

## CHEMICAL WARFARE

### 1. Chemical Warfare

Weapons of mass destruction have received increased attention recently. Terrorist groups, rogue states, and foreign governments possessing these weapons have raised major concerns to stability in different regions across the globe, and about homeland security in the United States. Weapons of mass destruction are defined as nuclear, chemical, or biological weapons. While categorized together due to their potential destructive power, the nature of the threat of each of these types of weapons is very different, and defensive measures taken in response to each varies greatly. This article focuses on the details of chemical warfare, and deals primarily with U.S. capabilities. Concerning the role of chemical warfare in U.S. strategic planning, all modern chemical warfare capabilities are defensive in nature. Due to the fact that the first step of defending against any threat is understanding the threat, a discussion of chemical agents follows. However, from there discussion turns to classes of chemicals that, among other uses, can be utilized to thwart attempts to detect the presence of chemical agents. Rapid and accurate determination of the presence of exceedingly small amounts of a chemical substance on a battlefield, an environment that is far from pristine, is a difficult task. However, certain chemicals can be used to further complicate detection by orders of magnitude, and a sample of those are included in this work. A short discussion describing contamination avoidance, protection, and

decontamination materials is also included. None of the material covered in this article should be considered to be comprehensive, even within the framework of what constitutes the U.S. military equipment or capabilities.

Chemicals used in the context of chemical warfare fit into five categories: toxic agents, riot control agents, flame agents, incendiaries, and smokes and obscurants. Toxic chemical agents, used to achieve military objectives by producing casualties and discouraging enemy troops from certain areas of the battlefield (terrain denial), may be incapacitating or lethal. Army Field Manual 8-285 defines a chemical agent as "a chemical substance. . . intended for use in military operations to kill, seriously injure, or incapacitate humans (or animals) through its toxicological effects." Army and Department of Defense doctrine specifically excludes from this definition riot-control agents, which are considered to be legitimate law-enforcement tools. Also excluded are chemical herbicides and smoke and flame materials, all of which are considered legitimate military assets (1). Riot control agents are nonlethal tear agents most effective against unprotected personnel. Flame and incendiary agents can be used to harass and inflict casualties, and to destroy structures and material. Smokes and obscurants are employed for screening, signaling, and target marking, in both offensive and defensive applications.

The use of chemical agents and weapons in war is commonly thought to be a modern military technique. However, several historic uses are reported (2) including the contamination of drinking water and an attack against ships with earthen pots filled with live serpents, both before the birth of Christ.

Chemical warfare, a term used since 1917, is of vital interest not only to the world powers, but also to many developing countries. The relative simplicity of production and ease with which existing pesticide or other chemical plants can be converted to a weapons facility, make chemical weapons a continuing threat. Iraq and Libya, each of which possesses chemical weapon production facilities, have been known to use chemicals in war during the latter part of the twentieth century. The Geneva Convention of 1925 prohibited the use of chemical agents in war. The United States did not sign the Geneva Convention. The Paris Conference on Chemical Weapons in 1989 reaffirmed the prohibition on nerve agents (3–5). Thus, chemical weapons are not, as of this writing, banned. However, whether employed or not, these materials exist as a potential weapon in any conflict. Toxic chemical agents may exist as chemical substances in gaseous, liquid, or solid state intended to produce casualty effects ranging from harassment through varying degrees of incapacitation to death. A few such agents are true gases but most are solids or liquids that are converted in use into a gaseous state or disseminated as aerosols (qv). For contamination of terrain the agent can also be disseminated in bulk form with or without additives to modify physical properties.

Since 1944, the DoD Nuclear Biological and Chemical (NBC) Defense Program has been overseen by the Office of the Secretary of Defense, Chemical and Biological Defense Steering Committee, and the Joint NBC Defense Board. The Joint Service Integration Group generates joint NBC requirements, including inputs of the geographic commanders in chief. The Joint Service Material Group takes those priorities and coordinates planning for all NBC nonmedical research. Development and Acquisition (RDS). Medical RDA is coordinated

through the Armed Services Biomedical Research and Evaluation Management Committee (6).

According to the U.S. General Accounting Office, in its report 'Chemical and Biological Defense: Coordination to Nonmedical Chemical and Biological R&D Programs', August 1999, the United States budgeted ~\$1 billion/year on military defense against chemical and biological weapons in 2000, with an additional \$1.4 billion for civilian preparedness (6).

## 2. Lethal Agents and Incapacitants

The modern history of the military use of toxic chemical agents (2,6–8) dates from the first full-scale (chlorine) gas attack on April 22, 1915, near Ypres, Belgium in World War I. Some estimates put the number of casualties of World War I to chemical warfare agents at 5 million (1). There have been a few reports of the limited use of toxic chemicals since that time. Historically, the most important of the tactical agents, and the one still used most often in battle, is sulfur mustard. Although it is chemically similar to the cytotoxic nitrogen mustards used in contemporary medicine, it has little commercial value other than its role in warfare. The first heavy military use of mustard occurred in the summer of 1917 (9). It is estimated that during 10 days of a German attack on the French town of Armentieres in September of that year, more than 1 million mustard shells were fired (10). While sulfur mustard was stockpiled by the warring nations of World War II, there is little evidence of its deliberate use in combat (9). In December 1943, an Allied ship carrying large quantities of mustard and other munitions was attacked by German planes and exploded in the harbor of Bari, Italy, disseminating mustard over a wide area. The incident resulted in more than 600 casualties due to mustard exposure (11). The Italians employed mustard, a blister agent, during the Ethiopian war in 1935 and 1936; the Japanese used toxic chemicals in a number of small-scale engagements in the early years of their war with China; and Iraq purportedly employed both mustard and nerve gases in the 1980s. The Iran-Iraq war produced at least 45,000 casualties to chemical agents (1).

Research on chemical agents after World War I led to the elimination of all but a handful of chemicals as being of practical battlefield significance. Some of the criteria used in the selection of a suitable agent are effectiveness in extremely small concentrations; time to onset of action; effectiveness through various routes of entry into the body, such as the respiratory tract, eyes, and skin; stability in long-term storage; and ease of dissemination in feasible munitions. At the time of World War II, the only chemicals considered to be of practical significance included the mustard gases and phosgene.

Discovery of nerve agents in Germany led to the availability of a class of compounds at least one order of magnitude more lethal than previously known where death might occur in a matter of minutes instead of hours.

An excellent survey of the many factors involved in the use of toxic chemicals in war, including historical background, legal aspects, attempts at international agreement, and reasons why toxic chemicals were not employed in World War II or the Korean Conflict, is available (12).

**2.1. Mustard and Related Vesicants.** Mustard, bis(2-chloroethyl) sulfide [505-60-2] (Chemical Agent Symbol HD),  $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{Cl}$ , is a colorless, oily liquid when pure. Most samples have a characteristic garliclike odor. Known as the “king of war gases,” it is a potent alkylating agent that causes severe vesication of epidermal surface. It is favored for its ability to incapacitate opponents, lower their mobility, restrict the use of terrain, and *reduce* their ability to flight. At high-dose levels, it exerts systemic cytotoxic effects, in particular involving the rapidly proliferative cells of the hematological system and intestinal mucosa. It is also genotoxic, mutagenic, and a dose-related carcinogen (8). Sulfur mustard is an oily liquid that becomes aerosolized when dispersed by spraying or by explosive blast from a shell or bomb. In temperate climates, it vaporizes slowly, posing particular risk in prolonged, closed-space, or below-grade exposures. At higher temperatures, vaporization increases markedly and contributes to more severe clinical effects. Because of its low volatility, mustard is persistent. At temperate climates, in open areas with little wind, it is expected to persist for >1 week. By contrast, persistence for only a day is likely at temperatures >37.7°C in the Saudi desert (9).

Battlefield air concentrations during World War I mustard gas attacks were estimated in the range of 19–33 mg/m<sup>3</sup> (13). At such concentrations, exposure for several minutes causes skin and eye injury, and exposure for 30–60 min can result in severe respiratory injury, systemic poisoning, and death (42).

In the period following World War I and during World War II, a wide variety of sulfur analogues of mustard were investigated and many potent vesicants were discovered. Each had two 2-chloroethyl groups attached to a sulfur atom. Examples of such compounds are 1,2-bis(2-chloroethylthio)ethane [3563-36-8] (Chemical Agent Symbol Q),  $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{Cl}$ ; and bis(2-chloroethylthioethyl) ether [63918-89-8] (T),  $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{Cl}$ . It is noteworthy that each 2-chloroethyl group is associated with a separate sulfur atom, not with the same one as for mustard. Both Q and T are more vesicant than mustard, but neither is as volatile. For that reason, neither is as effective by the vapor route. One disadvantage of sulfur mustard, however, is that it freezes at ~10°C, so that solidification in airplane spray tanks presents a serious problem.

The procedure by which mustard is manufactured can be modified to yield either a mixture of mustard and Q (HQ) or a mixture of mustard and T (HT). These mixtures have several advantages over mustard alone, unless the agent is used only for vapor effects. HQ and HT are more toxic, more vesicant, more persistent, and have lower melting points than mustard alone.

In 1935, nitrogen analogues of sulfur mustards were first synthesized and found to have marked vesicant action (14). These are tertiary amines containing at least two 2-chloroethyl groups,  $\text{RN}(\text{CH}_2\text{CH}_2\text{Cl})_2$ . The most important of these compounds were tris(2-chloroethyl)amine [555-77-1] (Chemical Agent Symbol HN3),  $\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_3$ ; *N*-methyl-2,2'-dichlorodiethylamine [51-75-2] (HN2),  $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$ ; and 2,2'-dichlorotriethylamine [538-07-8] (HN1),  $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$ . The nitrogen mustards are colorless when pure but turn yellow to amber in storage. These materials have faint odors varying from fishy or soft-soaplike to practically odorless, and they act on the body in a manner similar to sulfur mustard.

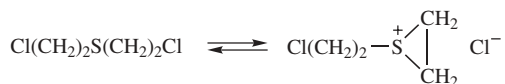
Table 1. Properties of Mustard Gases

Property	HD	Q	T	HN1	HN2	HN3
mol wt	159.08	219.08	263.25	170.08	156.07	204.54
bp, °C <sup>a</sup>	80 <sup>0.67</sup>		120 <sup>0.003</sup>	85 <sup>1.3</sup>	87 <sup>2.4</sup>	144 <sup>2.0</sup>
mp, °C	14.5	56	10	-34	-60	-4
density at 25°C, g/mL	1.2682		1.24	1.086	1.118	1.2347
volatility at 25°C, mg/m <sup>3</sup>	925	0.4	2.8	2s.29	3.581	0.120

<sup>a</sup> Pressure in kPa at which boiling point was determined is given as a superscript. To convert kPa to mm Hg, multiply by 7.5.

**2.2. Properties.** The physical properties of the mustards are summarized in Table 1. The sulfur mustards are only slightly soluble in water, whereas the nitrogen mustards are slightly soluble at neutral pH, but form water-soluble salts under acid conditions. Both sulfur and nitrogen mustards are extremely soluble in most organic solvents.

Although sulfur and nitrogen mustards have limited solubility in water at neutral pH, the small quantity that dissolves is extremely reactive. The reaction proceeds via a cyclic sulfonium or imonium intermediate



This intermediate attacks compounds containing a variety of functional groups, such as primary, secondary, and tertiary amino nitrogen atoms, carboxyl groups, and sulfhydryl groups (15).

With nitrogen mustards, the imonium ion, which apparently forms even in the absence of any solvent, readily attacks another molecule to form a dimer. For this reason, the nitrogen mustards are less stable than sulfur mustards in long-term storage.

An excellent reagent for detection and quantitative estimation of the mustards is *p*-nitrobenzylpyridine (16). On treatment of the reaction product with alkali, a blue color appears, which detects as little as 0.1 µg of mustard.

The mustards readily alkylate inorganic thiosulfates to form Bunte salt anions (17,18). For sulfur mustard, the product is  $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{SSO}_3^-$ . Phosphates react in a similar manner and the product isolated from sulfur mustard is  $\text{Cl}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OPO}_3^{2-}$ .

Sulfur mustard reacts rapidly with chlorine or with bleach, and this reaction is a suitable means of decontamination. Nitrogen mustards, however, chlorinate extremely slowly; thus chlorination is not suitable for their decontamination. The formation of water-soluble salts, such as by neutralization with sodium bisulfate, is the usual method for nitrogen mustard removal from contaminated surfaces. The mustard salts are much less vesicant than the corresponding free bases.

The mustards can be oxidized by such oxidizing agents as hydrogen peroxide or potassium bichromate in sulfuric acid. Oxidation occurs at the sulfur atom of sulfur mustard and at the nitrogen atom of nitrogen mustard. The product

formed on strong oxidation of sulfur mustard, bis(2-chloroethyl)sulfone, [471-03-4],  $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$ , exhibits vesicant properties.

**2.3. Physiological Effects.** The sulfur and nitrogen mustards act first as cell irritants and finally as a cell poison on all tissue surfaces contacted. The first symptoms usually appear in 4–6 h (7). The higher the concentration, the shorter the interval of time between the exposure to the agent and the first symptoms. Local action of the mustards results in conjunctivitis (inflammation of the eyes); erythema (redness of the skin), which may be followed by blistering or ulceration; and an inflammatory reaction of the nose, throat, trachea, bronchi, and lung tissue. Injuries produced by mustard heal much more slowly and are much more liable to infection than burns of similar intensity produced by physical means or by other chemicals.

Mustard's most important metabolic effect, at least for acute toxicity, is inhibition of cellular glycolysis. Disruption of that metabolic pathway is found after exposure to nearly all vesicant chemicals, usually due to interference with sulfhydryl-rich hexokinase enzyme systems (19). In the case of mustard, however, inhibition of glycolysis is an indirect result to nucleic acid damage and repair. Initially, sulfur mustard rapidly alkylates the purine bases (guanine and adenine) of DNA. Activation of endonucleases then leads to removal (depurination) of alkylated bases, leaving apurinic sites where DNA breaks occur readily. In turn, need for DNA repair activates poly(ADP-ribose) polymerase, an enzyme that rapidly depletes cellular  $\text{NAD}^+$  (20–22).

Depletion of cellular  $\text{NAD}^+$ , which begins within 1 h of exposure and is maximal after  $\sim 4$  h, inhibits glycolysis, leads to release of tissue proteases, and ultimately results in cell necrosis. These biochemical changes parallel the development of tissue injury (19,23). In animals, treatment with polymerase inhibitors (3-methoxybenzamide or nicotinamide) or  $\text{NAD}^+$  precursors (niacin or nicotinamide) increased cellular  $\text{NAD}^+$  levels, decreased the severity of skin damage, and delayed the onset of toxic effects after cutaneous exposure (20).

The rate of detoxification is slow, and the effects of even very small repeated exposures are cumulative or more than cumulative owing to sensitization.

**2.4. Uses.** The nitrogen mustards are used clinically in the treatment of certain neoplasms (21). They have been used in treatment of Hodgkin's disease, lymphosarcoma, and leukemia (see CHEMOTHERAPEUTICS, ANTICANCER).

**2.5. Nerve Agents.** Discovery of nerve agents in Germany led to the availability of a class of compounds at least one order of magnitude more lethal than previously known where death might occur in a matter of minutes instead of hours. Nerve agents are part of a class known as organophosphorus compounds, and were first synthesized in 1854, but their development as warfare agents did not occur until 80 years later (23). The first military nerve agent, ethyl phosphorodimethylamidocyanidate, known as tabun, or chemical agent symbol GA (Fig. 1), was synthesized in 1936 by Schrader while searching for

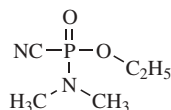
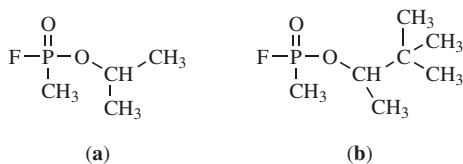


Fig. 1. Tabun.



**Fig. 2.** (a) Sarin (b) Soman.

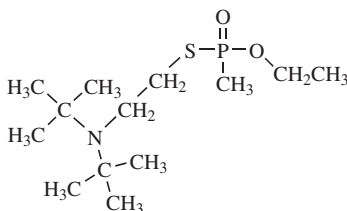
more effective agricultural organophosphate insecticides at the German chemical firm of IG Farbenindustrie.

Two years later, he synthesized a second nerve agent, isopropyl methylphosphonofluoridate, now known as Sarin or GB [Fig. 2(a)]. In 1944, a third nerve agent, pinacolyl methylphosphonofluoridate, now known as Soman or GD [Fig. 2(b)], was synthesized (14).

By the end of World War II, Germany had large stockpiles of nerve agents. Although estimates vary widely, as much as 30,000 tons of Tabun and 500 tons of Sarin may have been prepared in munitions ready for battlefield deployment (24). It is uncertain why these agents never were used by the German military; the Allies were not aware that Germany had synthesized these agents for use in battle and did not have antidotes (25). During the waning stages of war, Russian forces captured the German nerve agent-manufacturing facilities at Duhernfurt and moved the buildings and staff to Russia, where production and stockpiling of these agents continued (26). At approximately the same time, Allied forces discovered munitions containing nerve agents, and scientists elucidated the pharmacology and the antidotal activity of atropine. An excellent survey of the many factors involved in the use of toxic chemicals in war, including historical background, legal aspects, attempts at international agreement, and reasons why toxic chemicals were not employed in World War II or the Korean Conflict, is available (12).

In the early 1950s, a fourth agent of current military importance, *O*-ethyl-*S*-[2-(diisopropylamino)ethyl]-methylphosphonothioate, now known as VX (Fig. 3), was synthesized in England, again in a search for better insecticides (25). This and related compounds are a great deal more toxic than either mustard or chlorine and are capable of being disseminated by munition systems including bombs, artillery rounds, rockets, grenades, missiles, and aerial spray (27,28).

*Nerve agent* refers to two groups of highly toxic chemical compounds that generally are organic esters of substituted phosphoric acid (8,11,27). The nerve



**Fig. 3.** VX.

agents inhibit cholinesterase enzymes and thus come within the category of anticholinesterase agents (see ENZYME INHIBITORS). The three most active G-agents are tabun, ethyl phosphorodimethylamidocyanidate [77-81-6] (Chemical Agent Symbol GA),  $(\text{CH}_3)_2\text{NPOCNOCH}_2\text{H}_5$ ; sarin, isopropyl methylphosphonofluoridate [107-44-8] (GB),  $\text{CH}_3\text{POFOCH}(\text{CH}_3)_2$ ; and soman, pinacolyl methylphosphonofluoridate [96-64-0] (GD),  $\text{CH}_3\text{POFOCHOCH}_2\text{C}(\text{CH}_3)_3$ .

The G-agent liquids under ordinary atmospheric conditions have sufficiently high volatility to permit dissemination in vapor form. They are generally colorless, odorless or nearly so, and are readily absorbable through not only the lungs and eyes but also the skin and intestinal tract without producing any irritation or other sensation on the part of the exposed individual. These agents are sufficiently potent so that even a brief exposure may be fatal. Death may occur in 1–10 min, or be delayed for 1–2 h depending on the concentration of the agent.

Another class of nerve agents, discovered after World War II, is the V-agents. Nerve agent vapors are four to six times denser than air. As a result, they tend to remain close to the ground and pose a particular risk to people in low areas and below-ground shelters (25). These materials are generally colorless and odorless liquids that do not evaporate rapidly at normal temperatures. In liquid or aerosol form, V-agents affect the body in a manner similar to the G-agents. Although all four nerve agents are significantly hazardous by all routes and are percutaneous hazards, VX is least volatile and most efficiently absorbed through the skin (29,30). Their relative lethality as determined in animal studies is  $\text{VX} > \text{Soman} > \text{Sarin} > \text{Tabun}$  (30). Estimates of lethal doses vary. For inhalation exposure in a 70-kg adult breathing 15 L/min, approximate mean lethal doses are 150–400 mg min/m<sup>3</sup> for Tabun, 75–100 mg min/m<sup>3</sup> for Sarin, 35–50 mg min/m<sup>3</sup> for Soman and 10 mg min/m<sup>3</sup> for VX. Mean lethal doses due to skin exposure in a 70-kg adult are 1700 mg for Sarin, 1000 mg for Tabun, 100 mg for Soman, and 6 mg for VX (24,31).

**2.6. Properties.** Some physical properties of nerve agents are given in Table 2. The G-agents, miscible in both polar and nonpolar solvents, hydrolyze slowly in water at neutral or slightly acid pH and more rapidly under strong acid or alkaline conditions. The hydrolysis products are considerably less toxic than the original agent.

GB is unstable in the presence of water. Maximum stability in aqueous solutions occurs from pH 4.0–6.5 with the hydrolysis rate increasing as the pH increases. The half-life in distilled water at 25°C is ~36 h, but hydrolysis is accelerated in the presence of acids or bases. Because bases are far more effective in this respect than acids, caustic solutions are useful for decontamination.

Table 2. Properties of Nerve Agents

Property	GA	GB	GD	VX <sup>a</sup>
formula wt	162.13	140.10	182.18	267.38
bp, °C	246	147	167	298
mp, °C	–50	–56	unknown	below –51
density at 25°C, g/mL	1.073	1.0887	1.0222	1.0083
volatility at 25°C, mg/m <sup>3</sup>	610	21,900	3,060	10.5

<sup>a</sup> VX [50782-69-9],  $\text{C}_{11}\text{H}_{26}\text{NO}_2\text{PS}$ , is a phosphonothioic acid ester.



GB decomposes thermally to form a variety of phosphorus-containing products as well as propylene. The rate of decomposition increases with increase in temperature and in the presence of acids. At the boiling point of GB, under atmospheric conditions, decomposition is fairly rapid.

GB and other G-agents react with perhydriyl ions at pH 9–10 to form a perphosphonate ion,  $\text{CH}_3\text{P}(\text{O})(\text{OC}_3\text{H}_7)\text{OO}^-$ , which has a sufficiently high redox potential to oxidize indole or *o*-dianisidine to produce colored products. This reaction is thus useful as a method of detection, and  $<1\ \mu\text{g}$  of GB can be detected in this manner (32).

Another useful reagent for detection and estimation of G-agents is diisonitrosoacetone (33). A magenta color is produced with  $1\ \mu\text{g}$  of GB at pH 8.5. Coupling agents, such as *p*-phenylenediamine, increase the reaction rate.

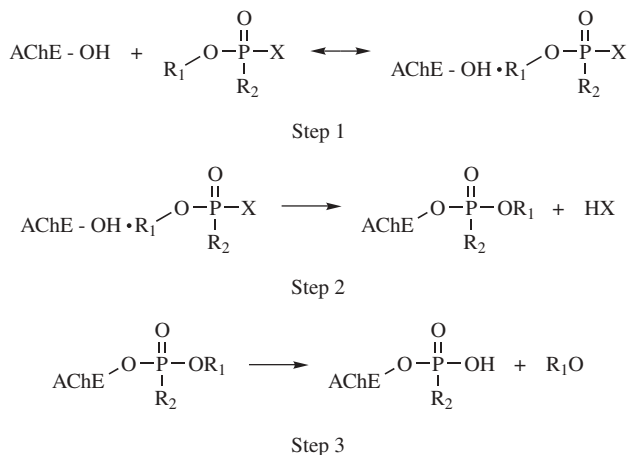
**2.7. Physiological Effects.** Inhalation of G-agent vapor at realizable field concentrations is immediately incapacitating. The symptoms in normal order of appearance are runny nose; tightness of chest; dimming of vision and pinpointing of the eye pupils (miosis); drooling and excessive sweating; nausea and vomiting; cramps and involuntary defecation or urination; twitching, jerking, and staggering; and headache, confusion, drowsiness, coma, and convulsion. These symptoms are followed by cessation of breathing and death.

Although GB is also effective by penetration through the skin, the dose required to produce toxic effects by this route is high. Thus a person wearing skin covering and a gas mask is reasonably well protected.

The toxicity of nerve agents is due primarily to irreversible inactivation of acetylcholinesterase leading to accumulation of toxic levels of acetylcholine. Like other organophosphorous compounds (pesticides), these agents act by binding to a serine residue at the active site of the cholinesterase molecule. The resulting accumulation of toxic levels of acetylcholine at the synapse initially stimulates and then paralyzes cholinergic synaptic transmission. Cholinergic synapses are found in the central nervous system, at the termination of somatic nerves, in ganglionic synapses of autonomic nerves, at parasympathetic nerve endings, and at some sympathetic nerve endings, such as those in the sweat glands (25,34). The reaction between organophosphorous compounds and acetylcholinesterase occurs in a three-step process (Fig. 4).

In step 1, a reversible enzyme-inhibitor complex is formed. The rate of complex formation depends on the structure of the organophosphorous compound, particularly the size and shape of  $\text{R}_1$  and  $\text{R}_2$ . In step 2, which results in phosphorylation and inactivation of the acetylcholinesterase molecule, the X moiety is displaced from the phosphorous atom by the hydroxyl group of the enzyme's target serine residue. The kinetics of this reaction is determined by the X moiety, which is referred to as the leaving group. Step 3 is a time-dependent reaction that modifies the enzyme-inhibitor complex in such a way that the organophosphorous compound and enzyme cannot be separated and the enzyme cannot be reactivated by oximes. This reaction, called "aging," involves the formation of a monophosphoric acid residue that is bound to the enzyme (25).

**2.8. Binary Munitions.** Binary munitions contain two nonlethal components that are mixed during flight to form a nerve agent. Each component is manufactured separately, remaining in its own container until the munition components are assembled just prior to use. Mixing and subsequent agent



**Fig. 4.** Activity of organophosphorus nerve agents.

formation occurs after firing or launch of the munition. In addition to greatly reduced storage and handling hazards, the binary components can be manufactured in ordinary chemical facilities, which need not be equipped with the stringent safety and environmental controls required for the older nerve agent munitions. The binary technology also overcomes the long-term storage problems associated with the unitary nerve agents.

**2.9. Other Lethal Agents.** There are a number of substances, many found in nature, which are known to be more toxic than nerve agents (27). None has been weaponized. Examples of these toxic natural products include shellfish poison, isolated from toxic clams; puffer fish poison, isolated from the viscera of the puffer fish; the active principle of curare; "heart poisons" of the digitalis type; the active principle of the sea cucumber; active principles of snake venom; and the protein ricin, obtained from castor beans (see CASTOR OIL).

**2.10. Incapacitants.** Incapacitating agents, or incapacitants, are just what the name implies. In wartime, soldiers and civilians must be physiologically, physically, and mentally able to perform their jobs. Thus, an agent rendering an individual incapable of job performance may be classified as an incapacitating agent (27,35).

Incapacitants are most suitable for consideration in limited warfare situations, eg, when enemy troops are intermingled with a friendly population, or in a city that is a key military objective. The purpose is to capture the enemy without killing the civilians. Incapacitating agents should produce no permanent after-effects and allow for complete recovery.

Agent BZ, 3-quinuclidinyl benzilate [6581-06-2],  $\text{C}_{21}\text{H}_{23}\text{NO}_3$ , is a typical incapacitant. BZ is one of a group of substances, many of them glycolate esters, sometimes known as atropinemimetics. Their action on the central and peripheral nervous systems resembles that of atropine [51-55-8],  $\text{C}_{17}\text{H}_{23}\text{NO}_3$ . The effects of BZ are those of an anticholinergic psychotomimetic drug (27). These effects follow  $\sim 1/2$  h after exposure to BZ aerosol, reach a peak in 4–8 hs, and may then take up to 4 days to pass. Effects include disorientation with visual and auditory

hallucinations. The agent disturbs the higher integrative functions of memory, problem solving, attention, and comprehension. There is a gradual return to normalcy.

By U.S. Army criteria, incapacitation agents do not include (35): (1) lethal agents that are incapacitating at sublethal doses, such as nerve agents; (2) substances that cause permanent or long-lasting injury, such as blister agents, choking agents, and those causing eye injury; (3) drugs that exert marked effects on the central nervous system, such as barbiturates, belladonna alkaloids (qv), tranquilizers, and many of the hallucinogens. These drugs are logistically infeasible for large-scale use because of the high doses required (see HYPNOTICS, SEDATIVES, AND ANTICONVULSANTS AND ANTIOLYTIC; NEUROREGULATORS; PSYCHOPHARMACOLOGICAL AGENTS); (4) agents of temporary effectiveness that produce reflex responses interfering with performance of duty. These include skin and eye irritants causing pain or itching (vesicants or urticants), vomiting- or cough-producing compounds (sternutators), and tear compounds (lacrimators); and (–5) agents that disrupt basic life-sustaining systems of the body and thus prevent physical activity. These include agents that lower blood pressure, paralyzing agents such as curare, fever-producing agents, and blood poisons. Such agents almost invariably have a narrow margin of safety between the effective and possibly lethal doses, and the basic purpose of an incapacitating agent is to reduce military effectiveness without endangering life.

**2.11. Use.** Owing to inherent physical characteristics, chemical agents can be adapted to a variety of munitions, including grenades, mines, artillery shells, bombs, bomblets, spray tanks, rockets, and missiles. Tactically, chemical agents have defensive and offensive capabilities in limited or general wars. Toxic chemical agents may be used alone or in conjunction with other types of weapons. Chemical weapons do not destroy matériel but allow physical preservation of industrial complexes and other facilities. Incapacitating agents may also be used to preserve life and avoid permanent injury.

The use of chemical agents in battle imposes a significant burden on troops because of the cumbersome nature of the protective clothing and the attendant heat load in hot climate situations. This factor alone imposes a burden on potential target personnel, lowering their effectiveness. U.S. troops in the 1991 Mideast war Desert Storm were provided with protective gear that did not deter them with regard to the outcome of the action.

### 3. Irritants

Irritant compounds such as the lacrimators and sternutators used in World War I are traditional examples of harassing agents, the effects of which are reversible and briefly incapacitating. Riot control agent CS, a modern irritant compound (27,35), causes physiological effects that include extreme burning of the eyes, accompanied by a copious flow of tears; coughing; difficulty in breathing; chest tightness; involuntary closing of the eyes; stinging sensation of moist skin; runny nose; and dizziness or “swimming” of the head. Heavy concentrations also cause nausea and vomiting.

The effects of agent CS are immediate, even in extremely low concentrations. The median concentration for respiratory effects is 12–20 mg/m<sup>3</sup>; for eye effects it is 1–5 mg/m<sup>3</sup>. The onset of maximum effects is 20–60 s, and the duration is 5–10 min after the individual has been removed to fresh air.

A water-soluble white crystalline solid, CS is disseminated as a spray, as a cloud of dust or powder, or as an aerosol generated thermally from pyrotechnic compositions. The formulation designated CS1 is CS mixed with an antiagglomerant; when dusted on the ground, it may remain active for as long as 5 days. CS2 formulated from CS1 and a silicone water repellent, may persist for as long as 45 days (12).

The principal uses of CS are in riot control and training; it has limited tactical use in defensive military modes (36).

## 4. Flame

In the modern weapons arsenal flame agents are defined as various hydrocarbons, blends of hydrocarbons, and other readily flammable liquids, usually thickened with additives, that are easily ignited and can be projected to military targets (35). Although flame agents may be employed against buildings and other flammable targets, their primary role is against personnel in hardened structures or emplacements. In the United States, the principal application of flame agents is now in flame throwers and flame projectors, including flame rockets. The firebomb is becoming obsolete. The replacement for the portable flame-thrower is the multishot flame rocket, which delivers an encapsulated flame warhead directly to the target from a significantly great and safe range. The large-caliber flame rounds could become all-weather, highly aimable replacements for the obsolete air-deliverable fire-bombs and the mechanized flame-throwers.

**4.1. Flame Throwers and Projectors.** One advance in flame-throwers since World War II was a mechanized flame-thrower kit for a variety of armored vehicles other than the main battle tank. The multishot, lightweight, shoulder-fired, four-tube flame system capable of firing one to four flame rounds semiautomatically is replacing the portable flame-thrower. Indeed the mechanized flame-thrower is expected to become obsolete because of the family of large-caliber flame rounds.

The U.S. Army's M202/M74 flame system is a shoulder-fired, four-tube launcher equipped with front and rear hinged protective covers. A folding sight and trigger handle assembly provide compact carrying and storage capabilities. An adjustable sling is used to carry the launcher over the shoulder. The rocket system is aimed and fired from the right shoulder from the standing, kneeling, sitting, or prone position. Ammunition for the launcher is provided in rocket clips preloaded with four rockets that slip-fit into the four launcher tubes. The user can fire from one to four rockets semiautomatically at a rate of one per second; the launcher can be reloaded with a new clip repeatedly. The flame agent payload is thickened pyrophoric agent TPA, a polyisobutylene-thickened metal alkyl formulation (37).

**4.2. Fire Bombs.** After World War II, the fire-bomb became a standard item of military equipment. A cigar-shaped, thin-cased tank similar in appearance to the aircraft fuel tank from which it evolved, the typical fire-bomb consisted of the basic tank, two igniters, two fuses, an arming wire, and the flame agent payload. Most fighter and fighter-bomber aircraft carried two, one under each wing. Ideal delivery was at low altitude, almost level flight, with the fire-bomb impacting along the aircraft flight path and producing a rolling wall of flame covering an area  $\sim 35$  m wide and 100 m in length. The initial fireball, a direct function of flame agent quality, burned for  $\sim 10$  s with intense heat. The dispersed particles could burn for up to 10 min but at greatly reduced intensity.

Upon the advent of high performance jet-powered aircraft, the fire-bomb became obsolete. When delivered at speeds approaching Mach one (345 m/s), the design characteristics were often grossly exceeded and many units broke up or functioned while still on the aircraft. Delivery from high altitude created craters and deposited most of the flame agent payload in those craters.

Studies of fire-bomb modifications and the corresponding flame agent payloads were terminated once the controlled fireball damage mechanism was developed. In field firings it was shown that large-caliber flame rounds could produce equivalent effects. The rolling wall of reacting flame could be generated, accompanied by a highly aimable, all-weather flame system capable of sustained fire.

**4.3. Flame Agents.** For some time after World War II, effort was expended in improvement of naplam-thickened hydrocarbons as the standard flame agents. The problem was the breakdown of the flame agent in the presence of traces of water and the need for peptizers in cold-weather applications. More recently, thickened pyrophoric flame agents (35) have been deployed in the field and as the payload for the U.S. Army's flame rocket system. Advantages of this newer flame agent include: the ability to prepackage warheads and other containers and store them for indefinite periods with no deterioration; and the fact that these pyrophoric flame agents do not require an ignition system to function on the target.

Computer-aided research by army personnel has resulted in development of the controlled fireball damage mechanism for efficient and effective coupling of heat energy to effect maximum thermal damage. Moreover, flame agents may be tailored to each candidate flame system. Optimization of several low viscosity metal-alkyl formulations has also removed the problem of temperature by making these flame agents relatively independent of temperature variations.

## 5. Incendiaries

Incendiary agents are designed for use in the planned destruction of buildings, property, and matériel by fire (35). Incendiaries burn with an intense, localized heat. They are very difficult to extinguish and are capable of setting fire to materials that normally do not ignite and burn readily. Although there are tactical applications for incendiary agents and munitions, they have played primarily a strategic role in modern warfare.

**5.1. Incendiary Requirements.** The mechanics of starting fires using incendiary agents involve a source of heat to act as a match to initiate combustion

in a larger mass; combustible material to serve as kindling; and fuel. The match and the kindling are provided by the incendiary munition; the target is the fuel. All incendiary munitions, except for those containing materials that are spontaneously combustible, must have some sort of initiator such as a fuse or an ignition cup. The second element of the incendiary munition, the kindling, is the important factor, and both the amount and the nature of the combustible material in the munition have been the subject of much research and development.

The maximum total heat output of an incendiary agent can be readily calculated and it is obviously desirable to use a filling that has a high heat evolution. The rate of the heat release varies with the agent and depends on: flash, fire, or decomposition temperature; particle size of the agent after ejection from the munition, which controls the surface/volume ratio of the agent; and oxidizing agents blended with the combustible material to increase the rate of heat evolution. The incendiary agent must be capable of heating the target or fuel until the ignition temperature, which can vary from 200–400°C, is reached. To be really effective, the incendiary agent must generate at least four times as much heat as is necessary to raise the temperature to this point.

**5.2. Metal Incendiaries.** Metal incendiaries include those of magnesium in various forms, and powdered or granular aluminum mixed with powdered iron(III) oxide. Magnesium is a soft metal that, when raised to its ignition temperature, burns vigorously in air. It is used in either solid or powdered form as an incendiary filling, and in alloyed form as the casing for small incendiary bombs.

Magnesium has an ignition temperature of 623°C and a burning temperature of ~1982°C. The burning temperature is variable; it depends on the rate of heat dissipation, rate of burning, and other factors. Magnesium, burning with a blinding white flame, melts as it burns and the burning liquid metal drops to lower levels, igniting all combustible materials in its path. Burning stops if oxygen is prevented from reaching the metal or if the metal is cooled to a point below its ignition temperature. Whereas magnesium does not have the highest heat of combustion of the metals, none of the other metals have been successfully used as air-combustible incendiaries. Some metals may be alloyed with magnesium without affecting its ignitability. The alloyed metal has the strength to withstand distortion, whereas pure magnesium does not. In massive form, magnesium is difficult to ignite. This problem is overcome by packing a hollow core in a bomb with thermite [8049-32-9]. This results in an easily ignited mixture that supplies its own oxygen and burns at a very high temperature.

Thermite is essentially a mixture of ~73 wt% powdered iron(III) oxide, Fe<sub>2</sub>O<sub>3</sub>, and 27 wt% powdered or granular aluminum. The aluminum has a higher affinity for oxygen than iron, and if a mixture of iron oxide and aluminum powder is raised to the combustion temperature of aluminum, an intense reaction occurs



Under favorable conditions the thermite produces temperatures of ~2200°C, high enough to turn the newly formed metallic iron into a white-hot liquid that acts as a heat reservoir to prolong and spread the heat or igniting action.

The thermate mixture, composed of thermite and various additives, is used in igniter compositions for magnesium bombs. A number of such compositions have been developed. Three of these were Therm-8, Thermate-TH2 (formerly Therm-8-2), and Thermate-TH3 (formerly Therm-64-C). Therm-8 was the precursor of later, improved igniting formulations TH2 differs from Therm-8 in that TH2 contains no sulfur and slightly less thermite. TH3 was found to be superior to the others and thus adopted for use in the incendiary magnesium bomb. The wt% composition of TH3 is thermite, 68.7; barium nitrate, 29.0; sulfur, 2.0; and as a binder, oil, 0.3.

The TH3 core is ignited by the primer, and the burning core then melts and ignites the magnesium alloy body of the bomb. The incendiary action on the target is localized. There is little scattering of the incendiary material.

**5.3. Oil and Metal Incendiary Mixtures.** PT1 is a complex mixture composed of magnesium dust, magnesium oxide, and carbon (qv), along with an adequate amount of petroleum (qv) and asphalt (qv) to form the paste (37). The U.S. developers have adopted the formula: type c paste (goop),  $-49.0 \pm 1.0$ ; IM polymer AE,  $3.0 \pm 1.0$ ; coarse magnesium,  $10.0 \pm 1.0$ ; petroleum oil extract,  $3.0 \pm 0.2$ ; gasoline,  $30.0 \pm 3.0$ ; and sodium nitrate,  $5.0 \pm 0.5$ .

PTV is an improved oil and metal incendiary mixture having the composition: polybutadiene,  $5.0 \pm 0.1$ ; gasoline,  $60.0 \pm 1.0$ ; magnesium,  $28.0 \pm 1.0$ ; sodium nitrate,  $6.0 \pm 0.1$ ; and *p*-aminophenol, 0.1.

Incendiary bombs containing PT1 or PTV mixtures are easily ignited by nose or tail fuses because they contain many combustible ingredients. These formulations contain both metal and an oxidizer, eg, sodium nitrate; thus condensed phase reaction products are obtained. The resulting heat flux conducted to the target is increased, resulting in greater potential target damage.

## 6. Smokes

Military smokes are aerosols (qv) of gaseous, liquid, or particulate matter that are tactically employed to defeat enemy surveillance, target acquisition, and weapons guidance devices. The traditional battlefield applications of smoke are screening and marking. Screening smokes are normally employed to obscure a military objective from enemy observation by creating an aerial blanket, vertical curtain, or ground haze. Signaling smokes are pyrotechnic mixtures that incorporate an organic compound dyed for target marking or for transmitting messages by pre-arranged color code (see PYROTECHNICS).

Battlefield smoke has a great significance in the countermeasure role. Threat weapons no longer rely simply on optical devices that operate in the visible spectrum. Modern lethal weapons are augmented with sophisticated surveillance, target acquisition, and guidance devices that operate throughout the visible, infrared (ir), and microwave (radar) regions of the electromagnetic spectrum. Accordingly, research and development is concentrated on nonvisual multispectral screening systems designed to defeat modern weaponry such as the antitank guided missile (ATGM), laser-guided munitions, and heat-seeking missiles.

**6.1. Screening Smokes.** Military smoke screens are produced by dispersing either finely divided solids or minute liquid droplets in air. To be useful, a smoke screen must be sufficiently opaque to provide the desired screening power and long-lasting enough to achieve effective military results. In designing a screen for the modern battlefield, it is necessary to defeat sophisticated surveillance technologies that operate in the near-, mid-, and far-ir as well as in the millimeter wavelength frequencies. Other factors considered in the evaluation of potential screening agents include cost, ease of dispersion, and efficiency of dispersion. Agents used for screening friendly areas must be as nonirritating as possible.

Both the opacity and persistency of smoke screens are largely dependent on the nature of the individual smoke particles. All present U.S. smoke agents produce aerosols. The principal mechanism of obscuration is the scattering effect. To optimize its effectiveness, the aerosol's particle size should be approximately in the same size range as the wavelength of the light to be screened. Many U.S. smoke agents produce aerosols having particle-size distribution that is log-normal having a mean diameter of  $\sim 0.6 \mu\text{m}$ , allowing maximum effectiveness in the visible and near-ir wavelength regions. More recently, fine fibers have been used as screens for longer wavelengths and in mixtures or combined usage to screen the entire region of concern.

The obscuring action of visual screening smokes is largely caused by reflection and refraction of light by the individual suspended particles of which the smoke is composed (35). Because this obscuring action occurs to the greatest extent in the absence of light-absorbing particles such as carbon, white smokes have the greatest screening action.

Chiefly wind and convection currents in the air determine the persistency of a smoke cloud. Ambient temperature also plays a part in the continuance or disappearance of fog oil smokes. Water vapor in the air has an important role in the formation of most chemically generated smokes, and high relative humidity improves the performance of these smokes. The water vapor not only exerts effects through hydrolysis, but it also assists the growth of hygroscopic (deliquescent) smoke particles to an effective size by a process of hydration. Smoke may be generated by mechanical, thermal, or chemical means, or by a combination of these processes (35).

**6.2. Types of Screening Smokes.** The generation of oil smoke is based on the production of minute oil droplets by purely physical means. The most desirable droplet size is  $0.5\text{--}1.0 \mu\text{m}$ . The tiny droplets of oil scatter light rays and produce a smoke that appears to be white, and any individual droplet would be transparent under magnification. These droplets are produced as the vaporized oil passes through the nozzle of a generator and is subsequently cooled by the surrounding air. The air cools the oil vapor so quickly that only very small droplets are able to form. The process thus depends on a high oil temperature followed by quick cooling. Proper selection of the smoke oil ensures that the final smoke cloud is stable, and the life of the cloud is determined almost entirely by meteorological conditions. The smoke generator uses a low viscosity petroleum oil (U.S. Army designation: SGF No. 2 smoke generator fog). SGF corresponds somewhat to an SAE 10 (light) motor oil in viscosity. Below  $0^\circ\text{C}$ , a mixture of SGF No. 2 and a paraffin-free kerosene is used.



Another type of smoke mixture, a volatile hygroscopic chloride for thermal generation, has the U.S. Army designation HC, type C. It is composed of ~6.7 wt% grained aluminum, 46.7 wt% zinc oxide ZnO, and 46.7 wt% hexachloroethane [67-72-1],  $C_2Cl_6$ . The ratio of zinc oxide to hexachloroethane is held between 1.04 and 1.00, but the aluminum may be varied slightly to regulate the burning time. Because this mixture is composed of solids, it can be compressed to provide high payloads in small volumes, and it is used as a filling for smoke grenades, smoke pots, and artillery shells. The initial heat needed to start the burning of HC is provided by a starter mixture, typically silicon, potassium nitrate, charcoal, iron oxide, grained aluminum, cellulose nitrate, and acetone. A burning HC mixture produces zinc chloride which, in turn, is volatilized by reaction heat and condenses to form a zinc chloride–water smoke.

A third screening smoke-type is white phosphorus [7723-14-0] (WP),  $-P_4$  (see PHOSPHORUS AND THE PHOSPHIDES), which reacts spontaneously with air and water vapor to produce a dense cloud of phosphorus pentoxide [1314-56-3]. An effective screen is obtained as the  $P_2O_5$  hydrolyzes to form droplets of dilute phosphoric acid aerosol. WP produces smoke in great quantity, but it has certain disadvantages. Because WP has such a high heat of combustion, the smoke it produces from bulk-filled munitions has a tendency to rise in pillarlike mass. This behavior too often nullifies the screening effect, particularly in still air. Also, WP is very brittle, and the exploding munitions in which it is used break it into very small particles that burn rapidly.

The disadvantages of WP have been overcome to some degree by absorbing WP into felt wedge submunitions that burn and release smoke at a lower rate and by the development of plasticized white phosphorus (PWP). PWP is produced by melting WP and stirring it into cold water, which results in a slurry of WP granules of ~0.5-mm diameter. The slurry is mixed with a viscous solution of synthetic rubber, so that the granules are coated with a film of rubber and thus separated from each other. When PWP is dispersed by an exploding munition, it does not break into such small particles; the burning rate is slowed, and the tendency of the smoke to pillar is reduced. WP and PWP are used as fill for grenades, artillery shells, mortar shells, bombs, and rockets.

Developments in several countries have resulted in red phosphorus (RP) as a screening smoke agent having less performance problems. RP is an allotropic form of elemental phosphorus, which is made by heating white phosphorus at high temperatures in the absence of air. RP is less reactive than WP and thus lends itself to the manufacture of presized subunits that can be packaged in artillery and mortar shells. These subunits, which are dispersed as multiple smoke-producing sources, enhance target effectiveness by the rapid formation of a large homogeneous and persistent screen. The pillaring phenomenon is thus minimized. Another advantage of RP is that it does not undergo a change of state at operational temperatures thereby precluding the munition instability problems that sometimes occur with WP, which liquefies  $> 43^\circ C$ .

A solution of sulfur trioxide [7446-11-9],  $SO_3$ , dissolved in chlorosulfonic acid [7990-94-5],  $ClSO_3H$ , has been used as a smoke (U.S. designation FS) but it is not a U.S. standard agent (see CHLOROSULFURIC ACID; SULFURIC ACID AND SULFUR TRIOXIDE). When FS is atomized in air, the sulfur trioxide evaporates from the small droplets and reacts with atmospheric moisture to form sulfuric acid

vapor. This vapor condenses into minute droplets that form a dense white cloud. FS produces its effect almost instantaneously upon mechanical atomization into the atmosphere, except at very low temperatures. At such temperatures, the small amount of moisture normally present in the atmosphere, requires that FS be thermally generated with the addition of steam to be effective. FS can be used as a fill for artillery and mortar shells and bombs and can be effectively dispersed from low performance aircraft spray tanks. FS is both corrosive and toxic in the presence of moisture, which imposes limitations on its storage, handling, and use.

**6.3. Signaling Smokes.** Screening smokes also can be adapted for signaling purposes. For example, phosphorus-filled artillery and mortar rounds can be used to mark targets and determine range corrections. However, a good signaling smoke must be clearly distinguished from the smoke incident to battle. The standard signaling smokes, described in Table 3, afford good visibility and unmistakable identity. Unfortunately, all colors become gray and indistinguishable at great distances, and even excellent signaling smokes have a maximum effective visual range that varies from  $\sim 1\text{--}3$  km, depending on the color intensity of the smoke and the type and size of the munition.

Volatilizing and condensing a mixture containing an organic dye produce colored signaling smokes. Of the dyes tested by the U.S. Army, the most satisfactory ones are the azo dyes (qv), the azine dyes (qv), the diphenylmethane dyes, and those of anthraquinone (qv) (35) (see DYES AND DYE INTERMEDIATES). The filling for a colored smoke munition is essentially a pyrotechnic mixture of fuel and dye, with a cooling agent sometimes added to prevent excessive decomposition of the dye. The heat produced by the fuel volatilizes the dye, and the dye condenses outside the munition to form the colored smoke. In U.S. munitions, the fuel is made up of a mixture of an oxidizing agent such as potassium chlorate,  $\text{KClO}_3$ , and a combustible material such as sulfur or sugar. The burning time can be regulated by adjusting the proportions of oxidant and combustible material and by use of coolants such as baking soda. A typical starter mixture is given in Table 3. Colored smoke mixtures are used in hand and rifle grenades and in canisters for use with larger projectiles.

## 7. Defense Against Toxic Agents

Defensive measures against toxic agents may be divided into four categories: agent detection and identification, individual and collective protection, decontamination, and medical defense. To these may be added a high degree of training in defensive measures and discipline in using them.

**7.1. Detection.** The utilization of various technologies to sample the environment in search of chemical weapons agents is known as detection, and two major classifications of detection exist. If the environment being probed for the existence of chemical agent concentrations is in the immediate vicinity, it is known as point detection. If the search for chemical agents is occurring at some distance from the detector, it is referred to as remote or stand-off detection.

The United States has deployed several chemical sensors. The Automatic Chemical Agent Detector and Alarm is a man-portable vapor alarm designed

Table 3. Colored Smoke Fillings

Ingredient	CAS Registry number	Molecular formula	Composition, wt%
<i>Red smoke</i>			
dye:			
85% 1- <i>N</i> -methylaminoanthraquinone;	[82-38-2]	C <sub>15</sub> H <sub>11</sub> NO <sub>2</sub>	
15% dextrin	[9004-53-9]		42
sodium bicarbonate	[144-55-8]	NaCHO <sub>3</sub>	19
potassium chlorate	[3811-04-9]	KClO <sub>3</sub>	28
sulfur	[7704-34-9]	S	11
<i>Green smoke</i>			
dye:			
70% 1,4,di- <i>p</i> -toluidinoanthraquinone;	[128-80-3]	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	
10.5% indanthrene golden yellow;	[128-66-5]	C <sub>24</sub> H <sub>12</sub> O <sub>2</sub>	
19.5% benzanthrone	[82-05-3]	C <sub>17</sub> H <sub>10</sub> O	40.0
sodium bicarbonate			22.6
potassium chlorate			27.0
sulfur			10.4
<i>Yellow smoke</i>			
dye:			
65% benzanthrone;	[82-05-3]	C <sub>17</sub> H <sub>10</sub> O	
35% indanthrene golden yellow	[128-66-5]	C <sub>24</sub> H <sub>12</sub> O <sub>2</sub>	38.5
sodium bicarbonate			33.0
potassium chlorate			20.0
sulfur			8.5
<i>Violet smoke</i>			
dye:			
80% 1,4-diamino-2,3-dihydroanthraquinone;	[83-61-0]	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	
20% 1- <i>N</i> -methylaminoanthraquinone	[82-38-2]	C <sub>15</sub> H <sub>11</sub> NO <sub>2</sub>	42.0
sodium bicarbonate			18.0
potassium chlorate			28.8
sulfur			11.2
<i>Starter</i>			
potassium nitrate	[7757-79-1]	KNO <sub>3</sub>	37.8
silicon	[7440-21-3]	Si	28.0
charcoal	[7440-44-0]	C	4.2
cellulose nitrate	[9004-70-0]		1.2
acetone	[67-64-1]	C <sub>3</sub> H <sub>6</sub> O	28.8

to have greater capability than the current M8A1 detector against standard blister and nerve agents. The first U.S. Army unit was equipped in 1998, and it is starting to be procured in numbers. The Improved Chemical Agent Monitor (ICAM) is a hand-held, real-time detector of nerve and mustard agents in vapor phase on personnel or equipment. The program is also based on a product developed by Graseby in the U.K., and is intended to replace the CAM, significantly improving that system's reliability and maintainability. The United States has bought ~5000 ICAMs (38).

The Joint Chemical Agent Detector (JCAD) is a pocket-sized detector for use especially on aircraft and ships. It is entering into the operational test and evaluation phase, with production of more than 250,000 expected to begin in

Fiscal Year 2003 (FY03). Manufactured by BAE Systems of Austin, Texas, it is expected eventually to replace all current U.S. point detectors (38).

In the area of stand-off chemical detection, The Joint Service Lightweight Nuclear, Biological, Chemical Reconnaissance System (JSLNBCRS) is a vehicle-mounted system designed to sample, detect and identify threats within a unit's area of responsibility. It is intended to replace the Fox Nuclear, Biological and Chemical Reconnaissance System vehicle made by General Dynamics Land Systems and Henschel Wehrtechnik (Germany). The Fox uses the M21 Remote Sensing Chemical Agent Alarm, e.g., while the JSLNBCRS will incorporate the Joint Service Standoff Chemical Agent Detector (JSLSCAD) that improves on the M21. Some advanced detectors are also planned to be integrated into the Block II Fox NCBRS. JSLSCAD prototypes for High-Mobility Multipurpose Wheeled Vehicles (HMMWVs) and Light Armored Vehicles are under going development and initial operational testing, with full-scale production of 700 vehicles scheduled to begin in FY03 (38).

Individual chemical sensors would be much more effective if integrated into a network. Multiple sensors would provide mutual support, and rapid attack characterization, as well as minimizing false alarms. The Joint Warning and Reporting Network (JWARN) is a command and control information system that will be used by NBC specialists in various headquarters units to analyze data and support commanders' decisions, while extending warning down to individual battlefield units. It will seek to integrate legacy systems and future detectors. Block I software has been developed. A new Block II Operational Requirements Document has just been issued, and a solicitation is expected from the U.S. Marine Corps Systems Command (38).

**7.2. Individual and Collective Protection.** The United States has in the past insisted its troops be able to "fight dirty," in a contaminated environment. The United States sets a high limit for chemical agent protection ( $10 \text{ g/m}^2$  for liquids;  $5000\text{--}10,000 \text{ mg min/m}^3$  for vapors). This was designated in light of the threat when the former Soviet Union stockpiled chemical munitions by the ton and a possible struggle for societal survival was envisaged. Current potential enemies have less well-developed toxic capabilities, and there are suggestions that the high standards for protection need to be eased. This would also facilitate contaminated environments, in that heat stress and cumbersome equipment could be diminished. While current and planned protective equipment is designed to meet the high standard, there has been an increased emphasis on trying to reduce the significant troop performance decrement associated with it. This includes developing decontaminant creams to wear on the skin under seams and gloves (38).

The primary item of individual protection is the protective or gas mask. The U.S. Army standard mask is the M17A2, which has as its basic components a molded rubber facepiece with large cheek pouches that hold filter elements. These elements consist of six sheets of core laminated between two sheets of backing layer. The backing layers are composed of vinyl chloride–vinyl acetate copolymer, cellulose, and glass fibers. The core layers are composed of these same materials plus 75% Whetlerite absorbent, a finely ground activated carbon impregnated by immersion in an ammoniacal solution of silver, copper, chromium, and carbon dioxide, and then dried at temperatures sufficient to expel

substantially all ammonia from the granules. Inhalation valves are attached to the filter element caps through the cheek-pouch portions of the mask faceblank. A voicemitter-outlet assembly, incorporating a speech diaphragm and an outlet valve, is attached to the faceblank at the mouth position. Large eyepieces in the faceblank provide a wide field of vision. The M17A2 mask provides complete respiratory protection against all known military toxic chemical agents, but it does not provide protection against some industrial toxics such as ammonia and carbon monoxide.

A newer improved mask developed by the U.S. Army is in production and is expected to be fielded in the 1990s. The M40 (Figs. 5 and 6) and M42 chemical-biological masks are to replace the M17A2 and several other specialty masks, making for greater logistical simplicity as well as better respiratory, eye, and face protection against field concentrations of chemical and biological agents. Improvements include an externally mounted NATO standard canister, front and side voicemitters, microphone compatibility, drinking capability for all personnel, compatibility with combat spectacles, and better fit and comfort.

The mask alone, however, does not provide protection from substances such as nerve and blister agents that penetrate through the skin. Thus protection for the entire body should be provided. Airtight, impermeable clothing is available for personnel who must enter heavily contaminated areas. Such clothing is cumbersome and enervating because it retards release of body heat and moisture, and personnel efficiency is drastically lowered when it is worn for a long time. Although resistant to liquid chemical agents, impermeable clothing may be penetrated after a few hours exposure to heavy concentrations of agent. Consequently, liquid contamination must be neutralized or removed as soon as possible.



**Fig. 5.** The M40 chemical-biological mask shown with hood that increases protection against liquid contamination.



**Fig. 6.** Overgarment issued to troops operating in forward areas (19) that do not have access to or time to use any type of decontamination procedures.

For field use, combat troops use the battledress overgarment (BDO) shown in Figure 6. This overgarment protects against skin contact with chemical agent vapors, aerosols, and droplets of liquid. It consists of a two-piece suit in a camouflage pattern: the jacket has a zippered front, and trousers have a fly front and zippered legs. The BDO, supplied in a vapor-barrier bag that protects it from rain, moisture, and sunlight, consists of a water-repellent outer layer of nylon-cotton and an inner layer of charcoal impregnated polyurethane foam. The overgarment is discarded once contaminated.

The BDO is being replaced with an effective lightweight suit, the Joint Service Lightweight Integrated Suit Technology (JSLIST). The BDO generated controversy previously as quality-control issues came to light. The BDO is being supplanted by JSLIST, as the military is procuring 300,000 of these suits annually. One of the great improvements is that soldiers are supposed to be able to work ~45 min/h while wearing this suit, as compared to only 15 min/h in the old one. There is also a preplanned improvement for JSLIST under development (38).

The U.S. approach is to enable donning increasing levels of protection over the uniform, going from Military Oriented Protective Posture (MOPP)-ready (having gear available) to fully protected (MOPP 4) in ~8 min. However, adding garments when one is already masked often causes the mask to break its seal temporarily but significantly. The new joint service general purpose mask is more comfortable, but may not remedy this problem. Other countries, such as

France, have a different approach, and have lightweight suits worn directly on the skin rather than over the uniform (39).

The protective clothing issued to military personnel provides protection against high concentrations for prolonged periods, but is constraining and, in a hot climate, increases the risk of heat stroke, especially in individuals treated with atropine (39).

The U.S. military now has a mission to support homeland defense. However, its Personal Protective Equipment is not compatible with that of civilian responders. National Institute for Occupational Safety and Health does not accept military MOPP gear for civilian first responders, mandating a self-contained breathing apparatus rather than air purifying respirators. The DoD may want to reconsider whether it should purchase some civilian protection equipment to meet some of its needs, in addition to its military-specific developments (38).

Collective protection enclosures are required for groups of personnel. Such enclosures must be airtight to prevent inward seepage of contamination. They can be independent units or can be formed by adequately treating the interior walls of structures, tents, airplanes, or vehicles. A supply of uncontaminated air, provided by passing ambient air through high efficiency aerosol and carbon filters, must be provided.

Simplified collection protection equipment (SCPE) (U.S. designation M20) provides such protection using lightweight elements consisting of an inflatable enclosure, a hermetically sealed filter canister, motor blower, protective entrance, and a support kit. The SCPE is designed to be used inside another structure or tent. The modular collective protection equipment (MCPE) is designed to support enclosures such as rigid wall shelters or vans. The MCPE comprises a family of items, consisting of four filter units of different sizes, external and internal protective entrances, and a motor controller. The entire system is flexible by choice of items to fit a large variety of adaptations.

**7.3. Decontamination.** If contaminated equipment or material does not have to be used immediately, natural aeration is an effective decontaminant procedure, as most chemical agents, including the blister and V-agents, are volatile to a certain degree. Wind accelerates their evaporation and hastens their dissipation. Rain and dew may also cause sufficient hydrolysis of some agents. Sunlight increases the surface temperatures of military equipment and thus accelerates agent evaporation.

If decontamination cannot be left to natural processes, chemical neutralizers or means of physical removal must be employed. In general, the neutralizers are of two types: chlorine-based oxidants or strong bases. Some neutralizers have been especially developed for the decontamination of chemical agents.

One such decontaminant is supertropical bleach (STB). STB is a mixture of chlorinated lime and calcium oxide containing ~30% available chlorine. It can be used either as a dry mix or as a slurry to decontaminate some equipment surfaces and terrain. The dry mix is prepared with two parts bleach to three parts earth by volume. A slurry typically consists of 40 parts STB to 60 parts by weight of water. This material is then sprayed or swabbed on the contaminated surface (see BLEACHING AGENTS). STB is an effective decontaminant for mustard, lewisite, and VX. It is less effective against nerve agents other than VX.

Decontaminating agent DS2 is a general purpose equipment decontaminant, consisting of 70 wt% diethylenetriamine, 28 wt% ethylene glycol monomethyl ether, and 2 wt% sodium hydroxide. DS2 reacts with nerve agents and blister agents to effectively reduce their hazards within 5 min. Important limitations in the use of DS2 include: irritation to the eyes and skin, and inhalation of the vapors may be harmful; it is a combustible liquid, therefore it must not be used on hot metal surfaces such as running engines or exhaust pipes; it is not suitable for use on personal equipment such as mask or clothing or on electrical or electronic equipment; in the pure state, DS2 is noncorrosive to most metals but it may cause corrosion of aluminum, cadmium, tin, or zinc after prolonged contact; and whereas it can be used on surfaces coated with polyurethane paint, it may remove other paints, especially fairly new ones.

The M258A1 decontaminant kit, personal, is used by the individual soldier for emergency decontamination of skin and partial decontamination of personal equipment. The kit consists of three Decon 1 towelette wipes and three Decon 2 wipes, which are individually sealed in impermeable foil packets. The Decon 1 packet contains a towelette prewetted with a solution of 72 wt% ethanol, 10 wt% phenol, 5 wt% sodium hydroxide, 0.5 wt% ammonia, and the rest water. The Decon 2 packet contains a towelette impregnated with dry chloramine B and glass ampuls filled with a solution 44 wt% ethanol, 5 wt% zinc chloride, and the remainder water. The glass ampuls are contained in plastic mesh bags to prevent injury when the ampuls are broken. The M258A1 is effective against all threat agents including biological agents and toxins. It is capable of three complete decontaminations of exposed skin (hand, neck, face) and partial decontamination of personal equipment. Storage and handling of the kits require special consideration. Each of the solutions are poisonous and present a caustic burn hazard. The wipes are not to be used on eyes, wounds, or mouth. Also the kits must be stored in a dry place away from direct sunlight and flammable materials.

The M258A1 is being replaced through attrition by the M291 skin decontamination kit. This item contains six individual skin decontamination packets for the emergency decontamination of skin. Each packet contains a nonwoven fiber polybacked applicator pad impregnated with 2.8 g of Ambergard XE-555 resin. Applicator pads have strap handles for ease of use. Individual pads are hermetically packaged in olive drab-colored, heat-sealed, polyester-foil laminate material, which is notched on each corner for ease of opening. The six packets are carried in a flexible, walletlike carrying pouch constructed of nonwoven fabric. Total weight is 45 g, and it fits easily into the trousers pocket of the battledress uniform (BDU) and the protective BDO.

Besides these specially designed decontaminants and kits there are a number of commercially available materials that will partially decontaminate chemical agents. Such materials are listed in the *U.S. Army Field Manual FM 3-5*, NBC Decontamination.

**7.4. Medical Defense.** The most important items of U.S. medical defense against organophosphorus nerve agents are atropine and pralidoxime chloride [51-15-0], (2-PAM),  $C_7H_9ClN_2O_2$ . These agents neutralize the effects of the anticholinesterase compounds and are capable of reactivating the inhibited enzymes. If adequate emergency treatment is immediately available, it is theoretically possible to save a high percentage of those affected by the agent. Oximes such as pralidoxime displace nerve agents bound to AChE, allowing



AChE to resume hydrolyzing ACh (40). Before aging has occurred, administration of nucleophilic oximes, such as pralidoxime chloride, can reactivate the phosphorylated acetylcholinesterase, but such treatment is ineffective after aging (34). Oximes are ineffective after aging has occurred (41). American soldiers carry three 600-mg autoinjectors for concurrent intramuscular use with atropine (39). Atropine competitively inhibits muscarinic effects and has a central role in the treatment of nerve agent poisoning. Soldiers carry three 2-mg autoinjectors for use when first symptoms appear (41). More recently the use of a pretreatment has been developed using pyridostigmine bromide [101-26-8],  $C_9H_{13}BrN_2O_2$ , when the threat or possibility of exposure occurs. During the 1991 Desert Storm action, over 40,000 U.S. troops were so pretreated. Presently, American soldiers are issued 30-mg tablets of pyridostigmine bromide to be taken, on order, every 8 h for up to 14 days when at risk of nerve agent exposure (42). Similar pretreatment compounds are in use in other countries (13,23).

Immediate treatment of an exposed individual is essential. The U.S. regimen includes the pretreatment, and after exposure atropine and 2-PAM are self-administered. Further treatment includes up to two additional doses, followed by the tranquilizer Valium. As required, artificial respiration is instituted, clearing the airway if necessary. The current standard U.S. Army atropine item is the automatic injector, Atropen, designed for self-administration by the individual in the field.

Research on other protective measures includes the use of excess circulating acetyl- and butyryl- cholinesterases as scavengers. Monoclonal antibodies and carboxylesterase are being investigated as means to deactivate nerve agents in blood before they reach synapses (29).

Vesicant agents, such as mustard, require no special treatment once the burns have occurred. Copious washing is quite effective when used early for liquid contamination of the eyes, and soap and water removes the liquid agent from the skin. Burns resulting from mustard agent are treated like any other severe burn. The pulmonary injuries are treated symptomatically; antibiotics are used only if indicated for the control of infection.

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