

CONSIDERATIONS FOR DESIGN AND SELECTION OF CHEMICAL-PROTECTIVE CLOTHING

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Summary

A number of limitations and misconceptions exist for the design and selection of chemical-protective clothing involved in hazardous chemical monitoring and spill response. Of primary concern are protective clothing material—chemical compatibility, decontamination, and garment design. Current compatibility information, used for making protective clothing recommendations, is not always adequately or properly used. New methods for assessing material chemical resistance are being developed to standardize compatibility data, but extensive criteria are needed to establish appropriate selection guidelines. Equally important in the design and selection of chemical-protective clothing are material physical properties and design features. The U.S. Coast Guard is establishing selection criteria for low level protective clothing while developing improved high level protective clothing (total encapsulating suits) supported with extensive material testing. This, combined with active participation in the American Society for Testing and Materials for setting minimum protective clothing performance requirements, is helping to reduce current deficiencies in chemical personnel protection.

Introduction

Unlike chemical industry, those in public hazardous chemical response cannot always predict which chemicals they are likely to encounter. Nonetheless, these are the same people who must be prepared to monitor and mitigate actual or potential releases for any number and combination of hazardous chemicals. Contingent on their capabilities is an adequate form of personnel protection. Yet, because of the wide range of chemicals that can be encountered in spills, derailments, and at chemical waste dumps, with the associated variety of potential hazards presented by these chemicals, the selection of chemical-protective clothing involves a multiplicity of problems. In some cases, the information to make a selection is available but not consolidated for easy reference. Often, there is a lack of information for the “best” choice, or the existing information is incorrect. But, more dangerously, there are serious misconceptions as to the proper employment and limitations of chemical-protective clothing. These shortcomings for adequate personnel protection can be overcome with a comprehensive program which examines

all levels of protective clothing to both identify and implement needed improvements in deficient areas. The U.S. Coast Guard in cooperation with other governmental organizations is attempting such a program.

Defining the problem

Classifying the nature of the hazard and the required levels of protection has allowed the Coast Guard and other agencies to devise manageable approaches to optimize personnel protection clothing systems. Of the chemical hazards listed below,

1. flammability,
2. reactivity,
3. corrosion,
4. toxicity, and
5. oxygen deficiency,

chemical-protective clothing is designed primarily for protection against corrosion and toxicity; together with a self-contained breathing apparatus (SCBA), the personnel protection system further protects against oxygen deficiency. Fire and explosion hazards must be dealt with separately since current technology does not allow either a practical or economic merger of fire/explosion and chemical toxicity protection. Within the chemical toxicity

TABLE 1

Protective clothing categories

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- Level A — Protective clothing that is used when the threat is the greatest, and no contact may be permitted. The level incorporates a totally encapsulated suit to prevent skin contact of any kind and a self-contained breathing apparatus (SCBA) inside, for two separate seals between the outside air and the user's respiratory system (Type I). Two variations of this level involve only one seal, with the SCBA worn on the outside (Type II), and using an airline breathing system (Type III).
- Level B — Protective clothing that is used in cases where limited skin contact with vapors may be acceptable. The garment covers most of the body, but not completely, and it is not completely sealed, so there is a possibility of the chemical making contact with the skin. The respiratory equipment is an SCBA.
- Level C — Protective clothing resembling Level B, but the respiratory protection is not critical and an air-purifying purifier (a filter-type "gas mask") replaces the SCBA. The garments for Levels B and C do not protect against vapors, but only against liquids that may splash on the individual. Levels B and C clothing are generally referred to as a "splash suit".
- Level D — This protective clothing is essentially a pair of coveralls with boots and gloves. Level D protection is used in the limited number of cases when there is no indication of hazardous conditions and the work function precludes contact with hazardous substances.
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and corrosion hazards, there are four accepted levels of personnel protection defined by the U.S. Environmental Protection Agency (EPA), ranging from a totally encapsulated suit with a SCBA to cotton overalls (see Table 1). Surveying existing commercial clothing and accessories at each of these levels reveals that adequate personnel protection is provided by many items in Classes B and C, but sometimes questionable protection is offered by encapsulated suits for Class A protection. Whereas guidelines can be established to wisely select Class B and C chemical protective clothing, extensive research, development, and testing is needed in conjunction with performance standards to provide greater confidence for the highest level of protection, Level A protective clothing.

Any research and development program to improve Level A protective clothing must examine both design improvements and extensive suit materials testing. Level A protective clothing includes total encapsulating suits that have the objective of completely protecting the user against any form of chemical exposure — via respiration, skin absorption, and ingestion. Generally commercial suits have the same salient features, but they are not consistently incorporated in all available versions. The design of these suits involves much more than simple tailoring; specific engineering is needed for the suit to maintain a leak-free, positive pressure atmosphere. Important design features include the construction of seams, the type and location of the zipper, and the suit exhaust valve. The suit must also integrate with either one or several types of breathing systems. Of fundamental importance are the materials of construction which provide the physical strength for the suits and protect against various hazardous chemicals. Each material used in an encapsulated suit must be assessed for its physical properties and chemical resistance. Particularly significant are the selection of test methods and the chemicals used to “challenge” the suit material. This task is especially difficult when an organization must consider an unknown number of hazardous chemicals.

Although any large list of chemicals remains diverse, it is still necessary to rank hazardous chemicals in priority order to achieve a workable approach to develop a personnel protection system. In 1974, the Coast Guard established the Chemical Hazard Response Information System (CHRIS) now listing over 1000 chemicals which might be discharged into inland or coastal waterways (CHRIS provides a complete description of the chemical and recommends appropriate response techniques for each listed chemical [1]). Over 40% of these CHRIS chemicals were found to require use of an encapsulated or sealed suit based on toxicological data [2] (using Sax's Toxic Hazard Ratings [3]). Still, not all these chemicals are likely to be encountered in hazardous chemical response on a routine basis. Table 2 shows the top 25 chemicals based on spill frequency to which the Coast Guard responded to between 1974 and 1983. Yet, developing a personnel protection system for only those chemicals seen in the field incurs potential risk since there will always be spills of chemicals which cannot be anticipated. For example, over the same period information in Table 2 was accumulated, 53 identified sub-

TABLE 2

Top 25 chemicals spilled from 1973 to 1983 involving U.S. Coast Guard response

Rank	Chemical name	No. of spills ^a	Reported quantities		Level A protection ^b
			(gal)	(lb)	
1	Sulfuric acid	128	525044	3895054	yes
2	Sodium hydroxide (caustic soda)	95	185652	145173	yes
3	Xylene	92	230054	1800	no
4	Polychlorinated biphenyls	92	6686	149	yes
5	Benzene	91	10836	400	yes
6	Ammonia	85	121847	181095	yes
7	Toluene	81	80616	26500	no
8	Hydrochloric acid	63	99896	635	yes
9	Styrene	59	136900	68563	no
10	Chlorine	35	14897	—	yes
11	Cresol	33	586	—	no
12	Phenol	26	19896	99	no
13	Ethylene glycol	23	8826	375	no
14	Phosphoric acid	22	31140	10210	no
15	Formaldehyde	17	29340	90000	yes
16	Cyclohexane	17	3909	—	no
17	Methyl chloride	15	290	3440	no
18	Acetic acid	13	1010810	—	yes
19	Acrylonitrile	12	105396	228880	yes
20	Tetrachloroethylene	12	1355	99	no
21	Acetone	11	3753	—	yes
22	Ethyl acrylate	11	305	—	yes
23	Methanol	11	1262551	—	no
24	Acrylic acid	10	9680	125	yes
25	Napthalene	10	22635	—	no

^aSource of data U.S. Coast Guard Pollution Information Response System.^bDetermination of requirement for Level A protective clothing based on findings in Ref. [2].

stances were involved in Coast Guard hazardous response only once. This does not justify development of the personnel protection system for every chemical encountered, but it does mean that any system developed must be flexible enough to accommodate a variety of spilled substances. As a result of these difficulties, the Coast Guard has adopted a priority list of compounds which not only takes into account commonly spilled chemicals, but also the amounts of chemicals transported (i.e., the likelihood of their being spilled), the forms in which they are transported, and the potential toxicity and dermal effects of these chemicals. Beginning with a priority chemical list, chemical compatibility information can be generated to cover the majority of expected situations; other chemicals can be added to the system once established to extend the system to additional situations.

Suit material compatibility

Probably the most important characteristic used in selecting or developing chemical-protective clothing is the choice of materials. The major premise behind chemical-protective clothing is that it acts as an "impervious" barrier to hazardous chemicals. Though much of this depends on how well the suit is constructed, the ability of the suit material(s) to resist chemical intrusion or "breakthrough" is paramount. In the past few years, especially with the formation of the American Society of Testing and Materials (ASTM) F23 Committee on "Chemical Protective Clothing" in 1977, numerous studies have revealed that a number of assumptions on the chemical protection offered by existing clothing do not hold true. With the advent of a new ASTM procedures for determining chemical resistance of materials, more limitations are being discovered which necessitate new approaches to designing, testing, and using chemical-protective clothing.

Types of chemical intrusion

When a suit material resists intrusion by a hazardous chemical, the material is said to be "compatible" with that chemical. The ASTM F23 Committee has defined three processes by which a chemical can affect a suit material and/or gain access into a suit or other forms of protective clothing:

1. *Degradation*. The deterioration in the material of one or more physical properties upon surface contact by a chemical. For example, a change in material tensile strength through surface contact of a chemical could be such an indicator.

2. *Penetration*. The flow of a liquid or gaseous chemical on a non-molecular level through closures, porous materials, seams, pinholes, or other imperfections in a protective clothing material.

3. *Permeation*. The process by which a liquid or gaseous chemical moves through a protective clothing material on a molecular level via:

- a. adsorption of the chemical onto the surface of the material,
- b. diffusion into the material, and
- c. desorption of the chemical from the inner surface of the material.

(This process is illustrated in Fig. 1)

Each phenomenon raises different concerns about the viability of a protective clothing material. Degradation is usually a detectable change of the material which can be observed visually or instrumentally. Visual changes to the material may be readily apparent such as swelling, discoloration, delamination (of composite materials), and shrinking. Two commonly used measures for determining degradation, in addition to visually observed effects, include material weight change and elongation. Other changes may not be as easily measured or noticed following a chemical exposure, such as changes in tear strength and abrasion resistance. Yet, changes in these material physical properties can also adversely affect the integrity of protective clothing.

The extent of penetration for a piece of protective clothing or its com-

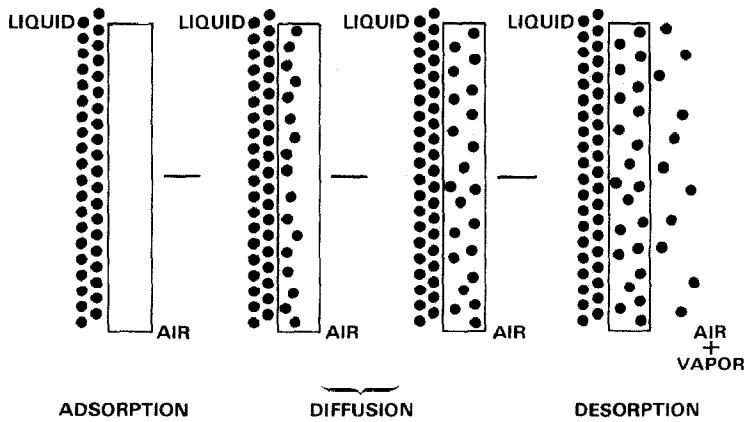


Fig. 1. Mechanism of permeation through protective materials.

ponents (zipper, visor, etc.) can be a measure of how well that item is put together. It is also an indicator of the material quality itself, particularly for coated fabrics. The process of laminating composite materials and coating fabrics can form imperfections in those materials due to improper curing or thin application of the polymer film; this can result in material pinholes and inconsistent layer thickness, providing an avenue for chemical penetration. However, chemical penetration is most likely to occur at seams, through the zipper, or around the exhaust valve(s) of Level A protective clothing. This phenomenon can be influenced by a number of conditions including design, wear, and temperature.

Permeation is the most insidious of the processes since a perfectly intact suit showing no visible adverse effects to a chemical can undergo permeation without the knowledge of the user. Furthermore, it is only after the material has accumulated within the suit at a detectable concentration, that it is first noticed by the user (if the chemical is detected by human senses). The time it takes for a chemical to initially adsorb, diffuse, and then desorb, and be detected on the other side of the material, is called the "breakthrough" time. The breakthrough time together with the rate of permeation are often used to characterize the permeation resistance of a material. In some cases, once breakthrough is achieved, the chemical may permeate at a constant rate for "steady-state" permeation. In other cases, permeation may continue to increase at a slow rate. Nevertheless, the breakthrough time is the most commonly used measure to establish chemical compatibility. It is important to note that permeation may occur without degradation and the opposing case is also possible.

Limitations of current compatibility information

Both degradation and permeation data are commonly used by manufacturers to establish material chemical compatibility recommendations.

Compatibility recommendations are an interpretation of the chemical resistance data based on exposure criteria. The exposure criteria are set by the particular application. For Level A suits, the material might have to successfully resist chemical attack or permeation for one to three hours; glove users often use an eight hour criterion. The criteria must be carefully established, particularly in response to a number of different chemicals, because there is no one suit material that has been tested that will resist degradation or permeation by all chemicals, much less by a majority of the common hazardous chemicals. Furthermore, nearly all plastic and rubber materials used in chemical protective clothing are permeable to some degree and for some chemicals, there is no acceptable garment that is currently available to provide adequate protection for the user. For Level A protection, this means that hazardous chemical response teams must carry an inventory of two or more encapsulated suits constructed of different protective materials. The Coast Guard has selected three — VitonTM/chlorobutyl laminate, butyl rubber, and chlorinated polyethylene with a fluorinated ethylene propylene visor to provide broad coverage against the hazardous chemicals they expect to encounter [4].

Data covering measurements for the above phenomena in most material—chemical combinations are not available. This is partly because the definitions or methods for their repeatable measurement did not exist until the last few years. As a result, many of the existing recommendations for using chemical-protective clothing may lack sufficient basis and should be regarded with caution. Table 3 shows a material—chemical matrix for some representative challenge chemicals and protective clothing materials. Each material in the table demonstrates incompatibility to a number of chemicals when the selection criterion is a one-hour exposure.

Serious misconceptions can arise from the way material—chemical data are

TABLE 3

Typical commercial material—chemical compatibility ratings

Chemical	CPE	Viton	Butyl	Vinyl	Nitrile	Neoprene
Acetone	A	X	A	X	X	B
Acetophenone	X	X	A	X	X	X
Acetyl chloride	A	A	C	X	X	X
Acetylene	A	A	A	A	B	B
Acrylamide	A	I	A	B	A	A
Acrylonitrile	A	X	X	X	X	C
Adipic acid	A	A	A	A	A	A

A — Recommended, little or no effect

B — Minor to moderate effect

C — Conditional, varies from moderate to severe under different conditions

X — Not recommended

I — Insufficient data.

presented. Material compatibility information is often presented for protective clothing items using simple rating formats; usually a system is employed using ratings of excellent, good, average, and fair with corresponding letters or numbers. In some cases, a recommended time period for the compatibility rating is given, e.g., "resistance time at least four hours; material slightly affected". Even when such information is provided, the method used to make that determination is not always documented. If a complete description of the testing and test results are available to support the recommendation, then some confidence in the recommendation can be assumed for the subject material. Such information is often unavailable for the materials in Level A protective clothing.

What remains a more serious problem is the basis for recommending a Level A encapsulated suit. Whenever a recommendation is made for the suit, it is made using the compatibility information of the primary material only. That is, secondary materials such as those used in the visor, boots, gloves, seams, and external suit fittings are not taken into account for recommending overall suit compatibility to a particular chemical. In reality, the integrity of a suit to resist chemical intrusion is only as good as its weakest material. This fact received widespread attention when the polycarbonate visors of two commercial butyl rubber encapsulated suits failed when exposed to vapors of dimethyl amine. The incident occurred when the fire department in Benecia, California responded to leaking tank railcars containing that substance. The facepieces of each suit "cracked open in a shattering manner" exposing the suit wearers to the chemical vapors [5]. Some sources show butyl rubber having limited compatibility with dimethyl amine; compatibility data are not available for polycarbonate. This example demonstrates the need for compatibility information for all external suit materials, with recommendations to use suits based on the least chemically resistant material for each particular chemical.

Another problem in the way chemical compatibility data are presented concerns the documentation of the material and testing procedures. Most material-chemical compatibility tables list ratings for materials like butyl, neoprene, and nitrile rubbers against several chemicals. Yet, these same material names are often "generic"; material product formulations/processing conditions can vary from manufacturer to manufacturer as well as lot to lot. For example, hundreds of formulations exist for neoprene rubber, a common protective material, each with various fillers and active ingredients that provide slightly different chemical properties [6]. Sometimes the differences can be significant, as shown in Table 4 for the permeation of two nitrile rubber formulations by carbon tetrachloride and propyleneglycol monomethyl ether. Other variations in the material, particularly thickness, can affect the applicability of chemical compatibility information. In essence, separate chemical compatibility data must accompany each protective clothing item because there is no certainty on how representative "generic" data may be.

TABLE 4

Permeation data for two different nitrile rubber formulations

Nitrile rubber manufacturer	Thickness (mm)	Breakthrough time (min)	
		Carbon tetrachloride	Propylene glycol monomethyl ether
A	0.43	127	59
B	0.46	63	96

Methods for assessing chemical resistance

In the past, both users and manufacturers employed different techniques to report overall compatibility of protective clothing to various chemicals. The inability to compare items with differing supporting data and the fact that some techniques employed did not yield repeatable results led the ASTM F23 Committee to seek development of standardized test methods. ASTM has drafted standard test methods which measure degradation, penetration, and permeation resistance for protective clothing materials. Of these, the methods for measuring permeation resistance with liquids and gases (ASTM F739-85) and penetration resistance with liquid chemicals (ASTM F903-84) have become established standards; a method for measuring degradation resistance with liquid chemicals is now undergoing round-robin testing and evaluation. These methods are constantly being reviewed and adapted to provide more flexibility for handling different test conditions. For example, the permeation resistance test method is being modified for intermittent contact by chemicals for "splash" tests; it may also be adapted for solid chemicals. A "Standard Guide for Test Chemicals to Evaluate Protective Clothing Materials" is being prepared to provide minimum requirements for material-chemical testing.

Degradation

In the past, most protective clothing manufacturers relied heavily on degradation testing to set up their recommendations in chemical compatibility tables. Many tests for degradation are relatively simple and inexpensive to perform. Essentially a material swatch of known dimensions and weight is exposed to a liquid chemical; observations and measurements are made at set time intervals from the beginning of the exposure. This is basis for the draft ASTM method. The draft ASTM method for measuring degradation is a qualitative method for rapidly screening materials by noting changes in visual appearance, weight, and thickness; it standardizes the way in which a material is exposed and how measurements and observations are to be made. Problems arise for some existing data since the exposure was often accom-

plished by complete immersion of the material swatch, sometimes without sealing the edges of the swatch. The ASTM method ensures one-sided exposure of the material to its normal outside surface, which realistically simulates chemical contact with the material. Future draft ASTM degradation methods may allow for measuring any physical property to denote a change in the material sample as the result of a chemical exposure. These physical properties can be chosen depending on available equipment and characteristics that are useful to the investigator. For example, one might want to know how tensile strength and flexibility are affected during chemical exposures. However, the greatest utility of the method is for "screening" materials prior to permeation tests; significant signs of degradation are usually an indication that the material will fail and costly permeation studies are not necessary.

Permeation

Measuring permeation with the ASTM F739-81 method also involves specified procedures for one sided exposure to "challenge" chemicals. In this case, the apparatus consists of a test cell, a sample pump, and sample analyzer (detector). The test cell (Fig. 2) consists of two chambers separated by the material to be tested. One chamber holds the challenge liquid chemical while the other chamber contains the collecting medium. The material is mounted

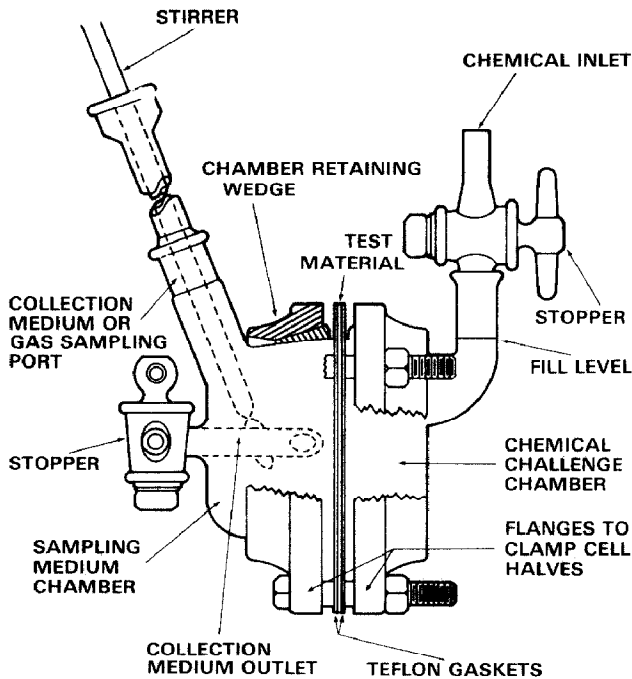


Fig. 2. ASTM F739-81 permeation test cell.

between Teflon[®] rings and clamped together. The collecting medium can be either gaseous or liquid, depending on the nature of the challenge chemical. Following exposure of the material to the challenge chemical, the collecting medium is either withdrawn continuously or discretely for analysis. Collection systems can be operated as open or closed. Chemical concentration is plotted versus time in a manner similar to that presented in Fig. 3 with subsequent determination of the breakthrough time and steady-state permeation rate. Variation does exist in the method; sometimes, different results can be obtained from the same technique. Yet, documenting the test method, equipment, and conditions can allow interpretation of this variance.

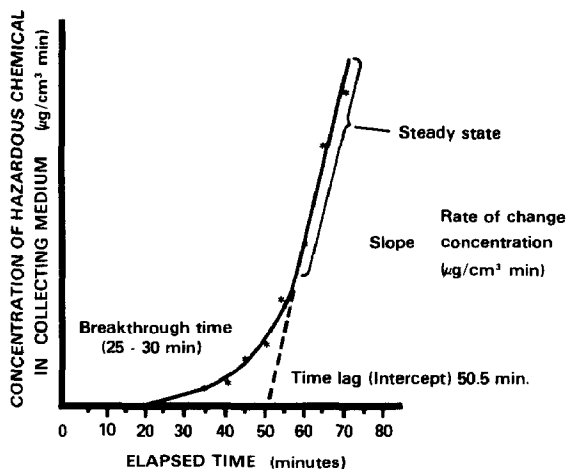


Fig. 3. Concentration of permeant as a function of time.

Variables affecting permeation

Permeation is affected by a number of variables which control accurate and precise measurements of breakthrough time and permeation rate using the ASTM F739-81 method. The equipment used to make the determinations can have a significant impact. For this reason, ASTM designed and adopted a standard test cell for exposing a protective material to a liquid chemical under repeatable conditions. However, other cells have been devised which use less chemical for testing and that are more easily adapted to multiple sample systems [7]. Methods have been established to determine the equivalency of test cells differing from the ASTM standard cell. Another variable involves the selection of the detector. Because breakthrough time is the time the chemical is first detected in the collection medium, it can vary with the sensitivity of the detector and the type of collection medium. The ASTM method does not specify the type of detector or collection medium in its procedures; it does require that reported results document the detector used and its sensitivity.

Other variables are related to the fundamental principles governing the permeation process. Many studies have shown that permeation is related to the solubility of the chemical in the clothing material [8, 9]. Material chemical solubility is a function of many factors such as temperature, concentration, and pressure. Table 5 shows the effect of slight changes in temperature on two protective clothing materials. The type of material, its thickness, and the method used for its manufacture can also affect chemical permeation [10]. Investigation of these variables are warranted because an understanding of the suit material/challenge chemical permeation process may allow prediction of breakthrough time and permeation rate for untested material—chemical pairs. Attempts that have been made to model known permeation data on the basis of the challenge chemical's solubility parameter, degree of hydrogen bonding, and molecular size show some correlation [11, 12, 13]. Several organizations are engaged in such studies including the National Institute for Occupational Safety and Health (NIOSH), the U.S. EPA, and the U.S. Coast Guard.

TABLE 5

Temperature effects on permeation breakthrough time

Test material	Temp. (°C)	Acetone breakthrough time (min)
Viton/Chlorobutyl Laminate	20	95—98
	26.5	43—53
30 mil Chlorinated Polyethylene	22	32—35
	24.5	27—31

The primary reason for investigating the effects of variable conditions on protective clothing permeation is to provide data which are more characteristic of actual use. The recommendation to use a particular protective clothing item of a specific material usually rests on the material's breakthrough time to a certain chemical. In nearly all cases, breakthrough times are measured for undiluted reagent grade chemicals in contact with the material. This type of material—chemical contact certainly does not represent a realistic exposure for the majority of protective clothing applications (industrial glove and boot use may be an exception). If a material has, for example, a two-hour breakthrough time for a particular chemical, then one could expect the material to fail after two hours of constant direct exposure to that chemical. This sort of testing is considered to be the "worst case". One could assume a large safety factor for using protective clothing in situations with less than 100% chemical exposure, but tests are still needed to approximate more realistic field conditions to determine the magnitude of safety factors that exist, and assist in establishing criteria for the interpretation of permeation data.

The permeation resistance test method (ASTM F739-85) was recently adapted for testing with challenge chemicals as either gases or vapors. An additional modification, when approved, will allow reproducible intermittent contact by liquid chemicals. Chemicals in the gaseous state are often encountered in the field. Depending on the temperature and the vapor pressure of "normal" liquids, the concentration of a chemical in the air can vary greatly. Of equal concern is intermittent exposure of a protective material to a liquid chemical representing the effect of a "splash". Preliminary experiments using these modified methods were conducted by the U.S. Coast Guard Research and Development Center. Generally, vapor and splash testing showed the expected results — pure liquid breaks through faster than saturated vapors at ambient or reduced temperatures; breakthrough also occurs sooner for the pure liquid than for multiple splashes, which break through faster than single splashes [14]. In some instances, however, breakthrough

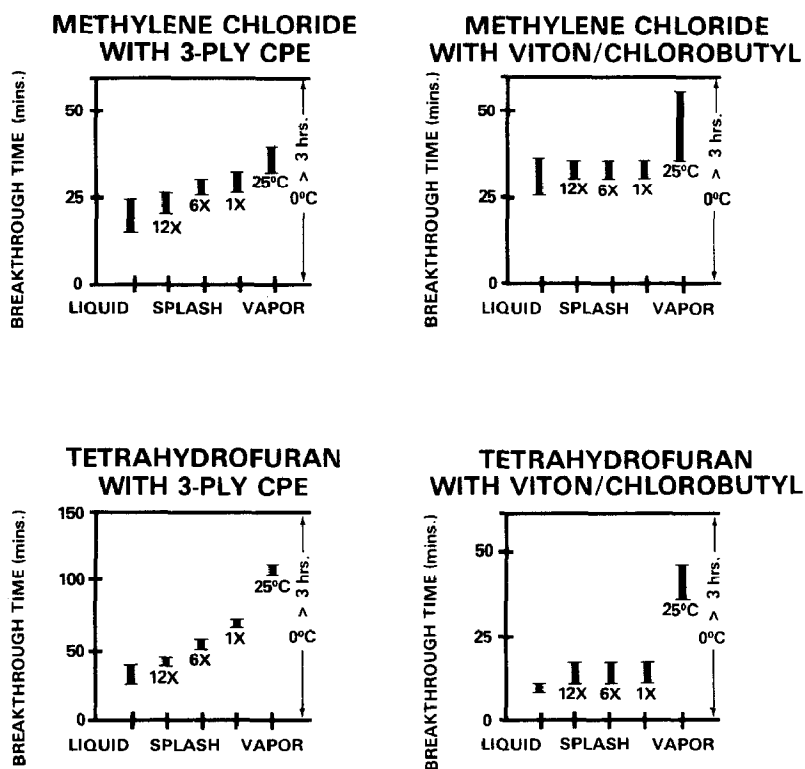


Fig. 4. Breakthrough times under different exposure conditions. Key:

Liquid — breakthrough time determined using ASTM F739-81.

Splash — 12X; 12 splashes at 15 min intervals over three-hour period; 6X; 6 splashes at 30 min intervals over three-hour period; 1X; one splash at beginning of test.

Vapor — saturated vapor at 0°C or 25°C in contact with material.

time did not vary significantly with challenge chemical contact time, suggesting wettability of the protective material as an important factor. These results are shown in Fig. 4.

Permeation by chemical mixtures

While little permeation information is available for most material-chemical pairs, even less information exists for chemical mixture permeation through protective clothing materials. Mixtures are commonplace in many chemical spill and monitoring situations. For a chemical mixture spill, there is little basis to assume that the material-chemical compatibility data and recommendations for each chemical can be applied separately to predict the overall effects of the mixture. For example, consider a two-chemical mixture. If

TABLE 6

Permeation breakthrough times of sample mixtures for representative protective clothing materials

A. Acetone and hexane mixtures for Viton/chlorobutyl laminate

Percentage acetone	No. runs	Breakthrough time ^a (min)
100	7	53-61
95	1	0-5
86	1	6-11
50	5	2-6
35	2	0-6
15	1	6-11
5	1	0-5
1	1	0-5
0 (100% hexane)	4	no BT (3 h)

^aBreakthrough times reported for both acetone and hexane.

B. Methylene chloride mixtures for Viton/chlorobutyl laminate

Percentage CH ₂ Cl ₂	No. runs	Breakthrough time (min)	
		CH ₂ Cl ₂	Second component
<i>hexane:</i>			hexane
100	1	25-36	—
50	2	42-47	57-62
0 (100% hexane)	4	—	no BT
<i>toluene:</i>			toluene
100	1	25-36	—
50	1	45-55	58-66
0 (100% toluene)	1	—	no BT

one chemical breaks through a material in 15 minutes and another chemical permeates through the same material in 1 hour, then either the mixture of the two chemicals or the most permeable chemical in such a mixture may not break through in 15 minutes. Research of the Coast Guard and other organizations has shown that some mixtures act predictably while others do not. Data in Table 6, provided by the Coast Guard Research and Development Center, indicate gross synergistic effects for hexane/acetone mixtures but "additive" permeation behavior for methylene chloride in hexane and toluene against Viton/chlorobutyl laminate [11]. Other studies show similar mixture permeation behavior involving different materials and chemicals [15, 16, 17]. One of the serious problems posed by mixtures is the selection of chemical-protective clothing. As illustrated above, even when the protective material provides protection against all chemicals in the mixture, there is no guarantee that the components acting together will not permeate the material. Furthermore, since chemical compatibility varies with material, mixtures may be encountered which contain chemicals compatible with some suit components but not with others. Clearly methods are needed to assess chemical mixture permeation.

Materials testing program

The U.S. Coast Guard has discovered many of the problems associated with material—chemical compatibility in the course of its efforts to develop new Level A protective clothing. For a three-hour exposure criterion (i.e., no chemical breakthrough in three hours), initial materials testing using the ASTM permeation resistance method have shown the Coast Guard selected materials (Viton/chlorobutyl laminate, butyl rubber, and chlorinated polyethylene) to be incompatible with a number of commonly encountered hazardous chemicals (see Table 7). As a consequence, a rigorous and detailed test plan has been developed by the Coast Guard Research and Development Center to thoroughly investigate the permeation process for these materials. The test plan addresses work on new procedures, the effect of several variables, and routine testing of priority chemicals that will provide realistic criteria for suit selection [11]. The end result of this effort will be a "manual of practice" to accompany deployed suits that informs Coast Guard responders as to the effectiveness and limitations of the protective clothing being used. The "manual of practice" will be specific to the design and type of suits employed and will be updated to cover more situations and chemicals as materials testing continues.

Though laboratory materials testing can take into account many variables and establish "reasonable" criteria for protective clothing selection, supplementary approaches are needed to handle situations for which no data exist. One alternative involves determining material—chemical compatibility at the site for unknown chemicals or mixtures. Due to the overwhelming number of possible mixtures in hazardous chemical response, techniques for on-site

TABLE 7

U.S. Coast Guard material permeation breakthrough times for various selected chemicals^a

Chemical	Breakthrough times ^b (min)		
	Viton/CB ^c	Butyl rubber ^c	CPE ^c
Acetaldehyde	30-40	—	10-30
Acetic acid	no BT ^d	no BT	no BT
Acetone	52-77	no BT	20-25
Acetonitrile	90-105	no BT	80-85
Benzene	—	—	71-75
Carbon tetrachloride	—	—	no BT
Chloroform	no BT	11-15	30-35
Cyclohexane	—	—	no BT
Dimethyl sulfoxide	no BT	—	no BT
Ethyl acetate	20-40	—	58-70
Ethyl acrylate	14-32	34-45	65-70
Hexane	no BT	13-16	no BT
Lindane in chloroform	no BT	0-10	—
Lindane in xylenes	no BT	80-90	—
Methanol	no BT	no BT	no BT
Methylene chloride	25-36	0-1	15-25
Methyl ethyl ketone	25-40	—	28-35
Styrene	no BT	0-1	60-70
Tetrahydrofuran	9-11	7-14	27-39
Toluene	no BT	0-6	69-75

^aThese reported breakthrough times are for illustrative purposes only and should not be used for selecting protective clothing in hazardous chemical response.

^bBreakthrough times measured using ASTM F739-81 Standard Method with a gas chromatograph/flame ionization detector (approximate sensitivity 1 ppb).

^cThe materials tested were as follows: Viton/CB — Viton/chlorobutyl laminate; 5 oz/yd² Viton (outer or exposed surface), polyester, and 5 oz/yd² chlorobutyl rubber (inner surface); 14 mil total thickness. Butyl rubber — nylon butyl cloth as per Military Specification Mil-C-12189 (13 mil thickness). CPE — chlorinated polyethylene, 30 mil thickness, unsupported.

^d“No BT” denotes no breakthrough within three-hour period.

permeation assessment may provide immediate protective clothing compatibility information. Portable “field-test” permeation kits are under development by both the U.S. EPA and NIOSH [18] for such purposes, and can also fill a gap for unavailable material-chemical pair data as encountered under actual conditions. As this sort of “field” data are accumulated, material-chemical compatibility tables and assessment methods can be revised to allow more judicious protective clothing selection.

Decontamination

Once a suit is exposed to hazardous chemical, there is no simple way to determine the extent of its contamination, and if decontaminated, the effec-

tiveness of the decontamination process. Herein lies the problem of protective clothing decontamination. Further complicating the issue is the fact that once a protective clothing item is exposed to a chemical, it may be permeated to some extent with residual chemical remaining inside but not breaking through the material for the duration of the exposure (material "matrix" contamination). However, following the exposure, the chemical may continue to permeate through the material while the item is in storage [19]. Subsequent exposure to the same chemical or a different chemical may drive the original residual chemical through the material, or have synergistic effects if the second exposure involves a different chemical. In essence, potential risk is assumed for reusing protective clothing that has been exposed to a hazardous chemical.

Any alternative to suit or clothing disposal following chemical exposure, i.e., decontamination, depends on the development of methods to determine the level of contamination for an exposed article. Additionally, the phenomenon of material matrix contamination must be verified and its significance determined. Because different decontamination processes may be involved, there must be an ability to distinguish between surface and matrix contamination. The Coast Guard intends to investigate this problem through two approaches. The first approach involves an in-depth analysis of materials exposed to chemicals with different contact times less than the established breakthrough time for the chosen material-chemical pair. Radioactive tracer chemicals will be employed to determine a concentration profile of the chemical in a cross-section of the material. This will show the extent of permeation and will help define the problem for evaluating decontamination methods. The second method addresses a survey of physical property methods to determine gross amounts of residual chemical within the material, and any changes occurring to the material as the result of the exposure. So far, thermal analysis techniques such as differential scanning calorimetry and thermogravimetric analysis show some promise for this application [20]. These methods may be easily applied to assess protective clothing contamination before and after a decontamination process, with the information used to determine the viability of reusing the clothing item.

Once protective clothing contamination can be measured accurately, decontamination methods may be found that can completely remove contaminants. Several methods are being employed which have potential for protective clothing surface decontamination. Water and certain detergents appear effective against many inorganic and some organic contaminants. A Freon-based "washing machine" or shower system (for encapsulated suits) may be suitable for removing many organic substances [21]. However, if the above studies yield results showing significant matrix contamination for most exposures, then development of decontamination methods will be difficult for cleaning protective materials without affecting the chemical resistance or physical properties of the material. Development of new materials may be considered which are more inert and which are only sur-

face contaminated. Such materials, in combination with effective decontamination methods, may offer an economic alternative to disposal of protective suit and clothing constructed of relatively cheaper materials.

Physical properties of protective materials

In addition to chemical resistance, the physical properties of a protective clothing material are also important in selecting the appropriate material for a particular application. The majority of materials used in protective clothing today have been around for the past decade, but many variations of each material exist, each with different physical properties. Protective clothing materials may be fabrics, thick polymer films, or coated fabrics. Some coated fabrics can be quite complex — a different coating may exist on either side of the fabric, more than one substrate can be used in a material, or films may be layered together to form composite materials. As polymer films vary (butyl rubber, neoprene, PVC, and Viton), so do substrates (nylon, polyester, Nomex™) which are both woven or non-woven. Level A protective clothing generally involves polymer-coated fabrics. These types of materials combine the chemical resistance characteristics of the polymer with the physical support of the cloth.

Some physical properties are characteristic of the entire material while others are attributed to either the coating or the substrate cloth. Physical properties that apply to the entire material include material thickness, typically measured in mils (thousandths of an inch), and weight, most often reported in ounces per square yard. The strength of a material (tensile, tearing, and bursting) and its ability to resist physical abuse (such as punctures and cuts) is mostly a function of the substrate. Material flexibility and brittleness is often associated with the polymer film, though sometimes the overall material can influence these properties. Flammability, a characteristic included in the list of physical properties, is highly dependent on the polymer coating. (Note: Favorable flammability properties of a material should not be used to infer any fire protective qualities for a particular item of protective clothing.) A list of physical properties and established test methods which can be used for their measurement is given in Table 8.

The requirements for these physical properties depend on the application of protective clothing employing the selected material. Weight and thickness are usually best kept at a minimum but tradeoffs are involved that pose advantages and disadvantages for other physical properties. Using a low weight and thin material might offer better comfort to the wearer in terms of flexibility and bending, but physical strength and resistance might be sacrificed (along with chemical resistance). Such lightweight materials are used in disposable commercial Tyvek™/Saranex™ type suits. Most chemical spill response teams use encapsulated suits made from materials that are relatively heavy and possess high strength characteristics for multiple use in either training or actual responses. Typical requirements for this application are given in Table 8.

TABLE 8

Example protective clothing material physical properties and test methods

Characteristic	Test method(s) ^a	Requirement ^b
Weight (oz/yd ²)	Fed Std 191,5051 ^c ANSI/ASTM D751-79	25 (maximum)
Thickness (mil)	ANSI/ASTM D751-79	20 (maximum)
Breaking or tensile strength (lb/in ²)	Fed Std 191,5102 ANSI/ASTM D412-80 ANSI/ASTM 751-79	80 warp (minimum) 80 fill (minimum)
Tearing strength (lb/in ²)	Fed Std 191A,5134 ANSI/ASTM D751-79 ASTM D2261-80	9 warp (minimum) 15 fill (minimum)
Bursting strength or hydrostatic resistance	Fed Std 191,5312 ANSI/ASTM D751-79	200 (minimum)
Abrasion resistance	Fed Std 191,5302 Fed Std 406,1091 H-18 wheel, 600 cycles	no loose fibers
Puncture resistance	ASTM F23 draft method	pass, no puncture
Flexibility	ASTM D1388-78	pass, no air bubbles
Brittleness	ASTM D1790-62 (1976)	pass at - 25 °F
Low temperature bending	ASTM D2136-66 (1978)	pass at - 25 °F
Flammability	ASTM D568-68	Non-burning

^aListed test methods apply to polymer-coated fabric materials.

^bRequirements are recommendations the Coast Guard uses for evaluating Level A encapsulated suit materials.

^cAbbreviations: ANSI — American National Standards Institute;
ASTM — American Society of Testing and Materials;
Fed Std — U.S. Federal Standard.

Encapsulated suit design problems

The basic configuration of an encapsulated suit varies from one manufacturer to another. An example of an encapsulated suit is shown in Fig. 5. Generally, total encapsulating suits have the same components — a full body garment with gloves, boots, visor, exhaust systems, entry location (e.g., zipper), space for a breathing system or an interface for one, and sometimes a cooling system. Most radical differences between suits involve the type of breathing system and how it interfaces with the suit, but several other differences can exist. This diversity of suit design offers different design features to accommodate the needs of chemical spill response teams. In some cases, variation in suit design is useful as called for by the particular application or operations of the user organization.



Fig. 5. Chemical response workers wearing typical total encapsulating suits (photograph courtesy of ILC Dover, Inc.).

Suit variation is often distributed between tailoring changes which do not affect the operation of the suit, and fundamental changes which can have a significant impact on the way a suit operates. Tailoring differences between suits typically deal with suit sizing and the space provided inside a suit for the variety of breathing systems and headgear (hardhats and communications). Another example of this design feature type would include whether the boots and gloves are permanently attached and the location of the zipper. These latter issues are not lightly considered and could conceivably be placed in the other category. Many response organizations, i.e., local fire department hazardous chemical teams, disagree whether the zipper should be accessible to the suit user or not (the zipper is commercially found either in the back or on the side). On the other hand, fundamental design changes might encompass the type of zipper, its sealing mechanism, and the way the zipper is designed. Additional features such as the type and number of suit exhaust valves, the visor/hood configuration, and provisions for cooling and breathing system interfaces all affect suit operation and differ in available commercial suits.

Certain design standards should be universal to all Level A protective

clothing. Extremely important are the design of seams, the zipper, and other items in which different materials interface (visor, gloves, boots, zipper, etc) or where an opening exists (e.g., exhaust valves, inflation valve, and zipper). These features all contribute to overall suit integrity for maintaining positive pressure operation; a deficiency in any item can seriously impair the protective capability of the suit as much as a chemically permeable material. The nature of designing such items is highly dependent on the materials used in fabricating the suit. Generally, there are two types of materials, which dictate two different fabrication procedures. Some materials, like chlorinated polyethylene (CPE) and polyvinyl chloride, are heat-sealable and are joined in seams dielectrically. Otherwise, materials such as butyl rubber, nitrile rubber, and Viton must be sewn together and then patched with a strip of material bonded over the seam with an adhesive. Modified or combined techniques exist for the many materials used in encapsulated suits, some specific for the material employed. Since there are a variety of suit construction methods each having its merits, standards must primarily apply to the performance of the suit and its components and less in the form of individual item design specifications.

The basis for many suit and suit component performance specifications now exists in the form of established or draft federal, military, and consensus organization standards including those of ASTM, the American National Standards Institute (ANSI), and the National Fire Protection Association (NFPA). For example, test methods are available to determine seam strength (ASTM D751-79) and establish quality control practices for sewing coated fabric seams (U.S. Federal Standard 751). The draft ASTM test method for measuring material chemical penetration resistance can be useful to assess seams, zippers, visors, and other material interfaces that affect suit integrity. Other standard techniques under development address total suit (ensemble) performance. One such method allows users to simply determine gross suit leakage by inflating the suit to a specified pressure and covering seams with a soap film. More standards will be necessary to address manufacturer quality assurance. But more importantly, it will be necessary to organize the individual standards and test methods in a comprehensive performance specification for encapsulated suits in multi-chemical response. Both ASTM and the National Fire Protection Association are attempting to do this. This kind of an overall standard can establish minimum requirements for Level A protective clothing, for which none currently exist. This would be especially useful to the smaller organizations that do not possess the resources to verify the quality of commercial chemical-protective clothing.

Chemical clothing selection guidelines

While a comprehensive specification for Level A encapsulated suits guarantees some minimum performance for such protective clothing, similar standards for Level B and C clothing might prove impractical due to the

diversity of clothing and clothing types, even in the application of chemical spill response. An alternative is the development of an information base and criteria which will allow users to select protective clothing such as non-encapsulated suits, gloves, aprons, and boots wisely for their own specific needs. In 1983, the American Conference of Government Industrial Hygienists (ACGIH) published "Guidelines for the Selection of Chemical Protective Clothing", consolidating chemical compatibility data and manufacturer information on protective clothing items [22]. This work was sponsored to assist EPA's internal Office of Health and Safety in providing clothing guidance to personnel, especially EPA employees, working on hazardous waste sites. The reference allows a user to select the "appropriate" protective material for a specific chemical, and then in selecting the clothing item needed (glove, suit, etc.), find out what manufacturers make the item in the recommended material. Shortcomings of the recommendations are explained and a full background on chemical protective clothing is given. This reference currently represents the largest public collection of chemical-protective clothing information.

Both the EPA and the U.S. Coast Guard intend to supplement the Guidelines with additional information to further promote their utility by assisting a protective clothing user in making wise decisions in procuring and using chemical-protective clothing. In many cases, actual material-chemical compatibility data for particular materials are necessary in lieu of recommendations to determine protective clothing applications not meeting the one-hour criterion used in the Guidelines. The EPA will provide these data in an appendix within a second edition of the ACGIH reference. The Coast Guard is addressing a need for listing material physical properties for specified common protective clothing materials. This will allow the user to characterize the materials for physical properties necessary to the particular application. Further, providing documentation to compare chemical clothing design features will assist organizations in making procurement decisions without relying on manufacturers' literature. To supplement this information, the Coast Guard plans on providing information on general quality assurance practices. A new edition of the "Guidelines for the Selection of Chemical Protective Clothing" would contain:

1. A material-chemical compatibility index,
2. A list of material physical properties,
3. A list of items made in each material for all manufacturers,
4. A design feature-manufacturer item matrix,
5. Quality assurance practices that are or should be used by manufacturers,
6. A vendor's directory,
7. Background information on chemical-protective clothing and permeation theory as provided in the first edition.

The U.S. EPA and the Coast Guard are seeking to devise a database for the above information with continual updating.

Suit selection guidelines must ultimately also cover suit usage practices as

well material or clothing performance characteristics. Protocols for donning and doffing suits, recommended periods of encapsulation, wearing conditions, and operating procedures should be established by those organizations in hazardous chemical response. Particularly important are the ergonomic considerations such as suit fit and heat stress. Information on the sizing of suits and the comfort of the fit should be available to aid in the selection and wearing of chemical suits. Impermeable encapsulating suits, while protecting the wearer from the chemical environment, prevent the evaporation of sweat and cause elevated temperatures inside the suit. Even in cases of low ambient temperature with moderate physical activity, high temperatures and severe physiological conditions can be reached by the wearer inside a chemical suit [23]. Response groups should determine ahead of time what practices to follow for various wearing conditions to minimize harm to the wearer from the physiological constraints of chemical-protective clothing. Each organization engaged in hazardous chemical response should use as much care in using chemical-protective clothing as in selecting it.

Conclusion

In the effort to provide adequate personnel protection during hazardous chemical monitoring and response, the U.S. Coast Guard and other response organizations have discovered many limitations of chemical-protective clothing in terms of design, material—chemical compatibility, and decontamination. These deficiencies have led to the establishment of a comprehensive hazardous chemical personnel protection program. This program entails two approaches: (1) setting up informative guidelines for the wise selection of Level B and C protective clothing; and (2) developing better Level A protective clothing through improvements in design and extensive materials testing. Concurrent with these efforts is strong participation in the ASTM F23 Committee on Chemical Protective Clothing and the National Fire Protection Association to establish standards which set requirements for protective clothing performance and testing. In the federal government, we have the unique position of making substantial advances in each area. We possess the resources to design equipment and clothing that meet chemical protection needs, we can perform the necessary background R & D to support those designs, and we can advocate our specifications to form the basis of standards for general industry to encourage minimum standards of personnel protection.

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