

## Permeation measurements of chemical agent simulants through protective clothing materials<sup>a</sup>

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### Abstract

Effective procedures associated with storage and disposal of chemical warfare (CW) agents are important for the protection of civilian populations from inadvertent release of these agents. Emergency groups as well as citizens in surrounding communities need to know the relative effectiveness of various chemical protective clothing (CPC) ensembles in the unlikely event of such releases. A method has been developed for studying permeation of chemical warfare agent simulants through CPC materials. The experimental results characterize some commercially available CPC materials. Thirteen different CPC materials having widely differing compositions were chosen to study the permeation of four different liquid CW simulants (dimethyl methyl phosphonate, diisopropyl methyl phosphonate, malathion, and dibutyl sulfide) through these CPC materials at 25 °C. This permeation study involved a newly developed analytical technique employing room temperature fluorescence quenching of an indicator compound, phenanthrene, on filter paper. Various experimental factors such as breakthrough time, rate of permeation and uptake were investigated. On the basis of breakthrough time, the 13 CPC materials could be divided into three groups: most resistant, moderately resistant, and least resistant. Materials in the most resistant category exhibited no permeation by any of the simulants for at least 24 hours. Breakthrough occurred in the least resistant materials in generally less than an hour, and sometimes as soon as a few minutes.

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## Introduction

Congress has mandated that the United States shall destroy its stockpile of existing unitary chemical warfare weapons and bulk stocks of chemical agents incorporated into such weapons. This destruction is directed by the Department of Defense Authorization Act of 1986 (PL 99-145) which was subsequently amended to require completion of the disposal process by April, 1997. (The Army and Congress have recently announced that the current projected date of completion is 2004.) Although this action does not eliminate U.S. chemical warfare capability (binary agents are excluded), the amount of material to be disposed of, along with its extreme toxicity, make the task of disposal one which should be approached prudently. Chemical warfare agents to be disposed of are currently stored at eight separate locations in the continental U.S., in a variety of munitions [1, 2], as well as in bulk storage.

The method of choice for disposal of these agents is high-temperature (1130–1400 °C) incineration on-site at each stockpile location [1]. Although the probability is low that a release of chemical warfare agent might occur during the disposal process, the extreme toxicity of these chemicals raises concerns regarding protection of individuals in adjacent communities. Civilians in these communities are unlikely to have ready access to specialized military protective clothing ensembles, nor is it likely that all civilian emergency response groups in these neighboring communities would have such protection available to them.

Many types of chemical protective clothing (CPC) materials have been developed for protection against a wide variety of potentially hazardous situations, including accidental release of hazardous chemicals, via spills, fires, explosions, gaseous releases, etc. The pertinent question is how well would these various protective materials shield humans from exposure to chemical warfare agents. This research group has analyzed the available open-literature information regarding some commercial CPC materials in a previous publication [3]. This report has identified wide data gaps in the characterization of CPC materials for either chemical warfare agents or chemicals with sufficient structural similarity and physical properties to serve as reasonable surrogates (i.e., simulants). The research reported in the current paper is an initial attempt to seek answers to the question posed above as part of the technical assistance support that Oak Ridge National Laboratory is providing the Chemical Stockpile Emergency Preparedness Program (CSEPP).

The goal of this study is to assess the protective capacity of various clothing materials by investigating their permeability and uptake when they are exposed to various undiluted liquid simulants. Use of actual agent entails such a degree of hazard to the experimentalist that only a very few laboratories are certified as surety facilities and permitted to perform warfare agent experiments. Oak Ridge National Laboratory is not a surety facility. Thus it is common practice to employ the use of simulants, which mimic the chemical agents sufficiently well to provide useful data, but do not exhibit the extreme toxicity of live agents.

The question of what testing protocol provides the best indication of chemical resistance for a given protective material is an important one. Visible changes in material properties (e.g., swelling, blistering, etc.) provide only crude indications of the effect of the chemical on the protective material, and permeation of the chemical through the material may occur long before visible outward signs of degradation. This study investigates two important endpoints, viz., breakthrough time, defined as the time required for a detectable amount of chemical to diffuse through the CPC material; and permeation rate, which is a measure of amount of chemical permeating the material as a function of time. Breakthrough time provides an excellent parameter for comparison of the resistance of various CPC materials to a given test chemical, i.e., the longer the breakthrough time, the more resistant the CPC. The permeation rate is of less obvious application, but provides useful information about the physicochemical resistance of the CPC material to the test chemical. This study also investigated the effect of a one-hour immersion of each CPC material in each simulant to determine the uptake of simulant. Other studies have used this approach [4], and it can provide additional useful information regarding resistance of laminated materials to solvation, changes in physical properties of the protective material following contact with the chemical, etc. It is certainly not to be taken as a direct indication of protective material resistance, since total immersion does not at all mimic the intended application of the material (i.e., on normal application, only the resistant surface of the material is exposed to the chemical). Although this information is of interest, it should not receive primary consideration in rating the effectiveness of CPC resistance to chemicals. Of course, all these endpoints are influenced by many other parameters such as thickness of the protective material, concentration of the challenge chemical, temperature, etc. Some permeation studies utilizing chemical solvent or low-molecular weight organic compounds have been reported in the literature, but these do not directly or indirectly relate to the chemical warfare agents [3].

This paper describes the results of permeation studies using a new, simple and sensitive procedure recently developed at Oak Ridge National Laboratory [5] to evaluate the efficacy of CPC materials against CW agent simulants using room temperature luminescence quenching of an indicator compound (phenanthrene) on standard filter paper. The procedure tested thirteen protective clothing materials for permeation resistance to four different simulants. Breakthrough time, uptake of simulants by the materials, and permeation rate were determined at 25 °C.

## Materials and methods

### *Chemicals*

Tables 1 and 2 list the principal chemical warfare agents in the unitary stockpile and the compounds used as simulants for each. The two major

TABLE 1

Structural formulas and selected physical properties of chemical warfare agents

Parameter	Agent		
	GB	VX	HD
Chemical name (formula)	Isopropyl methyl phosphonofluoridate (C <sub>4</sub> H <sub>10</sub> FO <sub>2</sub> P)	O-ethyl-S-(2-diisopropyl amino-ethyl) methyl phosphonothiolate (C <sub>11</sub> H <sub>26</sub> NO <sub>2</sub> PS)	Bis(2-chloroethyl) sulfide (C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> S)
Structure	$(\text{CH}_3)_2\text{CHO}-\text{P}\begin{matrix} \text{O} \\ \parallel \\ \text{F} \end{matrix}-\text{CH}_3$	$\begin{matrix} \text{CH}_3 & \text{O} \\ & \parallel \\ \text{C}_2\text{H}_5\text{O} & \text{P} \end{matrix} - \text{S} - \text{CH}_2 - \text{CH}_2 - \text{N} \begin{matrix} \text{CH}(\text{CH}_3)_2 \\ \text{CH}(\text{CH}_3)_2 \end{matrix}$	$\text{Cl}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{Cl}$
Molecular weight	140.1	267.4	159.1
Physical state (at room temperature)	Liquid	Liquid	Liquid
Boiling point	158 °C	298 °C	215-217 °C
Vapor pressure (25 °C)	2.9 mmHg	7 × 10 <sup>4</sup> mmHg	0.11 mmHg

categories of stockpiled chemical warfare agents, nerve agents and blister agents [1] are represented in Table 1 by GB (sarin, a nerve agent), VX (nerve agent) and HD (variously called sulfur mustard, mustard gas, mustard, etc.). The simulant chemicals chosen were recommended by the sponsoring agency (Office of Assistant Secretary of the Army) and research staff of the Chemical Research Development and Engineering Center (CRDEC) at Aberdeen Proving Ground, MD. Tables 1 and 2 also list pertinent physical properties of agents and simulants. The various simulants were obtained from the following sources and used without additional purification: Diisopropyl methyl phosphonate (DIMP) (98% pure) (Johnson Matthey Electronics); dimethyl methyl phosphonate (DMMP) (technical grade) (Alpha Products); malathion (MAL) (96% pure) (K&K Fine Chemicals, Inc.); dibutyl sulfide (DBS) (96% pure) (Aldrich); phenanthrene, the detection chemical for the permeation studies, was obtained from Matheson Coleman and Bell.

#### CPC Materials

Thirteen different CPC materials were chosen as representative materials from a broad selection of generic classes (e.g., only one material composed of butyl/nylon/butyl laminate, one of Viton<sup>®1</sup> polyester/Viton laminate, even

<sup>1</sup>Viton<sup>®</sup> fluoroelastomer is a registered trademark of E.I. du Pont de Nemours & Co.

TABLE 2

Structural formulas and selected physical properties of simulants used in this study

Parameter	Simulant			
	DIMP	DMMP	MAL	DBS
Chemical name (formula)	(GB Simulant) Diisopropyl methyl phosphonate (C <sub>7</sub> H <sub>17</sub> OP)	(VX simulant) Dimethyl methyl phosphonate (C <sub>3</sub> H <sub>9</sub> O <sub>3</sub> P)	(Organophosphorous pesticide) (Dimethoxy-phosphinothioyl) butanedioic acid diethyl ester (C <sub>10</sub> H <sub>19</sub> S <sub>2</sub> O <sub>6</sub> P)	HD simulant) (C <sub>8</sub> H <sub>18</sub> S)
Structure	$\begin{array}{c} \text{(CH}_3\text{)}_2\text{CHO} \quad \text{O} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{P} \text{---} \text{CH}_3 \\ \quad \quad \quad \diagdown \quad \diagup \\ \text{(CH}_3\text{)}_2\text{CHO} \end{array}$	$\begin{array}{c} \text{CH}_3\text{O} \quad \text{O} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{P} \text{---} \text{CH}_3 \\ \quad \quad \quad \diagdown \quad \diagup \\ \text{CH}_3\text{O} \end{array}$	$\begin{array}{c} \text{CH}_3\text{O} \quad \text{S} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{P} \text{---} \text{S} \\ \quad \quad \quad \diagdown \quad \diagup \\ \text{CH}_3\text{O} \end{array} \quad \begin{array}{c} \text{CH} \text{---} \text{COOC}_2\text{H}_5 \\   \\ \text{CH}_2 \text{---} \text{COOC}_2\text{H}_5 \end{array}$	C <sub>4</sub> H <sub>9</sub> —S—C <sub>4</sub> H <sub>9</sub>
Molecular weight	180	124	330	146
Physical state (at room temperature)	Liquid	Liquid	Liquid	Liquid
Boiling point	66 °C (3 mmHg)	181 °C	156–157 °C	188–189 °C
Vapor pressure	— <sup>a</sup>	—	4 × 10 <sup>-5</sup> mmHg (30 °C)	—

<sup>a</sup> Not available.

though there could be several CPC materials made by different manufacturers employing the same fabric composition).

Table 3 (see Results Section) lists the various CPC materials tested, their manufacturer and nominal thickness of the various materials. A number of the materials are laminates, and are so indicated in Table 3 by naming the individual laminating layers of the laminate "sandwich" (as butyl/nylon/butyl). In the case of some materials, no information regarding composition or lamination was available, and the material is simply listed. Samples from gloves were taken from the palm of the glove; samples from sheet material were cut from the edge, and samples from protective suits were taken from the suit sleeves. Duct tape was added to the original list of 12 CPC materials due to its extensive use to seal suits to gloves and suits to footwear.

### Experimental protocols

#### A. Breakthrough time studies

A 2.54-cm diameter circle of the CPC material was positioned over the open end of a glass vial (2.54 cm long with a 2 mL volume) containing approximately

1 mL of pure liquid simulant. A 1.0-cm circle of phenanthrene-treated (see Analytical Procedure Section) filter paper (Whatman 41) was centered over the bottle mouth on top of the material, and a second larger piece of filter paper acted to hold the 1.0-cm circle in contact with the material. This arrangement of bottle plus CPC plus indicator paper was mounted in a clamp (Fig. 1) to provide a seal between the CPC and the vial. To initiate a breakthrough measurement, the vial was inverted so that the liquid simulant contacted the outside surface of the CPC sample.

A series of specially designed exposure cells using glass vials [5] were set up and inverted at the same time. After selected intervals, individual vials were returned to the upright position, the clamp was loosened, and the indicator paper was removed and analyzed. Figure 2 schematically shows the principle of the fluorescence quenching technique. The time interval at which individual vials were selected for measurement varied considerably, depending upon the speed with which the simulant penetrated the CPC material. For extremely resistant materials, the sampling interval might be 1 h or more, while for easily permeable materials, sampling intervals of 30 s to 1 min were used. For a particular simulant, the first vial which showed a quenching of the fluorescence of

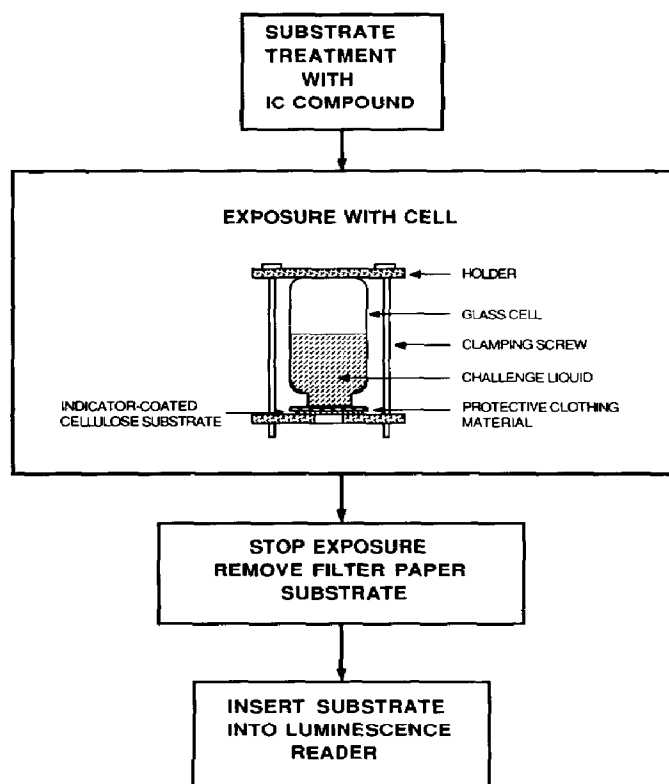


Fig. 1. Experimental apparatus schematic for breakthrough and rate of permeation study and schematic for fluorescence measurements (IC = indicator compound).

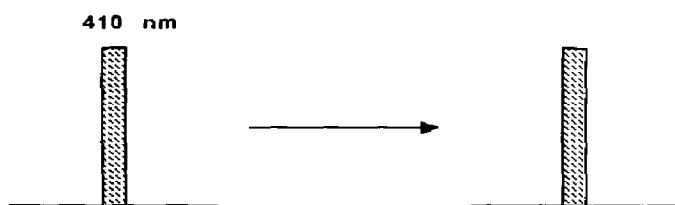
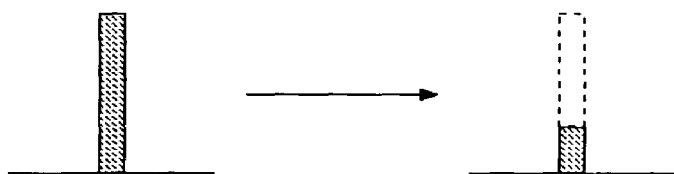
**A) UNEXPOSED IC COMPOUND****B) IC COMPOUND EXPOSED TO SIMULANT**

Fig. 2. Principle of the fluorescence quenching technique: (A) Representation of fluorescence emission of phenanthrene ( $10^{-2} M$ ) coated filter paper, excited at 352 nm and having a fluorescence maximum at 410 nm. (IC = indicator compound); (B) Representation of fluorescence intensity decrease of the phenanthrene-coated paper following exposure to simulant.

the indicator paper (see Analytical procedure Section) was taken as the “breakthrough vial.” The time at which this vial was sampled was therefore the breakthrough time. Each breakthrough time indicated in Table 3 was the average value of triplicate experiments. In the case of a few CPC materials, there was significant adhesion of the indicator paper to the CPC. In these circumstances, the indicator paper was analyzed on the opposite side from that which contacted the CPC (see Analytical procedure Section). Breakthrough times given in Table 3 as greater than some set time (e.g., > 24 h) correspond to solutions where the indicator paper/CPC sandwich left in contact with the chemical for the indicated period of time provided no measurable evidence of chemical contact during the period of 24 h observation.

**B. Permeation rate studies**

The basic experimental protocol consisted of measuring breakthrough (if any) of simulants after specific time intervals. The experimental set-up was the same as for the breakthrough time studies described above. A series of replicate exposure cells were all inverted at the specific time intervals following exposure. The indicator papers were removed from these vials and analyzed. A curve was constructed in which the amount of chemical which penetrated

the CPC material was plotted as a function of time after initial breakthrough. Each experiment was carried out in triplicate, and the curve was constructed using average values.

### C. Uptake studies

A 0.6-cm diameter circle of the CPC material was placed into 1 mL of the chemical simulant in a closed vial for 1 h [5]. The disc of CPC material was accurately weighed before and after immersion and the weight gain was considered an estimate of simulant uptake. In addition to this measurement, the change in physical characteristics of the CPC material following immersion was noted along with any other observations (e.g., leaching of colored dyes/adhesives from the CPC material).

### D. Analytical procedure

The analytical procedure developed for these permeation studies is described in detail in a previous report [5]. Briefly, Whatman No. 41 filter paper (11 cm circles) was treated with 1.25 mL of  $1 \times 10^{-2}$  M phenanthrene in ethanol and dried at room temperature. This served as our indicator paper. Following the simulant exposures as described above, the indicator paper circles were removed and directly analyzed for fluorescence. No chemical extraction was necessary for the analysis. This procedure therefore avoids the cumbersome separation techniques that would be required for a gravimetric (classical) analysis.

All fluorescence measurements were made using a Perkin-Elmer Model MPF-43A fluorescence spectrophotometer equipped with a 150-W xenon excitation source. To prepare exposed filter paper samples for measurements, the discs were mounted on a sample holder previously designed for surface emission measurements [6]. The indicator paper in the sample holder was transferred to the spectrofluorometer sample compartment for fluorescence measurement. All four simulants quenched phenanthrene fluorescence, but did so to differing extents (e.g., MAL caused the greatest degree of quenching, for a given concentration compared to equal concentrations of the other 3 simulants). Figure 2 illustrates the effect of MAL on the phenanthrene fluorescence. For a given simulant, the extent of fluorescence quenching on the indicator paper was related to the amount of simulant which had been absorbed by the paper. In this study, calibration curves for each simulant have been established, indicating a direct relationship between simulant concentration and fluorescence quenching. Figures 3 and 4 illustrate examples of calibration curves for DIMP and DBS. Note that there appears to be a linear relationship between the extent of fluorescence quenching and the concentration of simulant when this concentration is expressed logarithmically.

This fluorescence quenching procedure developed in this work was found to exhibit excellent sensitivity for detecting simulants. It is noteworthy that this



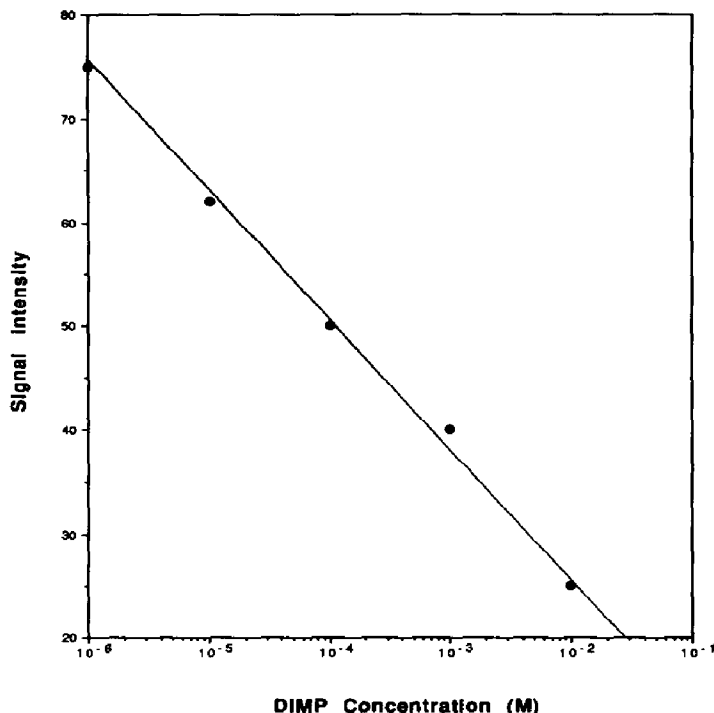


Fig. 3. Calibration curve for DIMP, using the fluorescence quenching of phenanthrene (see Experimental protocols, Section D). Aliquots of 2  $\mu\text{L}$  of DIMP, over the concentration range of  $10^{-2} \text{ M}$  to  $10^{-6} \text{ M}$  (diluted in ethanol) were added to the phenanthrene-treated paper, the paper was dried and the fluorescence was determined.

new quenching technique has been developed because a direct fluorescence measurement method cannot be used; CW agents and simulants are not fluorescent compounds such as polycyclic aromatic species [7]. The limits of detection for MAL, DIMP, DBS, and DMMP were found to be:  $10^{-12} \text{ M}$ ,  $10^{-6} \text{ M}$ ,  $10^{-5} \text{ M}$  and  $10^{-6} \text{ M}$ , respectively. This level of sensitivity allows one to readily detect very small amounts of simulant permeating the CPC. It should be emphasized that, in addition to phenanthrene, a wide variety of compounds (e.g., pyrene, naphthalene, anthracene, emodin, indole, fluorescein and diphenylamine) were also tested as possible indicator compounds. Only the fluorescence of phenanthrene was found to be uniquely quenched when exposed to any of the four simulants. Phenanthrene is a highly fluorescent compound, and there have been several studies in which investigators have examined the quenching of phenanthrene fluorescence by other chemicals [8, 9]. However, the effect of these particular chemicals on the fluorescence of phenanthrene has not been reported previously.

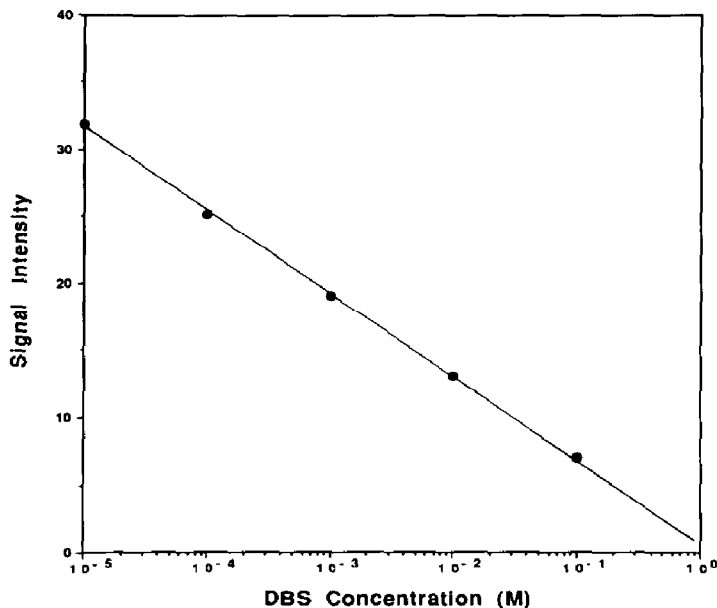


Fig. 4. Calibration curve for DBS, using the fluorescence quenching of phenanthrene (see Materials and methods, Section D). Aliquots of 2  $\mu\text{L}$  of DBS, over the concentration range of  $10^{-1} \text{ M}$  to  $10^{-5} \text{ M}$  (diluted in ethanol) were added to the phenanthrene-treated paper, the paper was dried, and the fluorescence was determined.

## Results and discussion

### *Breakthrough times*

The CPC materials tested displayed a variety of responses when tested for breakthrough time with the four chemical simulants (Table 3). Each of the simulants was tested undiluted, i.e., neat. Breakthrough time can serve to reflect relative estimates of protection provided by protective clothing [4, 5]. It is apparent that the CPC materials can be grouped into three categories, depending on the time required for breakthrough. The materials affording the highest degree of protection were CPC materials #9-13. For each of these materials, breakthrough times were in excess of 24 h, i.e., the test was carried out for at least 24 h, after which the test was terminated. In the case of CPC material #12, no breakthrough was detected even after 100 hours of exposure. The composition of the laminated fabric, and its thickness probably both contribute to the observed degree of chemical resistance. It is noteworthy that the thicknesses of materials #9-13 were greater than that of other CPC materials. Thickness alone, however, is not the most important criterion. It appears that laminates containing Teflon<sup>®2</sup> exhibit excellent resistance (see

<sup>2</sup>Teflon<sup>®</sup> is a registered trademark of E.I. du Pont de Nemours & Co.

TABLE 3

Breakthrough times of simulants through chemical protective clothing (CPC) materials

CPC Material	Thickness	DIMP <sup>a</sup>	DMMP <sup>a</sup>	MAL <sup>a</sup>	DBS <sup>a</sup>	Supplier
1. PVC/nylon/PVC (305 PVC/BA)	17 mil	10 min	4 min	3 min	4 min	Fyrepel Products Newark, OH
2. Neoprene plastic glove	No data	45 min	15 min	10 min	10 min	International Playtex, Inc. Stamford, CT
3. Tyvek® (Saranex®-coated)	8 mil	30 min	50 min	12 min	90 min	Kappler Safety Group Guntersville, AL
4. Butyl nitrile glove (Pioneer Gatorhide)	No data	60 min	45 min	50 min	55 min	Pioneer Industrial Products Willard, OH
5. Barricade® chemical barrier fabric	21 mil	50 min	80 min	90 min	60 min	Kappler Safety Group Guntersville, AL
6. Tyvek QC, Polyethylene-coated	6 mil	105 min	40 min	30 min	30 min	E.I. du Pont de Nemours & Co., Inc. Wilmington, DE
7. Viton® polyester/Viton (305 V/BA, 306 V/BA)	9 mil	140 min	140 min	> 100 h	> 100 h	Fyrepel Products Newark, OH
8. Duct tape	10 mil	210 min	210 min	> 24 h	> 7 h	Armco Company Michigan City, IN
9. Butyl/nylon/butyl (305 B/BA, 306 B/BA)	16 mil	> 24 h	> 24 h	> 24 h	> 24 h	Fyrepel Products Newark, OH
10. Butyl/polyester/chloroprene (Chempruf™ II)	19 mil	> 24 h	> 24 h	> 24 h	> 24 h	Mine Safety Appliances Pittsburgh, PA
11. Thf/Mws/Thf <sup>b</sup> ("First Team"™)	No data	> 24 h	> 24 h	> 24 h	> 24 h	Mine Safety Appliances Pittsburgh, PA
12. Teflon® Kevlar® Teflon (Force Field™)	17 mil	> 100 h	> 100 h	> 100 h	> 100 h	Fyrepel Products Newark, OH
13. Teflon/fiberglass/Teflon	10 mil	> 24 h	> 24 h	> 24 h	> 24 h	Chemical Fabric Corp. Merrimack, NH

<sup>a</sup>DIMP = Diisopropyl methyl phosphonate (GB simulant); DMMP = Dimethyl methyl phosphonate (VX simulant); MAL = Malathion (organophosphorus insecticide and generic nerve agent simulant); and DBS = Dibutyl sulfide (sulfur mustard simulant).

<sup>b</sup>Thermoplastic film/non-woven composite substrate/thermoplastic film.

materials #12–13). There are other laminate compositions, however, which also exhibit excellent resistance (i.e., butyl/nylon/butyl or butyl/polyester/chloroprene).

There is another group of CPC materials (Table 3) which exhibit relatively good resistance to one or more of the chemical simulants (materials #4–7). In general, these materials resisted simulant breakthrough for at least 1 h. Note that the Viton/polyester/Viton (material #7) provided excellent resistance to MAL and DBS. It is also important to note that CPC material #6 (Tyvek<sup>®3</sup>, polyethylene coated) did not show strong resistance against MAL and DBS. Note the different behaviors of materials #6 and #3. Even though both are Tyvek, they show differences in resistance to different simulants (see Table 3), perhaps due to differences in the coating material used over the Tyvek.

The last group of CPC materials in (materials #1–3) investigated in this study are those materials which exhibit poor chemical resistance (Table 3). With one exception, breakthrough occurred in less than 1 h. In the case of the PVC/nylon/PVC laminate, breakthrough occurred in a matter of a few minutes. It is also interesting to compare the chemical resistance of the two glove materials tested against this battery of chemicals. The material #2, commonly called Playtex<sup>™4</sup>, is widely used for domestic glove material in the kitchen and bath, while the butyl nitrile material is widely used in the chemical industry. Because of the extensive availability of Playtex, this material could be used for very short-term expedient protection. However, in our experimental system, the resistance to permeation of butyl nitrile is superior to that of Playtex. The butyl nitrile material provides a three-fold longer breakthrough time for DMMP, compared to Playtex, and a five-fold longer breakthrough time for MAL and DBS.

Also note that a special duct tape has been tested in the experimental assay. This duct tape is commonly used by hazardous material response teams to provide a seal between the protective suit and gloves, or around ankles to seal the suit to footwear. The experimental assay tested only one of many brands of duct tape, so the data cannot be used to evaluate the relative merits of different brands. The one particular brand tested demonstrated good resistance to the chemical simulants. As can be seen from Table 3, duct tape resists permeation of MAL and DBS for >24 h and >7 h, respectively. For the compounds DIMP and DMMP, duct tape provides greater resistance to breakthrough than CPC materials #1–7. Duct tape was one of the thinner materials tested (10 mil<sup>5</sup> vs. 19 mil maximal thickness for material #10).

#### *Rate of permeation studies*

This section briefly discusses data related to the permeation rate, which refers to how rapidly the chemical simulants diffuse through the CPC

<sup>3</sup>Tyvek<sup>®</sup> spun-bonded olefin is a registered trademark of E.I. du Pont de Nemours & Co.

<sup>4</sup>Playtex<sup>™</sup> is a trademark of International Playtex, Inc.

<sup>5</sup>1 mil =  $2.54 \times 10^{-5}$  m.

materials. This rate measurement provides a quite different index of CPC effectiveness against the simulants than breakthrough time. For some CPC materials, as the simulant begins to permeate the material, the resistance to permeation of the material changes. (In fact in certain instances, evidence of dissolution of CPC material constituents was seen, in that simulant solutions became colored, presumably with the material dye.) Therefore, by examining the slope of the rate of permeation curve, one can deduce valuable information about how the simulant affects the permeability of the material. Figure 5 shows an example of a permeation rate curve (DIMP against butyl nitrile) where the slope is initially very shallow, and then after 80 min, the slope increases dramatically. This behavior is in contrast to the curves of Figs. 6-9, where the slope is very steep. Representative curves showing the rate of permeation through various CPC materials by chemical simulants are shown in Figs. 6 through 9. In Figs. 6 and 7, we compare the rate of permeation of DIMP through material #1 (poor resistance) and material #7 (good resistance). In both cases, the steepest portion of the permeation curve shows the time at which maximum change in permeability occurs. Almost all of the permeation curves which we have generated exhibit a breakthrough time characterized by a rapid change in permeability with time. For material #1,

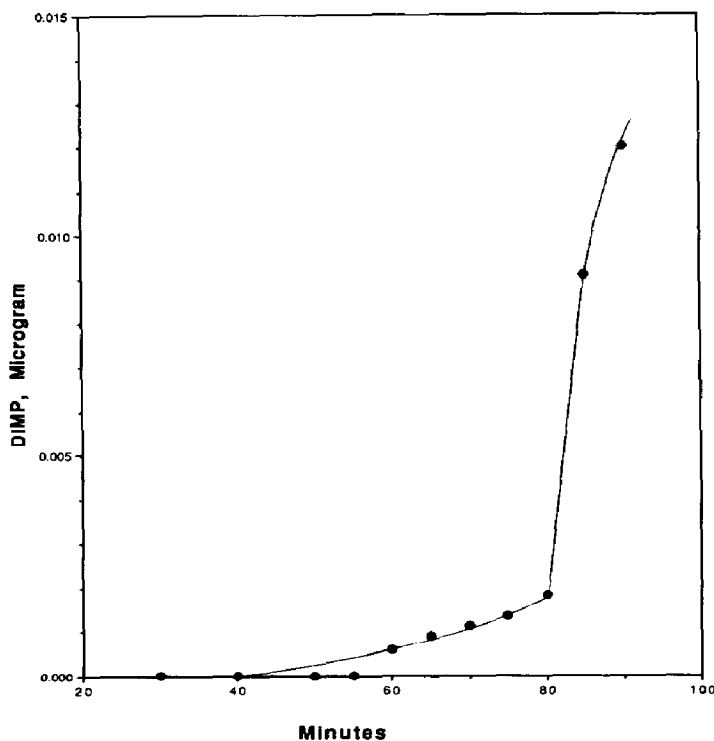


Fig. 5. Rate of permeation of DIMP through butyl nitrile glove material (#4, Table 3) (see Materials and methods for description of procedure).

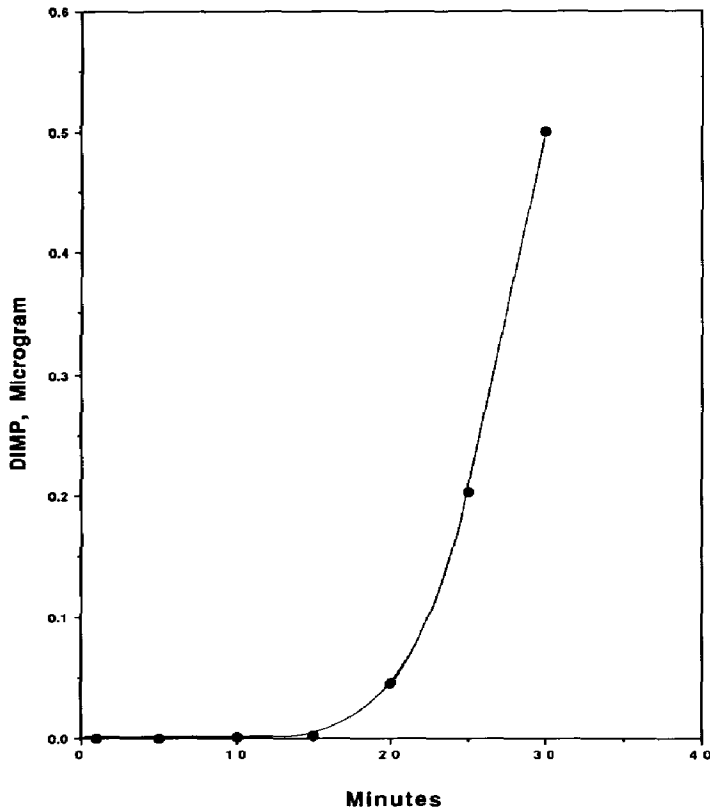


Fig. 6. Rate of permeation of DIMP through PVC material (#1, Table 3).

this change occurs about 15–20 min after initial breakthrough. For the resistant material (#7), the maximal permeability change occurs 20–30 min after initial breakthrough. This difference in time of maximal permeability change is probably consistent with the greater resistance to simulant permeation demonstrated by material #7. It is noteworthy that the permeation curves appear to level off after a steep increase. This effect could be due to saturation process of the detection system (i.e., the indicator-coated substrate became saturated with the simulations and could not absorb rapidly enough more simulant penetrating through the materials). Figures 8 and 9 exhibit some representative results of permeation rates of MAL through the two glove materials (#2 and #4) tested. In the case of the neoprene glove material, the maximal rate of change was measured after 20 min. These data may be of interest to workers who handle pesticides, as it demonstrates differences in permeability rates among two common commercial glove materials. This study has produced a large number of permeation curves for all combinations of simulant/CPC material. Although general conclusions from this wealth of data cannot readily be made, important and useful information can be derived from this study. The experimental results indicate that the breakthrough time could

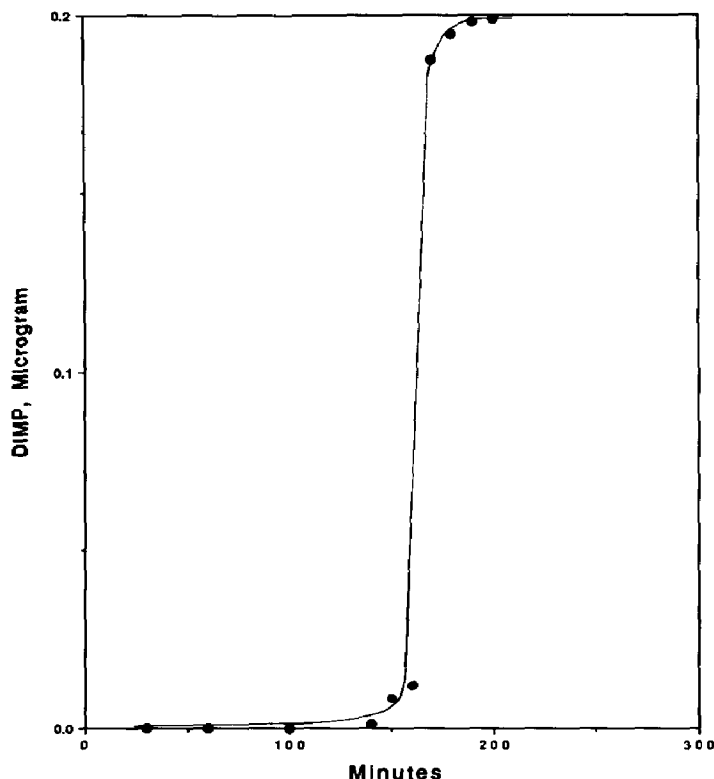


Fig. 7. Rate of permeation of DIMP through Viton laminate (#7, Table 3).

be used as a parameter for relative comparisons of CPC protection. Because most of the rate of permeation measurements show a rapid permeation of the simulant within a relatively short time of initial breakthrough, comparisons based on this parameter provide only qualitative differentiation regarding the effectiveness of the CPC materials tested.

#### *Uptake studies*

Table 4 presents the results of uptake studies, where a swatch of CPC material was immersed in undiluted simulant. Although certain immersion studies might take days to show detectable effects, our studies were limited to 1 h. The results from the uptake studies may have some relevance to the chemical protection afforded by the materials tested. However, it is noteworthy that, in the uptake studies, chemical impinges on the inside of the material as well as the outside, while in actual use, only the outside is intended to receive chemical exposure. Even more significantly, the process of cutting a small swatch of material to be immersed in a simulant solution for the uptake study results in exposed edges, which would be expected to exhibit little or no resistance to chemical permeation. Therefore, the uptake data can provide only qualitative information on physical changes of the materials immersed in

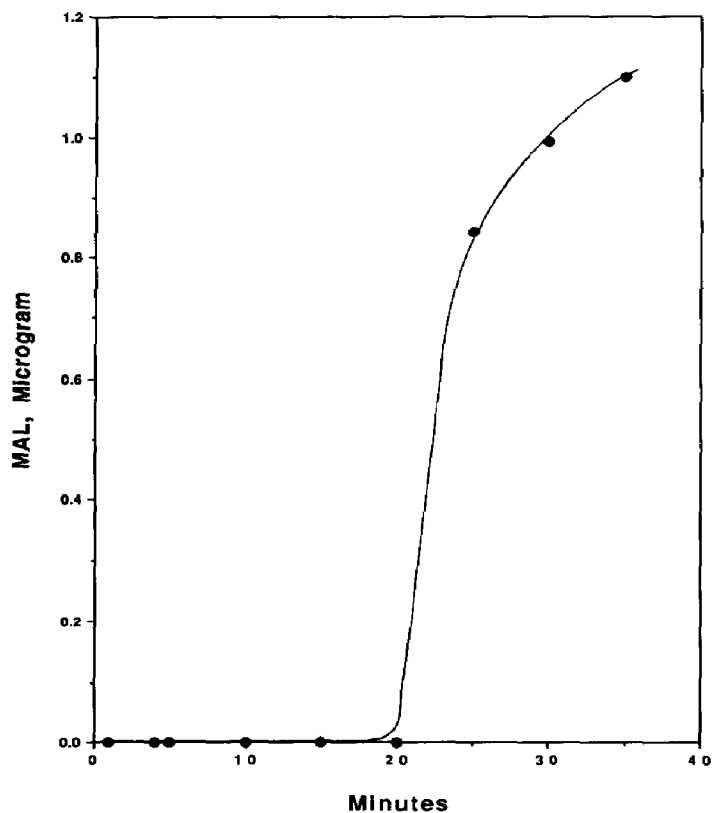


Fig. 8. Rate of permeation of malathion through neoprene glove material (#2, Table 3).

TABLE 4

Uptake of liquid simulant by CPC materials: 1 h study<sup>a</sup>

CPC material	Liquid (g/cm <sup>2</sup> )			
	DIMP	DMMP	MAL	DBS
1. PVC/nylon/PVC	— <sup>b</sup>	0.00686	0.00410	0.00166
2. Neoprene plastic glove	0.01329	0.00413	0.00349 <sup>c</sup>	0.09487
3. Tyvek®, Saranex®-coated	0.00486	0.00541	0.00592	0.00614
4. Nitrile glove	0.10028	0.00682	0.3163	0.00483
5. Barricade®	0.00404	0.00436	0.00737	0.00449
6. Tyvek QC	0.00426	0.00754	0.00491	0.00511
7. Viton®/polyester/Viton	0.04897 <sup>d</sup>	0.0110	0.00128	0.00038
8. Duct tape	— <sup>e</sup>	— <sup>f</sup>	— <sup>e</sup>	— <sup>e</sup>
9. Butyl/nylon/butyl	0.00167	0.00153	0.00201	0.03036
10. Butyl/polyester/chloroprene	0.00859	0.00351	0.02033	0.02033
11. Thermoplastic film	0.01012	0.00914	0.00798	0.00798
12. Teflon®/Kevlar®/Teflon	0.01598	0.01398	0.00994	0.00994
13. Teflon/fiberglass/Teflon	0.00127	0.00209	0.00118	0.00118

<sup>a</sup>0.86625 cm<sup>2</sup> of CPC material used.

<sup>b</sup>Disintegrated.

<sup>c</sup>CPC material expanded in two dimensions.

<sup>d</sup>Embrittlement and shrinkage.

<sup>e</sup>Adhesive dissolved; weight decreased.

<sup>f</sup>No significant change.



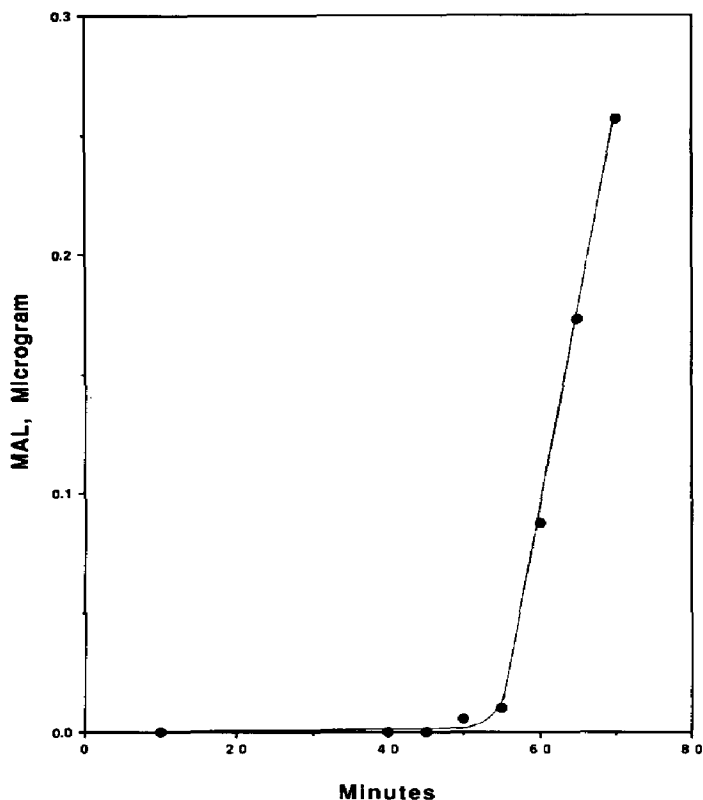


Fig. 9. Rate of permeation of malathion through butyl nitrile glove material (#4, Table 3).

simulant solutions. Among these changes we note the following. Material #1 disintegrated in DIMP, i.e., was reduced to a powder. Material #2 (Playtex glove) swelled in DBS without apparent disintegration. This effect was not seen with the other glove material (#4). Material #7 showed embrittlement and shrinkage in DIMP. Duct tape was found to undergo a weight loss upon immersion in DIMP, MAL and DBS, presumably due to dissolution of the adhesive. It is worth mentioning the importance of these uptake studies since they provide useful qualitative indications regarding physicochemical stability on the various materials.

## Conclusions

The experimental results of this work have produced many important conclusions on permeation properties of a wide variety of protective materials. The data indicate that some commercially available CPC materials provide excellent protection against permeation by the chemical warfare agent simulants evaluated. The most useful comparisons of the relative effectiveness

of the various materials are provided in Table 3. Materials #9-13, (viz., butyl/nylon/butyl, butyl/polyester/chloroprene, thermoplastic film, Teflon/Kevlar<sup>®6</sup>/Teflon, and Teflon/fiberglass/Teflon) all exhibited good resistance to permeation of the simulants (i.e., breakthrough times >24 h). All these materials are laminates and two of these utilize Teflon as a laminating material. The effectiveness of the other CPC materials tested against permeation by the simulants varied considerably, but no other material demonstrated the consistency of resistance toward all four simulants as demonstrated by materials #9-13. Duct tape exhibits reasonable resistance to permeation by the four simulants, although its resistance to DIMP (210 min) and DMMP (210 min) was not as good as its resistance to MAL (>24 h) and DBS (>7 h). Due to its wide availability, duct tape appears to be a useful expedient material to provide at least a temporary seal against permeation by the agents.

It should be emphasized that all these results were obtained during simulant challenge and should be confirmed with the unitary agents themselves. Although the authors expect that the agents will behave similarly to the simulants, this might not be true for a particular CW agent/CPC material combination. It is noteworthy that both permeation and penetration (of simulant through the pores of the materials) combined to account for the flow of liquid penetrating through the polymer. The results of this study do not distinguish between penetration and permeation but provide an overall parameter that can be related to the protective characteristics of the materials tested.

Finally, this work deals with an important application of a new analytical technique for permeation study of chemical agents and simulations through protective materials. The analytical technique, which is based on spectral modification of fluorescence, demonstrates high sensitivity, reproducible results, and simplicity. These features make it an attractive choice for future permeation studies of field monitors for protective garments.

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