulfosuccinate	Aluminum powder	Al ₂ O ₃	0.018	0.333
Glycerol monooleate	Ammonium perchlorate	NaCl	< 0.001	—
Pentaerythritol dioleate		Cu	0.009	—
		CH ₄	< 0.001	—
		H ₂ S	< 0.001	—
		CuCl	< 0.001	—
		Cr ₂ O ₃	0.001	—

*Quantitative data are protected by security classification

†Only the "boost" grain was tested. Test results are suspect because of discrepancies in predicted and observed combustion product values
Sources: (1) Bourke KS, Redstone Arsenal, Huntsville, Ala to CDR, US Army Environmental Hygiene Agency. 9 June 1986. Written communication. (2) Gross R, US Army Environmental Hygiene Agency, Aberdeen Proving Ground, Md., and Cox R, Redstone Arsenal, Huntsville, Ala. Telephone communication; 22 June 1992.

Some rocket scientists are advocating a return to liquid propellants or some modification of them. Using propellant chemicals like those found in the Lance missile system could eliminate the need for perchlorates and could therefore produce less-detectable combustion products when fired. However, as discussed earlier, the use of liquid propellants is associated with concerns about safety issues and, as they were used by the Iraqi forces in Operation Desert Storm, can cause operational delays because of the time required to fuel them in the field. The Lance missile system uses two liquids (in addition to other energetic propellant chemi-

icals): inhibited red fuming nitric acid and unsymmetrical dimethylhydrazine. When these two liquids come in contact with each other, a hypergolic (self-igniting) mixture is formed. Scientists currently believe that containers can be made leakproof, even when the rocket sustains combat damage. Rockets with leakproof containers could be charged with fuel at the factory and arrive at their destination ready for firing. Furthermore, the chemicals that combine to form the hypergolic mixture do not necessarily need to be liquids; using them as gels may provide an additional safety factor.²

COMBUSTION PRODUCTS OF PROPELLANTS

The qualitative and quantitative exhaust emissions from the firing of a gun or rocket to which a soldier or civilian worker will be exposed depend on a multitude of variables including

- the chemical composition of the primer, igniter, and propellant;

- the pressure and temperature in the gun or rocket motor;
- the density of loading of the energetic chemicals (g/cm³);
- thermal, chemical, and/or mechanical erosion of the combustion chamber, gun barrel, shell casing, and projectile; and

- the meteorological conditions during firing, including humidity, wind direction, and speed.⁹

The only sure way to determine the nature and degree of exposure is to collect samples for quantitative analyses from the person's breathing zone and/or to analyze solid residues and determine the extent

of contact between the residues and the person's skin and mucous membranes.

Emissions from burning energetic chemicals—for individual and all components in the ignition train—are measured in laboratories. However, the laboratory setting requires that arbitrary decisions be made about the types and sizes of test chambers or devices

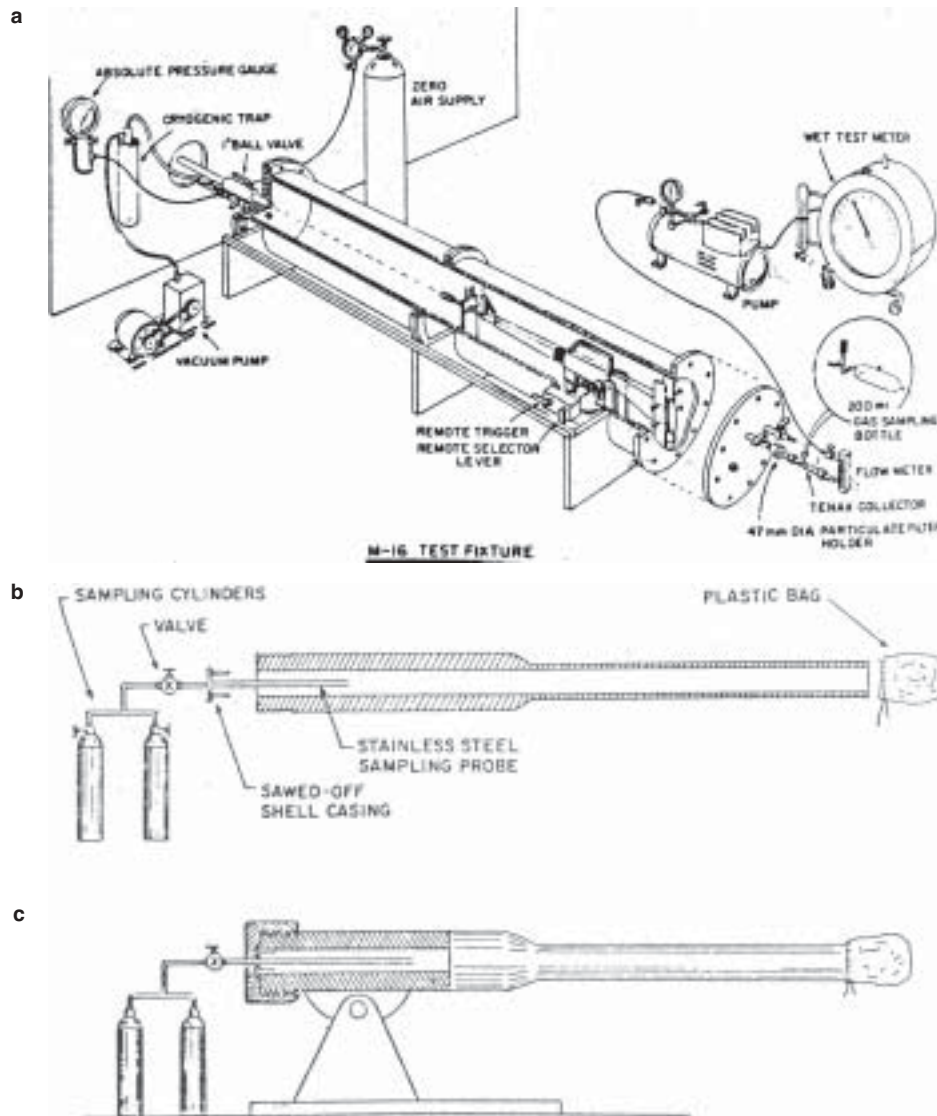


Fig. 10-8. Laboratory sampling systems for identifying propellant combustion products. The enclosure for studying emissions from the M16 rifle, shown in (a), was 6 ft x 11.75 in and contained 133 L. The chamber was Teflon coated to minimize gas absorption and was kept tight with O-ring seals and valves. After firing, chamber contents were evacuated and analyzed. The tank gun system was constructed in a bunker. A manifold for collecting specimens was connected to an adapter, which was a sawed-off shell casing. After firing, the end of the firing tube was covered, the spent shell casing was removed, and the sawed-off shell casing with manifold collection tube was inserted. In (b), the collection device is being inserted; in (c) it is fully inserted. Specimens were collected in the sampling cylinders. Source: Ase P, Eisenberg W, Gordon S, Taylor K, and Snelson A. Propellant combustion product analyses on an M16 rifle and 105-mm caliber gun. *J Environ Sci Health*. 1985;A20(3):337–368.

that will be used to collect emissions. Laboratory test conditions cannot and do not take into account all the potential variables that will influence the exposures received by personnel who operate the gun or rocket system. Two laboratory test systems have been used to evaluate propellant combustion products: one for rifle firing (5.56-mm M16 rifle) and one for 105-mm tank gun firing (Figure 10-8). Data collected from such laboratory test systems help in both assessing the potential for harmful exposures and investigating exposures that allegedly resulted in morbidity, mortality, or both. In drawing conclusions, however, the limitations of these data must be recognized. Additionally, in assessing reports of the qualitative and quantitative composition of energetic materials and their combustion products, it is usually difficult and often impossible for the AMEDD assessor to determine if the writer is addressing the primer, igniter, or propellant component, or a combination.

Primers and Igniters

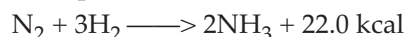
Data are not readily available on the chemicals emitted exclusively by the combustion of primers. This lack of data is probably explained by the quantity of primer used: primers contribute a very small proportion to the total amount of energetic chemicals in an ignition train. When evaluating total emissions using systems like those shown in Figure 10-8, it is often difficult to determine the specific source chemical for a particular product of combustion. However, primers often contain antimony, barium, lead, and possibly other chemicals that may not be found in other ignition train compounds.^{9,23}

Descriptive data on igniter combustion products also are not readily available in the scientific literature, probably for the same reasons that primer combustion data are scarce. However, black powder has been well studied and the approximate products of combustion are available (Table 10-7).

Gun Propellants

Carbon dioxide, water, carbon monoxide, hydrogen, nitrogen, and nitric oxide together typically constitute approximately 99% by volume of the total mixture of propellant combustion products.²⁴ The primary combustion products of most propellants are very similar and generally are considered to be predictable from the charge composition prior to combustion.²⁵ However, the total number of detectable, different chemical species formed during weapon firing is great. Ninety were reported from tests done on M16 rifle firing and 70 were associated with 105-mm tank gun exhausts.^{23,24}

During the 1980s, AMEDD emphasized the major combustion products: carbon monoxide (see Chapter 11), lead (see Chapter 12), and, to a lesser degree, ammonia.⁴ The irritant properties of ammonia could significantly detract from soldier performance on the battlefield. Other species (NO_x, the generic expression for oxides of nitrogen) can also be formed. Under the correct conditions, ammonia can be formed as shown in the equation



Iron particles in the exhaust, which are formed as a result of erosion of the gun tube, catalyze this reaction.^{9,25}

Weapons modernization occurred rapidly in the 1980s and with it grew concerns about the adverse health effects on soldiers who operated the new

TABLE 10-7
APPROXIMATE COMPOSITION OF
COMBUSTION PRODUCTS OF
BLACK POWDER

Component	Weight (%)
Gases (44% of total components)	
Carbon dioxide	49
Carbon monoxide	12
Nitrogen	33
Hydrogen sulfide	2.5
Methane	0.5
Water	1
Hydrogen	2
TOTAL	100.0
Solids (56% of total components)	
Potassium carbonate	61
Potassium sulfate	15
Potassium sulfide	14.3
Potassium thiocyanate	0.2
Potassium nitrate	0.3
Ammonium carbonate	0.1
Sulfur	9
Carbon	0.1
TOTAL	100.0

Adapted with permission from Lindner V. Explosives and propellants. In: Kirk RE, Othmer PF, eds. *Encyclopedia of Chemical Technology*. Vol 9, 3rd ed. New York: John Wiley; 1980: 660.

weapons systems.³ As a result, propellant combustion products were evaluated more thoroughly. Other inorganic emissions (hydrogen fluoride, hydrogen sulfide, cyanide, and sulfur dioxide) have been described and a large number of volatile organic combustion products have been studied qualitatively and quantitatively.^{9,23}

After they complete an artillery firing mission in the field, soldiers routinely burn any unused propellant. Large quantities of propellant and propellant-containing munitions have also been disposed of through a controlled process termed “open burning and open detonation.”²⁶ The emissions produced by open burning and open detonation have been extensively studied, and current results indicate that combustion products of tested propellants have been far lower than the levels specified by the U.S. Environmental Protection Agency (EPA).²⁷

Soot deposits generated from burning double-base propellants in laboratory ballistic ranges have demonstrated mutagenic activity as tested by the Ames *Salmonella* assay (see Chapter 9, Explosives and Propellants, and Chapter 14, Pesticides, for further discussion of mutagenic activity and the Ames assay).¹⁶ Because mutagenic activity had been detected under laboratory conditions (using a gun specifically designed for laboratory use) in an enclosed, indoor environment, field tests (using operational weapons fired in the outside environment) were conducted at Picatinny Arsenal, New Jersey. These tests, now completed, were designed to determine if the mutagenic activity occurs in operational settings and, if so, what dangers, if any, are posed to soldiers. Preliminary assessment of the data indicates no mutagenic activity associated with the 155-mm, 5.56-mm, or 9-mm weapons systems evaluated. However, data from other tests indicate that further study is required to evaluate the potential health risks from exposure to combustion products that are formed during both the firing of other, small-caliber weapons systems and the burning of unused propellant bags after the artillery-firing missions have been completed.

This discussion has pertained to propellant combustion products that are generated during the firing of small-, medium-, and large-caliber weapons. However, combustion products are also formed and released when stored ammunition burns as a consequence of battle damage or training accidents. The modernization of weapons that occurred during the 1980s was accompanied by an effort to evaluate vehicle vulnerability and survivability and soldier survivability on the battlefield. One area identified for critical evaluation was the ammunition storage com-

TABLE 10-8
MAXIMUM RECOMMENDED EMERGENCY
EXPOSURES FOR NITROGEN DIOXIDE

Time Limit (min)	Concentration (ppm)
30	10
10	25
05	50

Source: Davis DL, Executive Director, Board on Toxicology and Environmental Health Hazards, National Research Council Commission on Life Sciences, to Ranadive M. The Pentagon, Washington, DC. Written communication; 14 March 1985.

partment (bustle) in the M1A1 tank. The major objectives of this evaluation were to

- ensure that the bustle was properly placed, to reduce its vulnerability;
- ensure that the bustle doors and seals provided adequate protection for the crew in case of fire; and
- design the bustle and crew compartment so that the crew would have time to escape from the tank if an explosion occurred.

The OTSG identified carbon monoxide and oxides of nitrogen as the toxic gases of primary concern, and asked the Committee on Toxicology of the National Research Council to provide assistance. The committee used NO₂ as a surrogate for NO_x in their discussions and proposed maximum recommended emergency exposure guidance levels (EEGLs) (Table 10-8).²⁸

Rocket Propellants

The rocket propellant combustion product that has been of greatest concern for potential adverse health effects is hydrogen chloride (see Tables 10-4 and 10-6). Hydrogen chloride is released in significant quantities when propellants that include chlorine-containing compounds (such as ammonium perchlorate) are burned. In some cases, enormous quantities of hydrogen chloride are produced. For example, it has been estimated that 17 tons of the gas are released in the vicinity of a space-shuttle launch pad during a shuttle launch (Figure 10-9).²⁹ The amount of hydrogen chloride that soldiers or others could be exposed to depends not only on the amount generated in a given time but also on other variables including rocket speed, atmospheric conditions, and physical barriers



Fig. 10-9. The space shuttle Atlantis is shown being launched from the Kennedy Space Center, Florida, at 9:56 a.m. (EDT) on 31 July 1992. The large quantity of white smoke surrounding Launch Complex 39 is hydrogen chloride that was produced during combustion of the shuttle's perchlorate-based, solid rocket propellant. Photograph: Courtesy of National Aeronautics and Space Administration, Houston, Tex. 31 July 1991. Photograph STS046-(S)-082.

that will contain the gas. For example, a soldier firing a shoulder-held rocket with a perchlorate-based propellant in a stagnant airspace will be at greater risk than a soldier firing the same weapon in an open field.

In most cases, concern about the production of hydrogen chloride from military weapon systems will be confined to exposing young, generally healthy soldiers in the immediate vicinity of the rocket firing. However, this is not always the case. When large quantities of perchlorate-based propellant are fired within a relatively short time, weather conditions may carry the gas far beyond the firing area (or the military installation boundaries). These quantities and concentrations may not be a matter of concern for healthy, young soldiers. However, they could be a threat to certain civilians such as infants, children, the elderly, and those with cardiopulmonary or other diseases.

This situation occurred in the United States in 1988. The Intermediate-Range Nuclear Forces Treaty between the former USSR and the United States required that large Pershing missiles, which contained perchlorate-based solid propellants, be destroyed. The rocket motors were destroyed on the ground, by firing them while they were bolted to the ground horizontally. To protect those at risk off the military installation, prospective studies were conducted to determine the hydrogen chloride concentrations leaving the installation under defined firing conditions. Additionally, the Committee on Toxicology of the National Academy of Sciences (NAS) reviewed the data collected, procedures to be used, and exposure criteria. Specific restrictions were developed and followed during firing, and included permissible atmospheric conditions, times of firing, and frequency of firing.³⁰

CONTAMINANTS FROM AMMUNITION

Lead or tin foil is placed in the propelling charge of some artillery ammunition to protect the gun barrel from accumulations of copper. When these decoppering ammunition rounds are fired, metallic lead or tin may be measured in the breathing zones of crew members.³¹ Other elements included in shell casings, bullets, and projectiles can also vaporize or shear during firing and contaminate the breathing zones of soldiers

or civilians working in the firing area. The potential for lead exposure has long been recognized as a significant risk to those who fire lead bullets in poorly ventilated areas (see Chapter 12, Lead). Bullets may also have a copper jacket, although the jackets are sometimes made of steel.³² The full metal jacket that is required of all military bullets is something of a misnomer: the jacket on small-arms ammunition made in

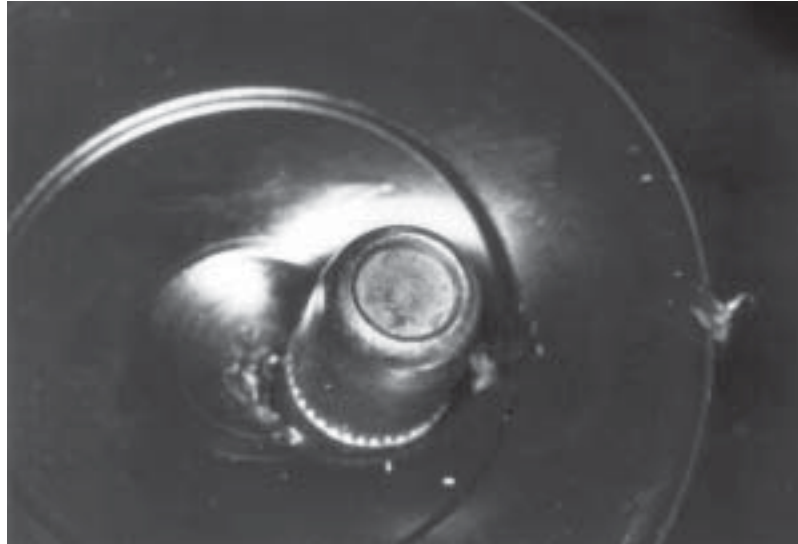


Fig. 10-10. The copper jacket does not completely surround this 5.56-mm bullet, the type fired by the M16 rifle; a portion of the lead core is exposed at the base. This exposed lead is subject to erosion from the hot gases that are produced during propellant combustion. However, this source of lead is minor; most of the lead in the environment surrounding the weapon comes from the combustion of the primer.

the United States does not cover the base of the bullet's lead core (Figure 10-10). Zinc bullets have been used and studied, and they have been recommended as a replacement for lead bullets to reduce lead exposure.³³

The only two components of bullets or projectiles that have raised concern about their potential for causing adverse health effects are lead and DU.¹⁷ DU, which is a mixture of ²³⁴U (0.0005%), ²³⁵U (0.2500%), and ²³⁸U (99.7500%), is a byproduct of the uranium-enrichment process and is of no use to the nuclear industry as a fuel for nuclear reactors. However, its high density and strength, ease and relatively low cost of fabrication, and availability make it desirable for use as the penetrator in antitank shells (the part of the projectile designed to actually penetrate the armor). DU emits alpha, beta, and gamma radiation, and may be contained in armor-piercing rounds of calibers 25 mm, 105 mm, 120 mm, and possibly other U.S. Army ammunition.^{17,34}

Studies to detect the presence of DU and related compounds have been conducted (a) at the barrel muzzle and the weapon breach during firing; (b) in gun barrels, after DU rounds have been fired; and (c) inside the crew compartment of an armored vehicle that has been hit by a DU round. (Soldiers inside the spall zone of the penetrating round will be killed. If

the ammunition or fuel cells do not explode, soldiers outside the spall zone will receive injuries to the tympanic membrane and ossicles, but will not be killed outright by the hit.) Detailed data from these studies are not available for public release. However, preliminary general information indicates that exposures are well below federal standards for soldiers conducting their military missions. This is not an unexpected finding, as DU-containing penetrators are completely enclosed within the round, and are not exposed at the muzzle or breach. Current assessments indicate that vehicle ventilation systems and personal protective equipment (PPE) available to soldiers will provide adequate protection in unusual situations where DU levels may exceed exposure standards.³⁴ However, DU could accumulate in and around vehicles that are used frequently as targets.

Release of DU into the environment can also occur if vehicles that are carrying DU-containing ammunition catch fire. These and all other incidents involving DU ammunition must promptly be reported to ensure that the correct emergency response, rapid and proper evaluation of any radiation hazard, and appropriate cleanup of any contamination occur. Procedures to be followed in these situations are outlined in a Department of the Army Technical Bulletin (DA TB).¹⁷

Penetrators and other material (DU metal, oxides, and other DU compounds or mixtures) from DU rounds fired during testing and training can accumulate in the ground. Assessment of the risk to health and

the environment from these situations and surveillance, if indicated, fall within the area of expertise of AMEDD health physicists and environmental health engineers.³⁴

IDENTIFICATION OF HAZARDS

Risk assessors seek to prevent injury arising from the use of propellants and ammunition. Their assessments are predicated on defining (a) the hazardous components of the combustion products, (b) the extent of soldier exposure to these hazardous products, and (c) the controls available to reduce harmful exposure. Identifying whether the components of combustion products are hazardous can best be facilitated by actual reports of adverse health effects. However, as discussed earlier, relatively few accounts in the literature describe the actual adverse health effects from exposure to propellant combustion products in the United States military.^{3,4,35}

In the absence of such data, the risks to soldiers can only be assessed by toxicological evaluation of the mixtures, or by assessing the risk based on knowledge of the individual components and combustion products of the mixtures. Obviously, the variability of the propellants' chemical composition and differences in firing conditions combine and cause differences in the types and quantities of combustion products formed—and thereby result in different risks to exposed soldiers.

Conditions of Exposure

The degree to which soldiers will be exposed depends on the amount and types of combustion products formed, the *dispersion volume* (the area contaminated by combustion products; for example, the inside of a tank or the vicinity of a rocket launching), and the relationship of the dispersion volume to the soldier's immediate environment. The amounts and types of combustion products formed depend on the chemical constitution of the propellant; the amount that is burned per firing (eg, rifle bullets contain only a few grams of propellant, whereas the propellant charge for howitzer rounds may be several kilograms); and other physical and chemical variables. High rates of weapons fire will produce higher concentrations of combustion products. These concentrations become hazardous when retained within the soldier's ambient environment, such as when guns or rockets are fired from enclosed bunkers, crew compartments, or rooms in buildings.

The conditions of exposure also depend on the measures initiated to limit the concentrations of combustion products, including ventilating enclosed

spaces and wearing respiratory protective equipment. Administrative controls to limit the duration of exposure, which are incorporated into operational safety procedures, are also very important and are discussed at the end of this chapter.

In general, combat and many training scenarios are characterized by brief periods of high-intensity fire; thus, exposures are likely to be high in concentration, but of limited duration. Carbon monoxide, for example, has been measured in excess of 6,000 ppm in crew spaces under rapid tank-firing conditions, but this concentration decays rapidly (Figure 10-11).⁴ The tank's vehicular ventilation system produces the rapid decay, returning carbon monoxide to concentrations at which the crew can continue to function without adverse effects on health or performance.⁴ The breech scavenging system prevents gases from entering the crew compartment, but once gases are in the crew compartment, the vehicle ventilation system must exhaust the compartment.

Industrial workers may be exposed to much lower, but often increasing and cumulative, carbon monoxide exposures over a workday. The Occupational Safety and Health Administration (OSHA) has established a permissible exposure level (PEL) of 50 ppm for carbon monoxide. At an end-of-shift exposure of 50 to 100 ppm, symptoms of headache, giddiness, and tinnitus could occur among the workers. A worker exposed to persisting carbon monoxide concentrations of 6,000 ppm would quickly become affected to the point of developing unconsciousness and coma, and could die if not removed from exposure.³⁶

Assessing Toxic Hazards

Before weapons enter full-scale production, the army requires that all systems being developed or undergoing major revision be evaluated for their potential deleterious effects on the health of the crew; this is known as the Health Hazard Assessment process (HHA) and is the subject of Chapter 6.³⁷ As part of this evaluation, the army has developed standardized testing procedures to determine potential toxic hazards of vehicles and other equipment.³⁸ Weapons mounted inside vehicles or on other weapons platforms are tested during sustained rates of fire and under various op-

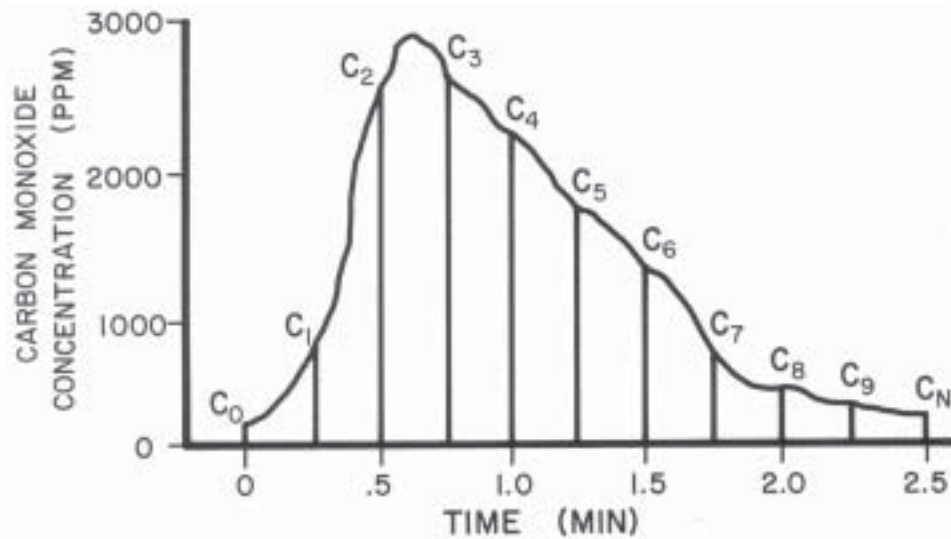


Fig. 10-11. This graphic example, based on actual measurements, shows typical carbon monoxide (CO) concentrations (in ppm) inside the crew compartment of an armored vehicle during a firing mission and the opening of the gun breech. Eleven air samples (C₀ through C_N) were obtained at 15-second intervals and analyzed for CO; the data were extrapolated to an expected, continuous concentration curve. The area under the curve may be represented by a definite integral and illustrates the total concentration of CO exposure for a given period of time. Increasing the number of measurement points improves the degree of accuracy in calculating the area. In this example, the firing and environmental conditions resulted in an estimated maximum CO concentration of almost 3,000 ppm at approximately 40 seconds after firing commenced. The ventilation system of the vehicle compartment, and perhaps a breech gas scavenging system, returned the CO concentration to near baseline level in about 2.5 minutes. This example also illustrates high baseline CO levels, exceeding 100 ppm, in the vehicle crew space. During actual field-firing situations, it is not unusual to find several armored vehicles in close proximity with their engines running, executing multiple firing missions. Therefore, high baseline levels may be obtained due to unexhausted CO from an earlier firing mission or CO from a gun muzzle or engine exhaust that has entered the vehicle being studied through an opened hatch or vent. In 1983, CO levels were monitored inside the crew shelters of a battery of M109, 155-mm self-propelled howitzers at Fort Sill, Okla. Firing was conducted with the hatches open; the environmental conditions, especially wind direction and speed, concentrated exhaust products around one particular vehicle in which the carboxyhemoglobin levels in the crew were higher than in crew members of the other vehicles. Sources: (1) Dalton BA, Deeter DP, Gaydos JC. Unpublished data from a field study performed at Fort Sill, Okla, 23–26 April 1983, by the Occupational Medicine Division, USAEHA. (2) US Army Combat Systems Test Activity. *US Army Test and Evaluation Command Test Operations Procedure: Toxic Hazards for Vehicles and Other Equipment*. Aberdeen Proving Ground, Md: DA; 1984. Report TOP 2-2-614. (3) Lucas TA. *Methodology Investigation of Toxic Gas Measurements During Weapons Firings from Vehicles While Moving: Final Report*. Aberdeen Proving Ground, Md: US Army Test & Evaluation Command. TECOM Project 7-C0-PB9-AP1-002; 1984. Report APG-MT-5896. (4) Dalton BA. Carbon monoxide in US Army tactical vehicles. *Medical Bulletin of the US Army Medical Department*. 1988;2:11–13. PB 8-88.

erational conditions, such as with their engines; ventilating systems; heaters; and nuclear, biological, and chemical (NBC) protection systems turned on and off.³⁸ The testing measures all sources of combustion products in the weapons system, including the weapon's propellant and the vehicle's fuel (combustion products of fuel could enter the crew compartment as exhaust gases). Vehicle crew compartments are sampled for carbon monoxide, ammonia, sulfur dioxide, nitric oxide, nitrogen dioxide, methane, hydrogen chloride, lead, and short-chain hydrocarbons such as acetylene or acetaldehyde. (Sampling decisions are based on the compo-

sition and conditions of combustion of the propellants and vehicle fuel, and depend on whether these chemicals are expected to occur.)

Studies That Predict Toxic Exposures

Relatively few studies have either assayed the actual propellant combustion products that form during firing in the field or assessed the risks experienced by soldiers. Within certain limitations, field studies can demonstrate the major toxic species in complex mixtures of combustion products. Field conditions

such as temperature, humidity, the maintenance of the weapons, and the chemical composition of the propellants that are employed all influence the mixture of combustion products. Instruments that are sophisticated enough to identify minor or trace species in these mixtures are not practicable in the field because they are too large, will easily be damaged under field conditions, or both.⁹

One study has highlighted the difficulties in sampling for combustion products in the crew compartment of the XM2 (the prototype for the Bradley Fighting Vehicle [BFV]) and the M198 howitzer.²⁴ Special portable collection equipment was designed to render reliable results given the time between field sampling and laboratory analysis. The sampling equipment failed during the XM2 field analysis, and accurate assessments of ammonia concentrations could not be made. Nevertheless, field analysis was able to demonstrate the major species produced following weapons firing (hydrogen, carbon monoxide, carbon dioxide, and methane) and the reduction of these concentrations after the vehicles' ventilation systems were activated (Table 10-9).

Due to the difficulties in field sampling, laboratory analysis of propellant firing has been conducted in laboratory-vented test fixtures such as those shown in Figure 10-8. These fixtures—specially designed chambers that allow weapons firing and sampling of combustion products—have permitted over 100 chemical species to be identified from the combustion of WC844 propellant, which is used in M16 ammunition, and

over 60 chemical species from XXX, which is the name of the propellant used in the MLRS motor.

In an attempt to characterize the concentrations of major combustion products from successive rocket-motor firings in urban terrain (eg, if shoulder-held rocket systems were fired from an enclosed room), a test facility was constructed circa 1973 at the U.S. Army Missile Laboratory at Redstone Arsenal, Huntsville, Alabama.³⁹ Tests performed at this facility clearly demonstrated that weapons crews could be exposed to carbon monoxide, lead, and nuisance particles in excess of the short-term exposure limits (STELs) established by the American Conference of Governmental Industrial Hygienists (ACGIH)⁴⁰ and OSHA.⁴¹

Several computer models are available to predict combustion products. These computer programs, developed by American Cyanamid Corporation, Wayne, New Jersey; Stanford Research Institute, Menlo Park, California; and the National Aeronautics and Space Administration, Washington, D. C., are under continual modification. While the primary purpose of these programs is to solve ballistic problems, they can also produce estimates of contamination from combustion products. The programs are used to complement chemical analyses or to alert chemists to species that must be looked for. The predictions have been compared to actual field and laboratory sampling of the exhausts of various propellants; the concentrations of the predicted major chemical species agree fairly well with those that are actually measured through laboratory firing. However, there is poor agreement for the minor and trace (especially organic) species produced because the computers are coded to produce results at thermodynamic equilibrium conditions and do not consider nonequilibrium processes such as incomplete combustion or condensation (soot-formation) processes.^{9,19} Continued research through field studies, laboratory simulations, and computer predictive modeling is necessary to generate the information needed to assess and reduce the risk to soldiers from propellant combustion products.

Toxicological Assessment of Combustion Products

Sophisticated chemical analyses have been developed for laboratory use that can identify hundreds of compounds found in weapons exhaust and analyze them for their toxicity. In most cases, the immediately toxic properties of the exhaust are determined by the predominant species in the mixture. Predictions of toxicological risks of exposure to the combustion products of propellants are made by comparing the measured concentrations of these individual components to the established health-based standards. The NAS

TABLE 10-9

ANALYSIS OF GAS SAMPLES WITHIN THE CREW COMPARTMENT OF THE XM2 AFTER WEAPONS FIRING

Compound*	Concentrations (ppm)	
	Pre-Active Vehicle Ventilation System	Post-Active Vehicle Ventilation System
H ₂	312 ± 2	39.9 ± 1.2
CO	942 ± 59	< 50
CO ₂	995 ± 26	313 ± 5
CH ₄	11.40 ± 0.25	3.41 ± 0.42

* Equipment failure prevented measurement of NH₃
Adapted from: Snelson A, Ase P, Bock W, Butler R. *Characterization of Combustion Products from Military Propellants*. Fort Detrick, Frederick, Md: US Army Medical Bioengineering Research and Development Laboratory; 1983. IIT Research Institute, Contract DAMD 17-80-C-0019.

EXHIBIT 10-1**EXPOSURE ASSESSMENTS**

Using the primer, igniter, and propellant compounds described in Exhibit Table 1, laboratory studies were done to qualitatively and quantitatively assess the combustion products generated during the firing of the M16 rifle and the 105-mm tank gun. Exhibit Table 2 lists the weight of selected combustion products per gram of propellant burned.

Let us say, as examples, that AMEDD personnel were asked to assess the following situations for their health risks:

- Firing 200 rounds/min of M16 ammunition over a period of 15 min in 100 m³ of air space
- Firing 4 rounds/min of 105-mm tank gun ammunition over a period of 15 min in 100 m³ of air space

These two situations are similar to many that are regularly presented to AMEDD health-risk assessors. These situations occur during the (a) design and testing of new or modified vehicles, guns and ammunition; (b) development of new training exercises; or (c) development or revision of test-firing laboratories where guns, gun parts, and/or ammunition are routinely tested. The standards or guidelines used in the evaluations may come from the Occupational Safety and Health Administration (OSHA), the American Council of Government Industrial Hygienists (ACGIH), the National Institute for Occupational Safety and Health (NIOSH), the Committee on Toxicology of the National Academy of Sciences, or may be developed by the U.S. Army Medical Department (AMEDD). In this example, let us say that AMEDD assessors, by agreement, will use the ACGIH's Threshold Limit Values (TLVs) as guidelines. The specific compounds of interest for the M16 will be limited in this example to carbon monoxide (CO) and hydrogen cyanide (HCN); for the 105-mm gun these will be CO and benzene (C₆H₆). However, assessments can be done for any emission product for which data or information is available.

The givens are (a) the propellant weights, (b) the number of rounds fired per minute, and (c) the number of minutes during which firing will occur. Therefore, using simple multiplication, the propellant mass required to generate combustion products can be calculated:

For the M16 Rifle:

Weight of Propellant: 1.65 g/cartridge (round)
Rounds per min: 200
Duration of fire: 15 min
Total mass of propellant burned: 4.95 kg

The total amounts of CO and HCN produced can be obtained by multiplying the total propellant burned times the amounts of CO and HCN produced per unit weight of propellant:

For CO:

3.37×10^{-1} g of CO are produced per g of propellant burned.
Therefore, 3.37×10^{-1} g \times 4.95 kg = 1.668×10^3 g of CO are produced.

For HCN:

8×10^{-4} g of HCN are produced per g of propellant burned.
Therefore, 8×10^{-4} g \times 4.95 kg = 3.96 g of HCN are produced.

Assuming that the shots are fired in a space of 100 m³ with no air dilution over the 15-min period, the amounts of CO and HCN produced by the M16 firings will accumulate. The accumulated values are first divided by 100 m³, then compared to the appropriate TLVs; these are found to greatly exceed the TLV values:

For CO: (TLV = 57 mg/m³)

$16.68 \text{ g/m}^3 = 292.6$ -fold greater than the TLV

For HCN: (TLV = 11 mg/m³)

$39.6 \text{ mg/m}^3 = 3.6$ -fold greater than the TLV

For the 105-mm Gun:

Weight of Propellant: 5.44 kg/shell (round)
Rounds per min: 4
Duration of fire: 15 min
Total mass of propellant burned: 326.4 kg

The amounts of CO and C₆H₆ formed when the 105-mm gun is fired are computed and compared to the appropriate TLVs:

For CO:

2.4×10^{-1} g of CO generated per g of propellant burned.
Therefore, 2.4×10^{-1} g \times 326.4 kg = 78.34×10^3 g of CO are produced.

For C₆H₆:

9.2×10^{-5} g of C₆H₆ are generated per g of propellant burned.
Therefore, 9.2×10^{-5} g \times 326.4 kg = 30.03 g of C₆H₆.
Again, the TLVs are exceeded (assuming an undiluted air space of 100 m³).

For CO: (TLV = 57 mg/m³)

$783 \text{ g/m}^3 = 13,737$ -fold greater than the TLV

For C₆H₆: (TLV = 32 mg/m³)

$300 \text{ mg/m}^3 = 9.4$ -fold greater than the TLV

Exhibit 10-1 (continued)

EXHIBIT TABLE 1
COMPOSITION OF ENERGETIC MATERIALS FOR TWO WEAPONS

M16 Rifle (Propellant in 5.56-mm Ammunition)				105-mm Caliber Gun			
Olin WC 844 Propellant (1.65 g)		Primer (0.032 g)		Propellant (5.44 kg)		M-83 Igniter (32 g)	
Component	Weight (%)	Component	Weight (%)	Component	Weight (%)	Component	Weight (%)
Nitrogen in nitrocellulose	13.05–13.20	Lead styphnate	35 ± 5	Nitrocellulose	28.55	Nitrocellulose	60.0
Graphite	0.4	Tetrazene	4 ± 1	Nitrogen in nitrocellulose	12.6	Unmixed black powder*	40.0
Sodium sulfate	0.5	Barium nitrate	32 ± 5	Nitroglycerin	22.23		
Calcium carbonate	0.2	Antimony sulfide	15 ± 2	Nitroguanidine	47.00		
Nitroglycerin	8.0–11.0	Aluminum powder	7 ± 1	Cryolite	0.31		
Diphenylamine	0.75–1.50	PETN	5 ± 1	Ethyl centralite	1.54		
Dibutylphthalate	3.0–6.0	Organic binder	small	Ethanol	0.24		
Total volatiles	< 2.0			Carbon	0.13		
Nitrocellulose	balance						

*The specific composition of the unmixed black powder was not defined. Black powder compositions typically lie in the following ranges: charcoal, 14%–18%; sulfur 10%–16%; and potassium or sodium nitrate, 10%–74%. The composition and amount of primer was not given. The primer mass would probably be < 0.1 g and would have a negligible impact on the overall combustion production generation.

Sources: (1) Ase P, Eisenberg W, Gordon S, Taylor K, and Snelson A. Propellant combustion product analyses on an M16 rifle and 105-mm caliber gun. *J Environ Sci Health*. 1985;A20(3):337–368. (2) Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1.

EXHIBIT TABLE 2
GASES DETECTED AND QUANTIFIED IN COMBUSTION PRODUCTS OF TWO WEAPONS

Number of Experiments	Compound	M16 Rifle		105-mm Caliber Gun	
		Mean*	± SD†	Mean*	± SD†
5	Carbon monoxide	3.37 × 10 ⁻¹	5	2.4 × 10 ⁻¹	11
7	Hydrogen cyanide	8.00 × 10 ⁻⁴	52	—‡	—‡
6	Benzene	1.74 × 10 ⁻⁴	18	9.2 × 10 ⁻⁵	41
6	Acrylonitrile	2.36 × 10 ⁻⁵	57	8.5 × 10 ⁻⁶	59
6	Toluene	1.82 × 10 ⁻⁵	9	2.2 × 10 ⁻⁵	28
6	Cyanobenzene	9.91 × 10 ⁻⁶	26	0–3.1 × 10 ⁻⁶ §	—‡
6	Crotonitrile	1.43 × 10 ⁻⁶	24	0–1.3 × 10 ⁻⁴ §	—‡
6	Furan	1.10 × 10 ⁻⁶	90	0–4.6 × 10 ⁻⁷ §	—‡
6	Dimethylnitrosamine	8.5 × 10 ⁻⁷	39	0–3.0 × 10 ⁻⁷ §	—‡
6	Methacrylonitrile	7.6 × 10 ⁻⁷	38	0–1.4 × 10 ⁻⁶ §	—‡
6	Quinoline	5.1 × 10 ⁻⁷	50	0–1.4 × 10 ⁻⁷ §	—‡
6	Nitrobenzene	4.5 × 10 ⁻⁷	44	0–2.3 × 10 ⁻⁸ §	—‡
6	2-Furfural	3.5 × 10 ⁻⁷	52	0	—‡
6	Carbon disulfide	1.8 × 10 ⁻⁷	56	5.2 × 10 ⁻⁶	69
6	Hexane	1.7 × 10 ⁻⁷	60	5.5 × 10 ⁻⁷	50
6	Indane	3.0 × 10 ⁻⁸	73	1.1 × 10 ⁻⁷	69

*Grams of compound per gram of propellant burned

†SD is given as the percentage of the mean

‡No attempt to measure

§Where a range of values is indicated rather than the percent standard deviation of the mean, the range covers minimum and maximum values measured

Source: Ase P, Eisenberg W, Gordon S, Taylor K, and Snelson A. Propellant combustion product analyses on an M16 rifle and 105-mm caliber gun. *J Environ Sci Health*. 1985;A20(3):337–368.

has established standards—applicable to short, intensive periods of weapons firing—in the form of STELs that are especially relevant to the U.S. Army.⁴²

The effects of each combustion product on different target organs determine the total potency of chemical mixtures. Interactions between these effects can be additive, synergistic, or antagonistic, and can produce acute and chronic medical problems. For example, in animal testing, carbon dioxide may have a protective effect in high concentrations in reducing carbon monoxide deaths (an antagonistic effect). Particulate matter may interact with sulfur dioxide to enhance bronchospasm over that expected from sulfur dioxide alone (a synergistic toxicological effect).⁴³

Currently, the military's primary emphasis is on the identification of the major chemical species produced so that the acute effects on a soldier's performance in combat can be predicted. The level of exposure to these major species can be used to produce an assessment of risk with regard to incapacitation, morbidity, and mortality. The emphasis on immediate performance is necessary to ensure that soldiers can effectively perform their tasks and accomplish their missions; but exposure to minor or trace amounts of combustion products is also important and could serve as a risk factor for delayed health effects such as toxic effects on the reproductive system, the produc-

tion of chronic disease, or carcinogenesis.

Risk assessments of combustion products should be and, eventually, will be based on the total mixture.⁴³ Nevertheless, until methods are established, validated, and standardized to toxicologically evaluate all propellant combustion products simultaneously, the current method of basing risk assessment on the major species produced will have to suffice.

An example of the types of calculations a risk-assessor might use in assessing health risks to soldiers is shown in Exhibit 10-1, in which the known weight of the propellant is integrated with data obtained from test firings of the M16 rifle and the 105-mm caliber gun. Often, the calculation of an exposure at any given time, or over an interval, is complicated by the episodic nature of weapons fire and by the dilution of the soldier's ambient air with clean air. In situations like these, it will probably be necessary to (a) plot the concentrations of the toxic chemical over the interval of interest and (b) determine the exposure over the entire time through a process of integration (define the area under the curve). Consultation with toxicological experts may be required when attempting to estimate the combined effect of multiple toxic chemicals. Such consultation has been obtained in the past from the Committee on Toxicology of the NAS⁴⁴ and the Armed Forces Epidemiological Board (AFEB).⁴⁵

HEALTH EFFECTS OF EXPOSURE TO AIRBORNE PRODUCTS OF PROPELLANT COMBUSTION

Properly assessing the potential for adverse health effects associated with the operation of military weapons systems is often difficult or impossible because exposure data from operational settings are lacking. There is a pressing need for expanded, systematic study of field exposures to develop precise guidelines for both preventing adverse health effects and managing casualties of overexposures.

To diagnose and treat victims of overexposure in a timely fashion, field medical personnel should be alert for any medical sequelae arising in soldiers who may have been exposed to the products of propellant combustion. What may initially appear to be coincidental headaches or routine acute respiratory diseases in soldiers must take on new importance should an occupational history reveal problems with the ventilation system of the soldier's vehicle, that the soldier has been firing a new type of ammunition, or that the soldier has participated in missions with prolonged firing times. Reports of suspected health effects arising from exposure to combustion products are needed; these should be forwarded through medical command channels so that proper evaluations of the events can be made.^{6,7}

As previously noted, exposure to the combustion products of propellants includes coming in contact with gases and particulate matter. The greatest hazard to soldiers is from the inhalation of these substances. In turn, the health effects that develop depend on whether and where deposition in the respiratory tract occurs. Deposition could result in direct damage to tissue or absorption of the material, which could result in a systemic health effect.

The major combustion products of most propellants are classified as (a) tissue asphyxiants (carbon monoxide, nitric oxide, and minor amounts of hydrogen cyanide), (b) irritant gases (ammonia, nitrogen dioxide, sulfur dioxide, nitric oxide, and hydrogen chloride), or (c) inhalable metal particulates (lead, copper, and others).

Tissue Asphyxiants

Because asphyxiants can quickly produce incapacitating central nervous system effects without warning signs, these compounds are of major immediate concern to the army. Asphyxiants act to interfere with the

delivery of oxygen to tissue cells or with the ability of the cell to use oxygen. Carbon monoxide and nitrites decrease hemoglobin's oxygen-carrying capacity. Carbon monoxide is a competitive inhibitor of the ferrous binding sites for oxygen in the hemoglobin molecule. Because carbon monoxide has a higher affinity for hemoglobin than does oxygen, the amount of oxygen available for transport to organs is reduced. Nitrites and nitric oxide also decrease the oxygen-carrying capacity of blood through the production of methemoglobin, which is less efficient than hemoglobin in releasing oxygen to the tissues. Hydrogen cyanide, which is produced by nitramine propellants such as RDX, acts to produce cellular asphyxia by interfering with the cells' cytochrome oxidase system, which disrupts oxidative metabolism.

Irritant Gases

When inhaled, the acute effects of irritant gases on the respiratory tract (eg, pulmonary edema, bronchoconstriction, and bronchorrhea) can cause an immediate decrement in a soldier's performance. Delayed effects include reactive airways dysfunction syndrome (RADS) and airway cellular destruction.⁴⁶

RADS is characterized by continuing airway hyperresponsiveness, typically after an acute, high-level exposure to an irritant. This airway hyperresponsiveness is usually detected by physiological measurement of expiratory airflow or an increase in airway resistance after the administration of histamine or methacholine by inhalation. Although many such individuals will remain asymptomatic, some may develop overt asthmatic symptoms, often after exposure to other irritants or cold air. Airway hyperresponsiveness may persist for months or years. Case reports of RADS after exposures to chlorine, hydrochloric acid, sulfur dioxide, and ammonia have been described. The long-term health consequences of this condition are unknown. Healthcare personnel attending soldiers who may have been exposed to these irritants, especially if acute pulmonary conditions resulted, should remain cognizant of the potential late development of asthmatic symptoms and the implications of continuing exposure to irritant agents.⁴⁷

The absorption of gases depends mainly on their solubility in the aqueous layer lining the mucosa in the upper and lower respiratory tracts. For example, both sulfur dioxide and ammonia are highly soluble and are normally absorbed in the upper airways; they are rarely deposited in the lower tract unless exposure to these gases has been overwhelming. On the other hand, gases like nitrogen dioxide are less soluble; they can bypass the upper airways and injure the lower

airways. Because these relatively insoluble gases may not irritate the upper airway, they do not produce warning symptoms. However, in conditions of high humidity or moist mucous membranes, nitrogen dioxide may dissolve and form nitric and nitrous acids, which can irritate the upper passages. Additionally, certain cells in the airway may be more susceptible to these gases. An example is the Type I pneumocyte, found in the alveoli, which is thought to be particularly susceptible to damage because of its high surface area-to-volume ratio.

Particles, either solid or liquid, are deposited in the airway depending on their size. Particles greater than 10 μ are filtered out in the upper respiratory tract. Particles less than 0.5 μ are rapidly exhaled. Particles between 0.5 μ and 3.0 μ are deposited efficiently in distal airspaces, either through impact against the bronchiolar walls or through gravitational settling.⁴⁸

Short-duration, high-intensity exposures to combustion products can lead to both immediate and delayed health problems. A fire in 1929 at the Cleveland Clinic in Cleveland, Ohio, burned 50,000 nitrocellulose films (then used for X-ray films, but now used in military propellants). The combustion of nitrocellulose liberated carbon monoxide, nitrogen oxides, and hydrogen cyanide. Ninety-seven people died immediately, probably due to asphyxiation from carbon monoxide and hydrogen cyanide. Two hours to 1 month after the fire, 26 more people died from pulmonary complications that were suspected to have been caused by exposure to nitrogen oxides.⁴⁹

Ammonia

Ammonia is formed from the combustion of propellant compounds that contain nitrogen, especially those that contain nitroguanidine. All single-, double-, and triple-base propellants can produce ammonia. The nitrogen is converted first to molecular nitrogen during combustion, but it then quickly combines with hydrogen gas to form ammonia. Iron particles originating from heat-induced erosion of the gun tube catalyze this reaction.⁹

Due to its high solubility in water, ammonia is an upper respiratory tract, eye, and skin irritant (Table 10-10). Its *odor threshold* (ie, the lowest concentration of a substance at which its odor can be detected by humans) is below concentrations at which the eyes, nose, and throat become irritated. Once the eyes have been irritated by exposure to ammonia, lacrimation occurs. Lacrimation at ammonia concentrations of 134 to 150 ppm may be militarily significant when visual discrimination tasks are important. Acute, high-dose exposure causes coughing and severe irritation of the

TABLE 10-10
SIGNIFICANT, IMMEDIATE, REVERSIBLE
EFFECTS OF AMMONIA

NH ₃ (ppm)	Effects/Comments
1,000	Produces coughing
150–500	Produces changes in ventilation minute and tidal volumes and respiratory rate*
150	Produces lacrimation in subjects previously acclimated at 25–100 ppm for varying durations
140	Tolerated for 30 min by all unaccustomed subjects; for 2 h by highly motivated subjects
134	Produces lacrimation in 50% of unaccustomed subjects
110	Tolerated for 2 h by all unaccustomed subjects
100	EEGL†
50–72	Produces moderate eye, nose, and throat irritation in most subjects
20–30	Odor easily noticeable

* Tidal volume • respiratory rate = minute volume

† Emergency exposure guidance level

Source: Legters L, Morton JD, Nightengale TE, Normandy MJ. *Biological Effects of Short, High-Level Exposure to Gases: Ammonia, Carbon Monoxide, Sulfur Dioxide, and Nitrogen Oxides*. Rockville, Md: Enviro. Control, Inc. 1980. Final Summary Report AD A094505, DAMD 17-79-C9086.

throat. Early deaths can occur from laryngeal edema and severe airway obstruction. Patients who survive the initial exposure can develop tracheobronchitis, bronchoconstriction, and hypersecretion of mucus.⁴⁸ Tolerance to higher exposure levels may develop over time, and eye and upper respiratory tract irritation will lessen. For example, individuals exposed in an industrial setting to an average daily workday concentration of 100 ppm of ammonia have demonstrated a tolerance to irritation after 1 week of exposure.⁵⁰ Skin and mucous membranes are also sensitive to airborne ammonia. Due to ammonia's high solubility in water, it dissolves in the moisture of the eyes and skin,⁵¹ and due to its alkalinity, it damages tissue by producing caustic burns.

The NAS has recommended an EEGL for ammonia of 100 ppm.²⁹ This value is based on limiting lacrimation and its consequent performance decrement. EEGLs represent levels at which reversible health effects may occur, but before judgment becomes impaired and responses to emergencies are inappropriate. No reliable information is available concerning inhaled ammonia's potential as a developmental, reproductive genotoxic, or carcinogenic agent.

The signs and symptoms associated with ammonia exposure partially depend on its concentration. Most soldiers can tolerate exposure to levels exceeding 140 ppm for short durations, but not for hours. However, asthmatics and those individuals who develop bronchospasm after exposure to other respiratory-tract irritants may be more sensitive to lower concentrations, shorter durations of exposure, or both. Exposure to levels exceeding 5,000 ppm have caused death due to airway obstruction in normal individuals.⁵² Bronchiectasis has also been reported in previously nonasthmatic individuals after exposure to an ammonia cloud after a tank-car derailment.⁵³ Mild-to-moderate (50–100 ppm) exposure to ammonia can produce headache, burning of the throat, nausea, vomiting, and substernal pain.

The treatment recommended for exposure to ammonia consists of removing the casualty from the source of ammonia and flushing the eyes with water if severe irritation or lacrimation develops. Severely affected casualties who have visual difficulties (such as blurring of vision or difficulty focusing), laryngeal edema, signs of pulmonary compromise, or an abnormal chest film should be hospitalized and monitored.

Nitrogen Dioxide and Nitric Oxide

Nitric oxide and nitrogen dioxide often occur together. Nitric oxide and nitrogen gas are the first products formed from the combustion of nitrogen-containing compounds. At high concentrations (> 50 ppm), nitric oxide is rapidly converted to nitrogen dioxide in the presence of oxygen or ambient air. Both gases are considered to be pulmonary irritants, but nitrogen dioxide is generally considered to be the most toxic. Nitric oxide can cause methemoglobin formation, although its potential conversion to nitrogen dioxide should be considered the more important hazard for most exposures.^{54,55}

Workers are exposed to nitrogen dioxide during welding, electroplating, and metal cleaning; nitrogen dioxide is also a combustion product of jet-engine fuels and a byproduct of blasting operations.⁴⁸ On the battlefield, nitrogen dioxide is formed by the oxidation of nitric oxide during high-temperature combustion of nitrogen-based propellants. Nitrogen dioxide can also be converted to nitric acid, which can damage and potentially cause fibrosis of lung tissue by denaturing tissue proteins. Tank crews can be exposed to nitrogen dioxide while they fire weapons, or, as a result of secondary fires and explosions, if tank rounds are ignited and burned inside the vehicles after battle damage or following vehicle accidents associated with fires. Nitrogen dioxide is heavier than air, reddish

brown in color, and has a pungent odor. It thus accumulates in the bottoms of enclosed spaces.⁴⁸ (This type of accumulation has occurred in the bottoms of poorly ventilated silos that contain grasses or hay, causing farmers to be exposed to nitrogen dioxide. The pulmonary damage that occurs is known as Silo-filler's disease.)⁵⁶

During the World War I era, German naval personnel experienced problems with "nitrous fumes" filling gun turrets when the gun breech was opened.^{13,57} These nitrous fumes were probably a mixture of nitrogen dioxide and nitric oxide. For protection, naval gunners wore respirator masks. These probably contained soda-lime and activated coconut-shell charcoal. Despite wearing the masks, some of the gunners were alleged to have developed methemoglobinemia, and death occurred. The masks probably did not remove nitric oxide and may have increased the nitric oxide in the inspired air through reduction of nitrogen dioxide. As a result of these incidents, German scientists conducted creative laboratory studies to differentiate the toxic effects of nitric oxide and nitrogen dioxide.^{13,57-59} Studies of these two gases and their toxic effects in military settings have continued to the present in the U.S. Army.^{60,61}

Because nitrogen dioxide has limited solubility, it causes negligible irritation in the upper airway tract. Acute exposure may cause little effect on the mucous membranes of the eye or throat, and thus there is little immediate warning of exposure. Exposed persons can apparently continue to breathe concentrations of up to 50 ppm for several minutes without cough, throat irritation, or chest discomfort (Table 10-11). The onset of respiratory symptoms may be delayed for 3 to 30 hours, at which time cough, dyspnea, acute pulmonary edema, fever, and peripheral blood leukocytosis may develop.⁴⁸

Nitrogen dioxide reacts with lung tissue by oxidizing cellular lipids and inactivating surfactant. Type I pneumocytes lose their integrity and allow interstitial fluid to enter the alveoli. Type II pneumocytes are then activated, become hyperplastic, and may fill up the alveolar spaces, leaving no space for gas exchange to occur. Untreated pulmonary edema may progress to death.

Death from pulmonary edema can occur at nitrogen dioxide exposures of 150 ppm for less than 1 hour. Furthermore, even if the casualty apparently recovers from an acute exposure, he or she could present 2 to 3 weeks later with signs and symptoms of *bronchiolitis obliterans*. This condition is noted for its fibrotic destruction of the bronchioles, and its signs and symptoms include fever, cyanosis, and dyspnea.⁵² No specific X-ray findings are associated with this condition.⁴⁸

The deleterious respiratory changes induced by exposure to airborne nitrogen dioxide are partially dependent on its concentration. Mild, irreversible effects on lung function can be observed at exposures below 5.0 ppm. At 1.0 ppm, symptoms such as coughing, chest tightness, and laryngitis can appear, but these symptoms are reversible. Individuals with asthma or chronic bronchitis may experience mild, reversible symptoms at nitrogen dioxide levels of 0.5 ppm over a 2-hour period. This level is the odor threshold for nitrogen dioxide.⁵³

Little evidence is available to assess concentration-time exposure parameters in relation to observed health effects for nitrogen dioxide. The army uses OSHA PELs or recommendations of the ACGIH, whichever are more conservative. However, the standards set by OSHA and the ACGIH are more applicable to industrial settings. In militarily unique equipment, systems, and operations, special DA standards are devised.⁶ These may be based on guidance documents that the army has asked the AFEB or the NAS of the National Research Council (NRC) to draw up. If the

TABLE 10-11
TOXIC EFFECTS OF HUMAN EXPOSURE TO NITROGEN DIOXIDE

NO ₂ (ppm)	Exposure Time (min)	Effects/Comments
1,000	15	Immediate incapacitation; respiratory and eye injury followed by death
100	60	Immediate respiratory and eye injury with progressive respiratory injury and death
50	60	Immediate respiratory and eye irritation with possible sub-acute and chronic pulmonary lesions
25	60	Immediate respiratory irritation with chest pain
5	60	Acute reversible respiratory function effects
5	15	ACGIH's STEL
~1	60	Equivocal respiratory function effects and impaired dark adaptation of vision

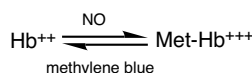
STEL: short-term exposure limit

Source: Davis DL, Executive Director, Board on Toxicology and Environmental Health Hazards, National Research Council Commission on Life Sciences, to Ranadive M. The Pentagon, Washington, DC. Written communication; 14 March 1985.

question is one of toxicology, the NAS Committee on Toxicology will consider the question or issue. If there are engineering implications, the multidisciplinary NRC may be asked to evaluate this situation. In 1985, at the army's request, the NAS Committee on Toxicology reviewed a situation involving tank-gun ammunition. The army recognized the need to develop blast-proof door seals on the bustle, to ensure that combustion products of burning propellants (a situation that could occur with battle damage) would not reach tank crews in significant concentrations. The NRC's committee studied the potential problem and recommended maximum exposure levels (see Table 10-8). These limits, which are essentially EEGLs and pertain to the ability to escape a contaminated environment, can be compared to those established by the ACGIH for civilian workplaces. The ACGIH standard is more conservative (their 15-min STEL is 5 ppm).⁴¹ In a military training situation, exposures should be kept as low as possible, but at a minimum should be below the ACGIH criteria. For emergency escape purposes, the NRC guidelines should be used to assess the efficacy of hazard-control systems. However, the NRC notes that sensitive individuals may experience mild wheezing and chest tightness on exposure to 0.5 ppm of nitrogen dioxide for 2 hours.²⁸

The treatment of casualties who are exposed to nitrogen dioxide consists of removing them from the offending source, keeping them at rest, and administering oxygen.⁵⁶ Because of the danger of pulmonary edema even in the absence of acute pulmonary irritation, close observation for 24 to 36 hours is also indicated after any significant exposure. Hospitalization is necessary for any person who has symptoms of pulmonary irritation manifested by increased pulse and respiratory rates. Supplemental oxygen may be indicated and corticosteroids may be given in life-threatening situations, but documentation of the beneficial effects of steroids is lacking.^{48,53,62}

Blood methemoglobin should be measured as soon as possible after a casualty has been exposed to nitrogen oxides, *especially if the casualty is cyanotic*. Methemoglobin cannot transport oxygen efficiently; therefore, hypoxemia cannot easily be corrected with supplemental oxygen when methemoglobin is present. The patient may require intravenous treatment with methylene blue [3,7-bis(dimethylamino)phenazathionium chloride in a dosage of 1–2 mg/kg body weight],⁵³ which reduces methemoglobin's ferric iron back to the ferrous state found in normal hemoglobin:



Sulfur Dioxide

Sulfur dioxide may be formed when antimony sulfide (used in primers), sulfur (used in black powder igniter), and potassium sulfate (a flame retardant used in propellants) are oxidized.⁹ Sulfur dioxide is a heavy, irritating gas with a characteristic pungent odor. It reacts with water to form sulfurous acid and therefore mucous membranes in the eyes, mouth, and upper respiratory tract are at risk for injury. Sulfurous acid will also burn the lungs.⁴⁸

Sulfur dioxide induces bronchoconstriction; the stimulation probably occurs via an afferent nerve after direct stimulation of its sensory end organ in the airway wall. This stimulation leads to efferent vagal-induced contraction of smooth muscle in the airway. Asthmatic subjects exposed to sulfur dioxide at 5 ppm for 5 minutes while exercising have developed bronchospastic attacks.⁶³ However, research performed with normal adult subjects has shown that

- continuous exposure to sulfur dioxide at 3.0 ppm may occasionally produce a reversible decrease in small-airway compliance⁵³;
- exercise can also potentiate functional airway impairment in the presence of atmospheric sulfur dioxide⁶⁴;
- an estimated 10% to 20% of the adult population will exhibit hyperreactive airways after exposure to sulfur dioxide⁶⁴; and
- exposure to less than 25 ppm can also cause other symptoms, including irritation of the mucous membranes, increased respiratory rate and depth, and coughing.⁶⁴

Workers who are chronically exposed to 5 to 20 ppm can become acclimatized to these effects: their sense of smell becomes less acute, their reflex cough is lessened, and they are less aware of the irritation in their upper airways.⁵³ This acclimatization will not occur in soldiers who experience only intermittent high-level exposures. In general, 20 to 30 ppm of sulfur dioxide is very disagreeable.⁶⁵

Exposure limits and an EEGL have been established for sulfur dioxide; the NAS recommends an EEGL of 10 ppm for a 1-hour exposure.⁶⁴ In addition, the ACGIH and OSHA have established time-weighted average (TWA, an average 8-hour exposure within a normal workday) exposure values of 2 ppm.^{40,41}

The treatment of casualties who are exposed to sulfur dioxide is to remove the victim from the source and flush the eyes with water if they are irritated or lacrimating. However, severely symptomatic individuals should be hospitalized and monitored for the

signs of pulmonary edema. Bronchiolitis obliterans can occur within days or weeks after the patient has recovered from a moderate-to-severe exposure.

Hydrogen Chloride

Hydrogen chloride exists both as a gas and as an aqueous acid aerosol (microdroplet solutions of hydrogen chloride and water). Hydrogen chloride has an extremely high affinity for water, and its acidic properties make it a strong irritant of mucous membranes.

Although the odor threshold of hydrogen chloride is 1 to 5 ppm, 10 ppm is a noxious concentration. In fact, inhalation of hydrogen chloride causes an individual to promptly leave the offending environment. Inhalation of hydrogen chloride causes several respiratory tract signs and symptoms, including noticeable pain, coughing, inflammation, edema, and, at high concentrations, laryngeal or bronchial constriction (Table 10-12 and Figure 10-12).

Early test-firing of the MLRS, in which a perchlorate-based propellant is used, showed that hydrogen chloride was produced in large quantities, and was present at levels of 25 to 50 ppm in the crew compartment. This level irritates the eyes, and the resultant lacrimation would have prevented the crew from performing its mission effectively. During the late 1970s, the MLRS was reengineered: the crew compartment

of the subsequent version could be overpressurized, and gas and particulate filters were included on its air intake.⁶⁶

The shoulder-held Stinger, an anti-aircraft missile, also produces high concentrations of hydrogen chloride when it is fired. Soldiers who fired the Stinger were required to wear chemical protective masks to reduce their exposures to hydrogen chloride, but the masks obstructed their views through the missiles' sighting devices. To sight their targets, soldiers took off their masks and held their breaths while they fired the weapons. Their intention was to improve their tracking capability while reducing the irritating effects of hydrogen chloride in the upper airways.

Several governmental regulatory agencies have established limits for exposure to hydrogen chloride. Both OSHA and the ACGIH recommend a ceiling of 5 ppm.^{40,41} The NRC proposed a 10-minute EEGL of 100 ppm, but because this level is not likely to be tolerable for any sustained duration (up to an hour), a 1-hour EEGL of 20 ppm was adopted.²⁹

The treatment of casualties who have been exposed to hydrogen chloride is mostly palliative: remove the casualty from the source and treat the symptoms. Little information is available concerning the long-term effects on health that may arise after acute exposure to hydrogen chloride.⁴⁸

Inhalable Metal Particulates

The inhalation of metal particulates can, over time, be expected to cause chronic health problems. Of the mass of inhalable metal particulates formed when an M16 round is fired, lead constitutes approximately one-half, and copper approximately one-third (the effects of inhaled lead particulates are described in Chapter 12, Lead). Inhalable copper comes from brass cartridges and copper jackets of bullets. Another source of copper is the rotating band on artillery shells.⁹ Although most particles still consist of lead, the relative percentage of inhalable copper increases and that of lead decreases as more rounds are fired.²⁴ To reduce the amount of copper deposited in the barrel bore, lead foil has been added to artillery rounds, which, of course, also increases the amount of particulate lead produced. Tin foil is being considered as a replacement for lead foil, and no adverse health effects are expected from this substitution.³¹

The signs and symptoms of copper inhalation include nasal congestion, nasal septum perforation, nasal ulceration, and metal fume fever, which is characterized by a sudden onset of fever, chills, malaise, and headaches.⁵³ Therefore, OSHA has established an 8-hour TWA for copper dust of 1.0 mg/m³ air.⁴⁰

TABLE 10-12
TOXIC EFFECTS OF HUMAN EXPOSURE TO HYDROGEN CHLORIDE

HCl (ppm)	Exposure Time	Effects/Comments
1,000–2,000	Brief	Dangerous for even short exposures (pain; laryngeal and bronchial constriction)
50–100	1 h	Tolerable
100	10 min	EEGL*
91	—	Median concentration for odor detection
10–50	Few hours	Maximal tolerable concentration
35	—	Throat irritation after short exposure
10	Prolonged	No adverse effects
1–5	—	Odor threshold

*Emergency exposure guidance level
Source: National Research Council Committee on Toxicology. Ammonia, hydrogen chloride, lithium bromide, and toluene. In: *Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants*. Vol 7. Washington, DC: National Academy Press; 1987.



Fig. 10-12. This chest X-ray film was made 6 hours after a 19-year-old soldier was exposed to hexachlorethane smoke when a hexachlorethane grenade was thrown into her tent. The smoke is generated in the thermochemical reaction of zinc oxide, hexachlorethane, and aluminum metal, and is composed predominantly of zinc chloride with 1% to 2% aluminum chloride. Zinc chloride is a potent respiratory irritant with pulmonary effects similar to those caused by inhaled hydrogen chloride. This film shows bilateral, diffuse, air-space opacities, with an interstitial component consistent with pulmonary edema.

Antimony, barium, and zinc together constitute less than 5% of the metallic inhalable particulates that are produced when an M16 round is fired.⁹ In normal firing conditions, these metallic particles are expected to occur in low concentrations, and their health effects are expected to be negligible.⁶⁷⁻⁶⁹

Antimony trioxide is a combustion byproduct of antimony sulfide, which is used in primers and antimonial-lead alloy bullets. (Because lead antimony has a higher melting point than lead alone, its use in the bullet's core allows the weapon to be fired at a faster rate.) Antimony trioxide is an irritant to mucous membranes, and acute inhalational exposure can cause coughing, loss of appetite, and gastrointestinal pain. Chronic exposure has caused lung fibrosis.⁶⁷

Barium is a combustion byproduct of barium nitrate, which is also found in certain primers. Barium can also be a local irritant to mucous membranes and can cause coughing. Heavy industrial exposure to barium oxides or sulfates can produce a benign pneumoconiosis. Barium oxide is strongly alkaline and can cause eye and skin irritation. It is extremely toxic if ingested. No long-term health effects other than pneumoconiosis are known.⁶⁸

Zinc, like copper, comes from brass bullet cases. Zinc can be a mild mucous-membrane irritant during exposure. Zinc oxide causes metal fume fever; it often occurs during periods away from work and can last 6 to 24 hours. No chronic health effects are described for zinc.⁶⁹

Depleted uranium is a potential risk to personnel who may be exposed to the aerosolized products of a burning tank round (eg, during a fire in a tank bustle where the armor-piercing rounds are stored, or if a DU round has penetrated the armor into the tank's crew compartment). In these cases, particulate uranium oxide would form, some of which would be respirable ($< 10 \mu$). Because DU contains both uranium ^{238}U and ^{234}U , both of which are alpha emitters, a theoretical risk of lung cancer exists for those who inhale these particulates. (Exposure to DU in this circumstance would be expected to be short-lived, however, and the far greater risk to the crew would be from the conflagration or the ballistic properties of the armor-piercing projectile.) Toxicity studies with animals have not borne out hypothesized carcinogenicity, although fi-

brotic lung changes have been noted with exposure to uranium oxides. These changes have not been noted in humans. The primary hazard of exposure to elemental uranium would be heavy metal toxicity in the form of nephrotoxicity, if ingested. However, feeding studies in rats have failed to demonstrate toxicity from the insoluble uranium oxide.^{34,70,71}

Allied troops received wounds from fragments of DU during Operation Desert Storm. In some soldiers, the fragments were not removed. This raised a concern that the solubility of uranium in body fluids may exceed the solubility of uranium in water and therefore pose a greater health threat than was originally considered. In vitro solubility is being studied and soldiers with retained fragments of DU are being followed medically to detect any adverse effects.³⁴

CURRENT MEASURES TO CONTROL EXPOSURE

The measures that the army uses to control soldiers' exposure to propellant combustion products are not unlike the measures that civilian industrial operations take to control their workers' exposures. Engineering controls (such as incorporating appropriate ventilation into the design of weapons systems) are the best for limiting exposure, followed by administrative controls (such as limiting firing or personnel exposure times), and finally, by providing PPE (such as respirators) if the other measures are inadequate. The health hazard assessment process identifies potential health hazards that arise from the accumulation of combustion products so that these controls can be implemented.

Currently fielded protective masks may efficiently remove chemical-warfare agents, but they may be unable to efficiently filter out nitrogen oxides, carbon monoxide, and low-molecular-weight aldehydes.^{72,73} This caveat is important for medical officers to consider when they evaluate casualties who have been exposed to the products of propellant combustion. For example, during Operation Desert Storm, the protective masks that tank crews were issued to wear against the threat of chemical warfare may not have protected them against propellant combustion products inside their own tanks; these crews would have been particularly at risk had their tanks sustained battle damage and their own munitions caught fire.

Several engineering mechanisms are used in modern army fighting vehicles to limit the crew's exposure to propellant gases. The bore evacuator was an earlier engineering approach that was designed for large guns (Figure 10-13). Another system, the M81 closed-breech scavenger, used an inert gas to flush out the gun

tube. The principal guarantor of the crew's safety is the vehicle's ventilation system, however, which can purge the pollutants by exhausting either the entire crew area, the area of the breech of the individual weapons, or both.⁹

Other possible means of limiting exposures include placing the gun breech outside the crew compartment, reformulating the propellant chemicals or other components of the shell (eg, adding more zinc to bullets to reduce the production of lead particulates), or redesigning military small-arms ammunition so that the metal jacket completely encloses the bullet.

The U.S. Army, primarily as a cost-saving measure, is considering using liquid propellants such as hydroxylammonium nitrate (HAN) in its artillery weapons. Computerized projections of the theoretical combustion products of HAN indicate that the major chemical species produced will be carbon dioxide and nitrogen in relatively low concentrations, water vapor, and minor amounts of carbon monoxide and mixed nitrogen oxide gases.⁷⁴ However, the reduced threat to soldiers' health from exposure to these combustion products may be offset by the potential for soldiers' direct exposure to the propellant liquid or its vapors. Not only can HAN cause methemoglobin formation, direct exposures to this propellant or its vapor have also produced respiratory distress, splenic enlargement, and anemia in laboratory animals.⁷⁵

The air force and army are now evaluating gel propellants to replace the current, solid propellant, aircraft emergency escape systems (aircrew ejection systems). The system consists of a gas generator that applies pressure to separate gel fuel and gel oxidizer

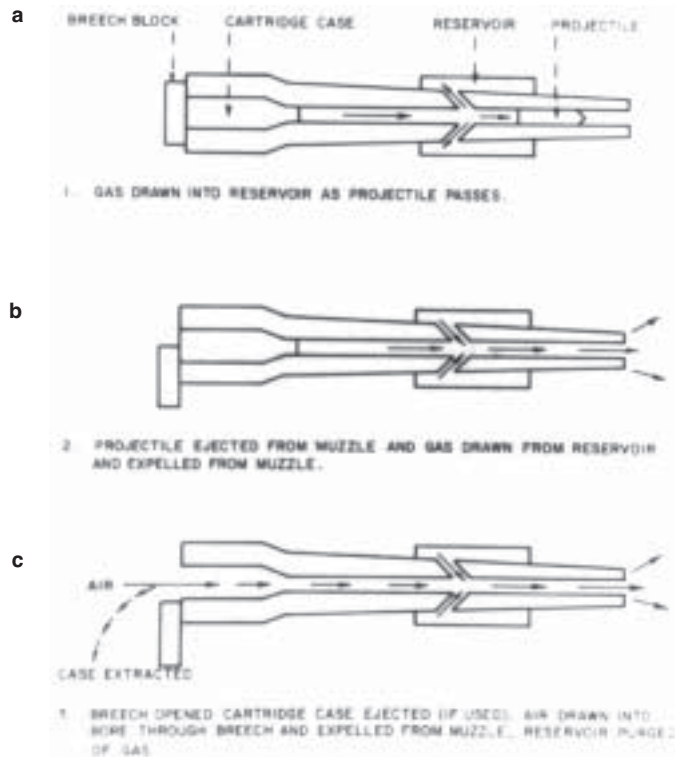


Fig. 10-13. (a) Following the firing of the weapon, gases are drawn into the reservoir as the projectile passes. (b) After the projectile is ejected from the muzzle, the gas previously drawn into the reservoir is expelled from the muzzle. (c) As the breech is opened to eject the cartridge case or reintroduce another round, air from the crew compartment is drawn into the bore and expelled, along with any combustion gas remaining in the reservoir, through the muzzle. Source: Ross RH, Pal BC, Lock S, et al. *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. Vol 1. Oak Ridge, Tenn: Oak Ridge National Laboratory; 1988. Final Report AD-ORNL-6334/V1.

tanks, which combine in combustion chambers to produce a significant thrust advantage over the current solid propellant systems. The gel fuel consists of aluminum powder, monomethyl hydrazine and hydroxy propyl cellulose as the gelling agent. The oxidizer gel consists of inhibited red fuming nitric acid, lithium nitrate, and fused silica. This gel propellant offers advantages over its liquid version in that it is insensitive to detonation if the fuel and oxidizer tanks are penetrated by projectiles during combat. In this situation, partial operability of the system would

be maintained. Combustion products would not pose a threat to the aircrew who have ejected. However, some leakage of inhibited red fuming nitric acid could result in the leakage of nitrogen tetroxide, which quickly dissociates to nitrogen dioxide. In this situation, aviators would probably switch from their respirator's regular air supply to 100% oxygen to avoid exposure.⁷⁶ Overall, gel propellants offer distinct safety advantages over both solid and liquid propellants and could be considered as components of a wide variety of weapons systems in the future.

SUMMARY

Although soldiers have been exposed to the deleterious effects from propellant combustion products for more than 1,000 years, innovations in weapons and tactics during the 1980s have increased the potential for exposure to these health hazards. The wide variety

of gun and rocket propellants now in use have the potential to give rise to an even more complex array of combustion products during firing. In general, however, certain chemical species are thought to pose the greatest risk to soldiers, predominately through inha-

lation. These include asphyxiants (such as carbon monoxide and nitric oxide), pulmonary irritants (such as nitrogen dioxide, ammonia, and hydrogen chloride), and heavy metal particles (such as lead).

Evaluation of potential hazards has been assisted by computer modeling of predicted species; however, there have been few studies to validate the prediction capability. This is due to the difficulty of conducting appropriate chemical sampling under both laboratory and field conditions. Nevertheless, efforts are made during the health hazard assessment process to gather appropriate data, assess the health impact on soldiers, and design protection systems into military hardware while it is still being developed.

The potential for significant toxic effects is inherent in the firing of military weapons. Medical officers should thoroughly understand the occupational hazards that soldiers face, especially those from jobs that are performed within enclosed spaces. Combustion products of propellants encountered in training and battlefield conditions can have acute as well as long-term effects. Medical personnel must also recognize that engineering controls designed to reduce hazardous exposures (such as ventilation systems) may fail, administrative controls (such as limiting firing times) may be ignored, and PPE (such as respirators) may be discarded, worn improperly, or possess an inadequate protective factor.

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