13
Advances in chemical and biological protective clothing

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Abstract: Protection against hazardous chemical and biological (CB) materials is necessary in many aspects of everyday life and can be provided by the proper selection of protective clothing. Variables to be considered include weight, comfort, level of protection, and the duration of protection required. To cover the range of situations that may be encountered, a spectrum of CB protective materials and clothing systems has been developed. This chapter reviews the types of materials and clothing systems currently in use and the science and technology efforts underway to maximize protection and comfort.

Key words: chemical protective clothing, biological protective clothing, chemical protective materials, biological protective materials.

13.1 Introduction

Protection against hazardous chemical and biological (CB) materials is necessary in many aspects of everyday life. Proper protective clothing is needed during household chores and in industrial, agricultural, and medical work, during military operations; and in response to incidents of terrorism. This clothing generally involves a respirator or dust mask, hooded jacket and trousers or one-piece coverall, gloves, and overboots, individually or together in an ensemble. Many different types of materials and garment designs are used in these clothing items, and protection levels vary considerably. Choices must be made as to which items of protective clothing to select for a given situation or environment. Variables to be considered include weight, comfort, level of protection, and the duration of protection required. In addition, the nature of the challenges to be encountered is also of significant consideration. Due to the large number of variables involved, a spectrum of CB protective materials and clothing systems has been developed. Fully encapsulating ensembles made from air impermeable materials with proper closures provide the highest levels of protection. These latter ensembles are recommended for protection in situations where exposure to hazardous chemicals or biological agents would pose an immediate danger to life and health.

Chemical warfare agents (CWAs) such as chlorine, phosgene, and mustard gas (also known as blistering agent), were used in World War I (WWI). As

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Table 13.1 Formulae of some traditional chemical agents

Chemical agents	Formula
Sulfur mustard	$(ClCH_2CH_2)_2S$
Sarin	$C_4H_{10}FO_2P$
Soman	$C_7H_{16}FO_2P$
VX	$C_{11}H_{26}NO_2PS$

a result there were over a million casualties, with approximately 90 000 deaths.[1] Nerve agents, consisting of organophosphorus compounds, were developed during the 1930s.[2] CWAs were not used during WWII. There are many examples of CWA use from historical records. Italy sprayed mustard gas from aircraft against Ethiopia in 1935. Japan used CWAs when they invaded China in 1936. Egypt used phosgene and mustard gas bombs in the 1960s in the Yemeni Civil War. During the Iran–Iraq war between 1980 and 1988, Iraq used sulfur mustard and probably nerve agents on their own Kurdish civilians in northern Iraq and in the city of Halabja.[3] It was reported that 5000 civilians were killed. The Aum Shinrikyo cult used Sarin nerve agent to terrorize Matsumoto City in 1994 and then attacked the Tokyo subway system in 1995. The Tokyo subway incident exposed some 5–6000 people and killed 12.[4] In 2002, 115 people died as a result of the Russian government's use of the chemical BZ, a 'knockout gas,' to subdue about 50 Chechen armed guerillas holding about 800 Russians hostage in a Moscow theater. The chemical formulae of some traditional agents are provided in Table 13.1.

The use of biological warfare agents (BWAs) has been recorded as early as the 6th century BC when the Assyrians poisoned enemy wells with rye ergot. In 1937, Japan used aerosolized anthrax in experiments on prisoners. There were several cases of suspected 'yellow rain' incidents in Southeast Asia, and the suspected use of trichothecene toxins (T2 mycotoxin) in Laos and Cambodia. In 1978, ricin was used as an assassination weapon in London. In 1979, there was an accidental release of anthrax at Sverdlovsk. In 1991, Iraq admitted its research, development, and BWA weapons production of anthrax, botulinum toxin, Clostridium perfringens, aflatoxins, wheat cover smut, and ricin to the UN. In 1993, a Russian BW program manager, who had defected, revealed that Russia had a robust biological warfare program, including active research into genetic engineering and binary biological weapons.[5]

Recent military concerns have included toxic industrial chemicals (TICs) as emerging threats where TICs include chemicals such as common acids, alkalis, and organic solvents. However, it should be noted that TICs have long been a concern for military personnel, civilian emergency responders, and industrial chemical handlers. Next generation CB protection is being developed with TIC protection very much in mind.

13.2 Current chemical and biological (CB) protective clothing

There are many different types and designs of CB protective clothing that are available to both the military and civilians for use in particular circumstances and threat scenarios. Currently, the US military uses a CB protective ensemble known as the Joint Service Lightweight Integrated Suit Technology (JSLIST) overgarment.[6] The JSLIST, when worn with gloves and boots as shown in Fig. 13.1, provides protection against CWAs for 24 hours. It is

13.1 Joint Service Lightweight Integrated Suit Technology (JSLIST).

designed for extended use, can be laundered every seven days, and is disposable after 45 days of wear, even if not contaminated. It contains a clean and breathable sorptive liner material as part of its textile structure. The JSLIST overgarment has an integral hood and raglan sleeve design which allows more freedom of movement. Its integrated suspenders (braces) allow individualized fitting for individuals of diverse sizes. Its wrap-around hook and loop leg closures allow ease of donning and doffing. Similar carbon-based, air permeable overgarments are used by many other countries.

Another US military clothing system is the chemical protective undergarment (CPU).[7] The CPU is a two-piece, snug-fitting undergarment worn under any standard duty uniform. It is a stretchable fabric that is designed to provide up to twelve hours of vapor protection, and it has a 15-day service life. The CPU is shown in Fig. 13.2. Civilian variants of these garments are also available.

13.2 Chemical protective undergarment (CPU).

Recent R&D efforts in individual CB protection have been on the development of advanced CB protective clothing systems that are lighter in weight with reduced thermal burden. The aim is to enable the future soldier to operate longer in a CB contaminated environment comfortably, safely, and effectively. One of the current emphases is on the use of selectively permeable membranes (SPMs) as a component in future soldier systems. SPM-based CB protective clothing systems are about a third to half the weight of the standard CB clothing systems, depending on the clothing system's specific materials and design. The development of such systems has demonstrated that it is possible to limit or eliminate the need for activated carbon, the use of chemical protective overgarments, the use of chemical protective undergarments, the use of rubber gloves, and the use of overboots. The elimination of any or all of these clothing items would represent significant weight, logistics concern, and cost reductions, as well as an increase in comfort. In addition to membranes in the form of films, electrospun nanofiber membranes and fabrics are being extensively investigated for applications in CB clothing.

Soldiers as well as civilians use special-purpose clothing such as the Improved Toxicological Agent Protective (ITAP) ensemble and the Self Contained, Toxic Environment Protective Outfit (STEPO) during emergency operations for chemical spills, toxic chemical maintenance, and cleanups in environments with higher threat concentrations. The ITAP and STEPO are shown in Figs 13.3 and 13.4, respectively. The ITAP is used in Immediately Dangerous to Life or Health (IDLH) toxic chemical environments for up to one hour. It is used in emergency and incident response,

13.3 Improved Toxicological Agent Protective (ITAP) suit.

13.4 Self-contained Toxic Environment Protective Outfit (STEPO).

routine chemical activity, and initial entry monitoring. ITAP is a suit that offers splash and vapor protection, and dissipates static electricity. It can be decontaminated for reuse after five vapor exposures, and it has a 5-year minimum shelf life. US Air Force firefighters use the ITAP with a self-contained breathing apparatus (SCBA), a personal ice cooling system (PICS), and standard TAP gloves and boots.

The STEPO is a totally encapsulating protective ensemble that provides four hours of protection against all known CB agents, missile/rocket fuels, petroleum oil and lubricants (POL), and industrial chemicals. Explosive ordinance disposal (EOD) and chemical facility (depot) munitions personnel engaged in special operations in IDLH environments use the STEPO. It can be decontaminated for reuse after five vapor exposures. Since complete encapsulation is very cumbersome, the work duration in the suit is strictly limited because of the limited air supply, and microclimate cooling is necessary for comfort. The STEPO has four hours of self-contained breathing and cooling capabilities. It has a tether/emergency breathing apparatus option. It also has a built-in, hands-free communications system. If the major concern is liquid splash protection, then full encapsulation may not be necessary. The use of a coverall or apron may be more appropriate. Such items are typically fabricated from the same type of materials that are used in fully encapsulating suits. Vapor protection is then sacrificed for increased comfort and mobility. The STEPO is shown in Fig. 13.4.

Another item is the Suit – Contamination Avoidance and Liquid Protection (SCALP). The SCALP is made of polyethylene-coated Tyvek^R, and it is worn over the standard overgarment. It is designed to protect the user and their overgarment from gross liquid contamination during short-term operations for up to one hour. Decontamination personnel also use it. The SCALP is shown in Fig. 13.5.

Similar special purpose clothing is available commercially. As with combat clothing, the special purpose clothing has limited wear time. It can be repeatedly cleaned and re-used, and repaired if not contaminated. These suits have different designs and protective capabilities; thus potential users must understand their capabilities in order to use them properly in different operational environments for specific durations of use.

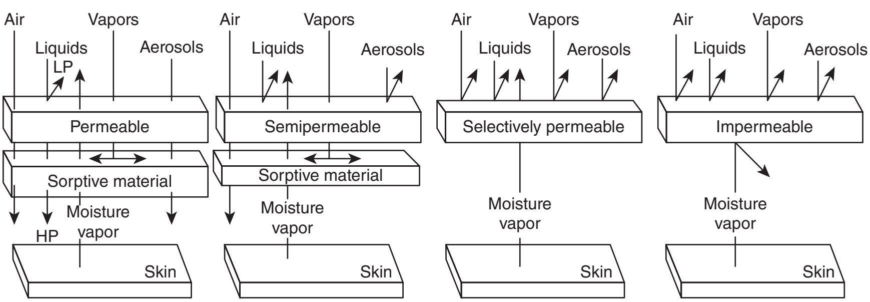
13.3 Materials for chemical and biological (CB) protective clothing

There are basically four different types of CB protective materials. These are illustrated in Fig. 13.6.

13.3.1 Air-permeable materials

Permeable fabrics usually consist of a woven shell fabric, a layer of sorptive material such as activated carbon impregnated foam or a carbon-loaded nonwoven felt, and a liner fabric. Since the woven shell fabric is not only permeable to air, liquids, and aerosols, but also vapors, a sorptive material is required to adsorb toxic chemical vapors. Liquids can easily penetrate permeable materials at low hydrostatic pressures; therefore, functional finishes such as Quarpel® and other fluoro-polymer coatings are usually applied to the outer-shell fabric to provide liquid repellency. Additionally, a liquid and/or an aerosol-proof overgarment such as non-perforated Tyvek® protective clothing must be used, in addition to permeable clothing, in a contaminated environment to provide liquid and aerosol protection. Many users like to use permeable clothing because convective flow of air is possible through the clothing and open closures. This action allows

13.5 Suit – Contamination Avoidance and Liquid Protection (SCALP).



13.6 Types of CB protective materials. LP, low hydrostatic pressure; HP, high hydrostatic pressure.

evaporative cooling to occur. Examples of air-permeable protective clothing containing activated carbon include garments used by the US, British, and Canadian military, as well as that of many other countries.

13.3.2 Semipermeable materials

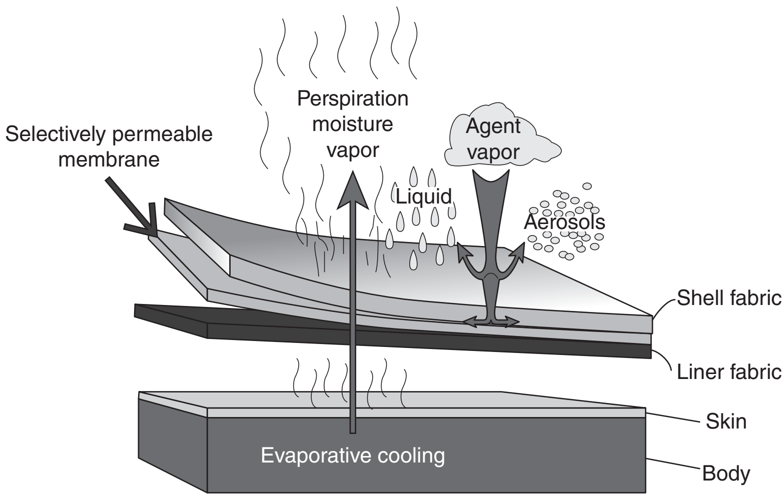
There are two different types of semipermeable membranes – porous and solution–diffusion membranes.[8] Porous membranes include macroporous, microporous, and ultraporous membrane structures. A macroporous membrane allows convective flow of air, aerosols, and vapors through its large pores. A microporous membrane follows Knudsen diffusion through pores, where pores with diameters less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through. An ultraporous membrane has also been referred to as a molecular sieving membrane, where large molecules are excluded from the pores by virtue of their size. A solution–diffusion membrane has also been called a nonporous or a monolithic membrane. This type of membrane follows Fickian diffusion through the nonporous membrane, where gas dissolves into the membrane, diffuses across it, and desorbs on the other side based on concentration gradient, time, and membrane thickness. Such membranes have found many applications in sports clothing and related active wear.

13.3.3 Impermeable materials

Impermeable materials such as butyl and halogenated butyl rubber, neoprene, and other elastomers have been commonly used over the years to provide CB agent protection.[9] These types of materials, while providing excellent barriers to penetration of CB agents in liquid, vapor, and aerosol forms, impede the transmission of moisture vapor (sweat) from the body to the environment. Prolonged use of impermeable materials in protective clothing in the warm/hot climates of tropical areas, significantly increases the danger of heat stress. Likewise, hypothermia can readily occur if impermeable materials are used in the colder climates. Based on these limitations, a microclimate cooling/heating system can be an important adjunct to the impermeable protective clothing system, to compensate for its inability to allow moisture permeation.

13.3.4 Selectively permeable materials (SPMs)

SPMs are extremely thin, lightweight, and flexible protective barrier materials to CB agents and selected TICs, but without the requirement of a thick, heavy, and bulky sorptive material such as an activated carbon material layer. They allow selective permeation of moisture vapor from the body to



13.7 Selectively permeable membrane.

escape through the protective clothing layers so that the body of a soldier is continuously evaporatively cooled during his missions while being protected from the passage of hazardous chemicals in liquid, vapor, and aerosol forms. SPMs have the combined properties of impermeable and semipermeable materials. The protection mechanism of selectively permeable fabrics relies on a selective solution/diffusion process, whereas carbon-based fabrics rely on the adsorption process of activated carbon materials. SPMs have been widely used for many years throughout the chemical industry in gas separations, water purification, and in medical/metabolic waste filtration.[10] SPMs consist of multi-layer composite polymer systems produced using various different base polymers such as cellulose, cellulose acetate, polyallylamine, polyallylimine and polyvinyl alcohol, among other gas or liquid molecular separation membranes. SPMs are expected to see increasing applications in CB protection as future garments and items are developed. A schematic of an SPM is shown in Fig. 13.7.

13.4 Technologies for next generation chemical and biological (CB) clothing

13.4.1 Self-detoxification

Catalysts are under development that are intended to cause the transformation of chemical warfare agents (CWAs) into less hazardous chemicals. Some of this work is aimed at improving methods of detoxifying contaminated vehicles and equipment following a chemical attack. The chemistry behind traditional methods of decontamination has been reviewed by Yang *et al.*[11] These agent-reactive catalysts can also be incorporated into fabric systems, where they serve to reduce the hazard from chemical contamination, particularly while doffing the contaminated clothing and disposing of it. The addition of catalysts to CB protective clothing systems is not a trivial matter. The catalysts can be applied as a coating onto fabrics or individual fibers; they can be incorporated within individual fibers; they can be chemically bonded to fiber surfaces; or they can be incorporated as particles or nanoparticles within a matrix such as an electro-spun nanofiber mat. Aspects of these approaches have been discussed by Sun *et al.*[12]

Numerous efforts to develop and incorporate catalysts are ongoing. Enzymes have been studied for this purpose for many years. Enzymes such as organophosphorus acid anhydrolase (OPAA) to neutralize G agents and VX have been developed. The widespread use of enzymes in these applications has been hindered by the lack of durability of the enzymes. The presence of water is also necessary for the successful hydrolysis of nerve agents. Work is ongoing to improve this property. This topic has been reviewed by DeFrank.[13]

Polyoxometallates (POMs) for neutralizing sulfur mustard (HD) have been studied extensively by Hill.[14] Recently, Song *et al.* reported that a POM has been incorporated into the pores of a metal-organic framework.[15] This novel catalyst has been found to dramatically increase the turnover rate of the POM in air-based oxidations.

One family of catalysts that has demonstrated effectiveness against a variety of hazardous chemicals are metal oxides, such as MgO, TiO_2, CaO, and Al_2O_3. The development and characterization of these catalysts have been reported by Wagner *et al.* In studies using solid-state MAS NMR, the nerve agents VX, GB, and GD, as well as HD, were reported to hydrolyze on the surface of metal oxide nanoparticles. In general, nontoxic by-products are formed.[16]

Bromberg *et al.* have studied the nucleophilic hydrolysis of organophosphorus compounds by polyacrylamidoxime (PANOx) and poly(N-hydroxyacrylamide) (PHA) and found these catalysts to be effective in degrading these chemicals.[17]

Halamines (R_2N-X, where X = Cl, Br, or I) are being investigated for use as biocides, as well as catalysts, in protective clothing.[18]

13.4.2 Super-repellency

When breathable clothing is contaminated by contact with droplets of hazardous chemicals, the droplets may 'wet' the fabric by soaking into it, or the droplets may remain on the surface and not wet the fabric. In either case, the vapors associated with the droplets will sooner or later permeate the fabric. To minimize the contact time between the droplets and the protective garment, the outer shell fabric is usually treated with a liquid repellent coating such as Quarpel^R. While these finishes do a good job repelling liquid water and certain other chemicals, they may not be effective in repelling a variety of hazardous chemicals. Work is underway to develop fabric treatments that are super-repellent; that is, superhydrophobic and superoleophobic.

Aspects of the fundamental science behind super-repellency in fabrics have been developed by Tuteja *et al.*[19] and Chhartre, *et al.*[20] The fabrication of such fabrics for applications in CB protective clothing has been discussed by Saraf *et al.*[21] The idea is to develop fabric treatments that are sufficiently liquid repellent to allow droplets of chemicals to be easily shed from protective clothing. Such clothing can also be described as self-cleaning, since dirt and oils will not adhere to the clothing.

13.4.3 Electronic textiles

The integration of electronics into textile systems has made it possible to incorporate sophisticated functions into clothing that were not previously possible. The development of wireless technology has added a new dimension to these advancements. Some of the new functions now possible include physiological status monitoring, resistive heating, wearable power, and the incorporation of CB sensors. Wearable electronic systems have been described by Park and Jayaraman.[22]

For individuals such as soldiers and firefighters to perform their missions optimally, they must be in good physical condition. It is now possible for commanders and medics to wirelessly monitor the status of their physiological condition using sensors that are integrated into their clothing systems. Sensors are currently available that can monitor skin temperature, heart rate, respiration rate, and hydration status. Such monitoring can lead to improved readiness in medical treatment and in the treating of casualties.

Numerous technologies have been developed and incorporated into a range of CB detectors for use in buildings, at transportation hubs, and on the battlefield. Many of these technologies can be miniaturized and incorporated as small sensors into clothing systems, either on or within the textile structure. These technologies typically detect the presence of organophosphorus compounds or other hazardous chemicals.

13.4.4 Thermal management

For operation in extreme climates, it may be desirable to integrate some form of active or passive heating or cooling into clothing systems. Increased warmth can be achieved through the use of layers and insulation materials.

Active heating, using traditional wires or conductive fibers incorporated into the textile system, can also be used. Heated handwear is especially useful and welcome in cold climates.

Cooling can be achieved on a short-term basis through the use of phase-change materials. These materials have been incorporated into boots, helmets, and backpack liners and typically provide around an hour of cooling. Cooling vests have been developed that are able to provide effective cooling indefinitely. These vests utilize tubing which is sandwiched between two fabrics and through which cold water circulates. The water is cooled by a vapor compression cooling unit that is operated on battery power or power supplied by a vehicle. Vapor compression units powered by portable batteries add weight to already overburdened users, so their use by dismounted individuals remains strictly limited.

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