

NIOSH

TECHNICAL REPORT

PERMEATION OF PROTECTIVE GARMENT MATERIAL BY LIQUID HALOGENATED ETHANES AND A POLYCHLORINATED BIPHENYL

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

ERRATA

for

Permeation of Protective Garment Material by
Liquid Halogenated Ethanes and Polychlorinated Biphenyls

It is important to note that pure Polychlorinated Biphenyls (PCB's) are rarely used commercially; they are generally diluted with chlorinated benzenes or other industrial solvents. As indicated in this report, the PCB used here was AROCLOR 1254 diluted with Trichlorobenzene (TCB). The analytical method employed in this study was not specific. Either or both chemicals in the PCB mixture could have permeated the garment material samples. NIOSH will perform additional studies in the near future to obtain permeation data for the individual components of the PCB mixture.

**PERMEATION OF PROTECTIVE
GARMENT MATERIAL BY
LIQUID HALOGENATED ETHANES
AND A POLYCHLORINATED BIPHENYL**

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PERMEATION OF PROTECTIVE GARMENT MATERIAL BY LIQUID HALOGENATED ETHANES AND A POLYCHLORINATED BIPHENYL

by

R. W. Weeks, Jr., and M. J. McLeod

ABSTRACT

The halogenated ethanes 1,2-dichloroethane; 1,1,1-trichloroethane; and 1,1,2-trichloroethane are used as chemical intermediates and in metal working operations, and polychlorinated biphenyls (PCBs) have in the past been used by the tens of millions of pounds in various roles in American industry. Because of the widespread use and hazardous or potentially carcinogenic nature of these compounds, a study was performed to determine the degree of protection which was afforded against these compounds by certain protective garment materials. The materials evaluated in these studies have included: butyl rubber, milled nitrile rubber, neoprene rubber latex, nitrile rubber latex, polyethylene, poly(vinyl alcohol), surgical rubber latex, Teflon, and Viton as well as the following composite or multilayered materials: butyl-coated nylon, polyethylene-coated Tyvek, polyurethane-coated nylon, and poly(vinyl chloride)-coated nylon. The breakthrough time at which each liquid phase compound permeated these materials was studied by the time lag method. For the noncomposite materials, the results of these breakthrough studies were correlated with their equilibrium weight changes following immersion in the test liquids. Results of these studies have shown that most materials currently used in the construction of protective garment material in the United States are of a generally unsatisfactory nature with respect to protecting the worker against the halogenated ethanes and the PCB used in this study.

I. INTRODUCTION

Chlorinated ethanes are chemical compounds of the general structure $C_2H_xCl_{6-x}$ ($x \leq 5$) and are widely used in the industrial world as solvents, chemical intermediates, cleaning fluids, fumigants, and for numerous other purposes including uses in petroleum refining. Likewise the chemicals in the class of compounds known as polychlorinated biphenyls $C_{12}H_{10-y}Cl_y$ ($2 \leq y \leq 10$) (PCBs) have found widespread use as fluids for heat transfer systems, hydraulic systems, and fire retardants, but by far their widest use has been as dielectric fluids in capacitors and transformers. Both the chlorinated ethanes and the polychlorinated biphenyls have shown evidence of chemical carcinogenicity and other toxic effects,¹⁻⁹ and as such must be handled and utilized with extreme care. Despite the hazards involved in the use of these compounds, the halogenated ethanes find continued widespread use and the PCBs are widely encountered, although their original roles are being satisfied through replacement by other substances and they are no longer being manufactured nor imported into the U. S.

Because of the wide scope of usage of these materials and their associated risks, the present study was performed to determine those protective garment materials which would afford the highest degree of protection against the halogenated ethanes and the particular PCB (Aroclor-1254) chosen for this study. Overview documents describing three halogenated ethanes of this study and polychlorinated biphenyls in general are given in Appendices A-D of this report.

II. EXPERIMENTAL

The work described here was performed in a laboratory which had been specially modified and equipped to handle chemical carcinogens.¹⁰ Strict care was taken to avoid worker exposure to hazardous chemicals during the course of these studies. Reagent-grade chemicals used for this work were: 1,2-dichloroethane (Alfa Products, Danvers, MA); 1,1,1-trichloroethane (Matheson, Coleman & Bell, Norwood, OH); 1,1,2-trichloroethane (J. T. Baker Chemical Co., Phillipsburg, NJ); n-heptane and n-hexane (Burdick and Jackson Laboratories, Inc., Muskegon, MI). Also used was polychlorinated biphenyl, whose chemical composition as determined by GC/MS was consistent with that of Aroclor 1254 (Monsanto Co., Inc., St. Louis, MO), which had been diluted with trichlorobenzenes (TCB, a common industrial PCB diluent) such that the final composition was 43% TCB and 57% Aroclor 1254. **Throughout the present report this PCB/TCB mixture will be referred to as simply Aroclor 1254 or PCB.** CAP/ASTM Type I water was used throughout these experiments. The protective garment materials (butyl rubber, surgical rubber latex, neoprene rubber latex, nitrile rubber latex, milled nitrile rubber, polyethylene (medium density), poly(vinyl alcohol) [unsupported], Teflon, Viton, and the composite/bonded materials butyl-coated nylon, polyethylene-coated Tyvek, polyurethane-coated nylon, and poly(vinyl chloride)-coated nylon) used in these studies were obtained from: Clean Room Products (Bay Shore, NY); David's Gloves (Springfield, OH); Edmont-Wilson (Coshocton, OH); Interex Corporation (Natick, MA); Norton Safety Products (Charleston, SC); Pioneer Rubber Co. (St. Louis, MO); and Surety Rubber Co. (Carrollton, OH). As such, these materials were broadly representative of those materials which were readily available from commercial sources, but their choice does not represent an endorsement by the Los Alamos Scientific Laboratory. Each of the halogenated ethane determinations was performed in duplicate to ensure statistical validity. For those studies in which polyethylene-coated Tyvek was employed, a single determination was run with Tyvek toward the water-containing side of the permeation cell and the second determination was effected with the polyethylene toward the water.

A. Protective Garment Material Weight Change Experiments Following Immersion in Solvent

Samples (2-20 g) of protective garment materials were immersed in the particular halogenated ethane or PCB at room temperature ($23 \pm 1^\circ\text{C}$) for total time periods of seven days. During this period, they were removed and weighed at 24 and 168 h post immersion to determine the materials percent weight increase or decrease. For post immersion weighings, the materials were patted dry immediately after being removed from the respective liquids in order to remove excess solvent, and weighings were taken within 5 min. The net gain (loss) of weight was noted and reported as percent weight change relative to the initial sample weight.

B. Volume Change of Protective Garment Material Upon Immersion in Solvent

To determine the volume change of a given material following immersion, 1" by 1" pieces of the subject materials were individually placed in beakers which contained the halogenated ethanes and the particular PCB of this study. At 1, 4, and 24 h following immersion, the material was removed from its solvent and dimensional measurements obtained within 1 min following removal. The reason for the rapid measurement was that certain of the test materials would begin to shrink very soon after removal from the solvent due to solvent evaporation from within. Thickness measurements were to the nearest mil whereas length and width measurements were to the nearest 1/64th inch. The change in volume of the glove following immersion was then calculated relative to its original volume.

C. Solvent Permeation Through Protective Garment Material

Experiments were performed to determine the rate at which the halogenated ethanes and the PCB used in this study permeated various protective garment materials. Discrete, rather than continuous, sampling was employed for these studies and because of the hazardous nature of the compounds employed, the experiments were performed in a chemical fume hood having a face velocity >125 linear ft./min.

The permeation cells employed in these studies were functionally identical to those described in the Arthur D. Little, Inc., report for Contract 210-76-0130 to the National Institute for Occupational Safety and Health¹¹ and are shown in Fig. 1. The cell was constructed of Pyrex 1720 glass with stainless steel membrane holders and stainless steel top covers. Gaskets for the cell were constructed from Teflon (trademark DuPont) with the test material placed between the gaskets and with the bolts tightened to a torque of 5 ± 2.5 in pounds. This torque was chosen because values less than 2.5 in pounds did not seal the protective material firmly and torques greater than 7.5 in pounds would put such pressure on the material that it would tear or degrade rapidly at the points of contact.

A constant temperature was maintained during each permeation test by immersing the cells in the water bath of an Exacal 300 constant temperature bath (Neslab Instruments, Inc., Portsmouth, NH) maintained at $26 \pm 1^\circ\text{C}$ as shown in Fig. 2. Stirring of the aqueous side of the cell was effected by a Teflon stirring bar driven by a Model MS-7 Micro-Submersible Magnetic Stirrer (Tri R Instruments, Rockville Centre, NY, or Ace Glass, Vineland, NJ). Breakthrough determinations were run with either one or two permeation cell units in the constant temperature bath.

A zero time base for the halogenated ethane permeation studies was established as follows: The aqueous side of the cell was filled with 100 mL of water and allowed to reach thermal equilibrium with the water bath. Likewise, the particular organic compound being tested was allowed to reach

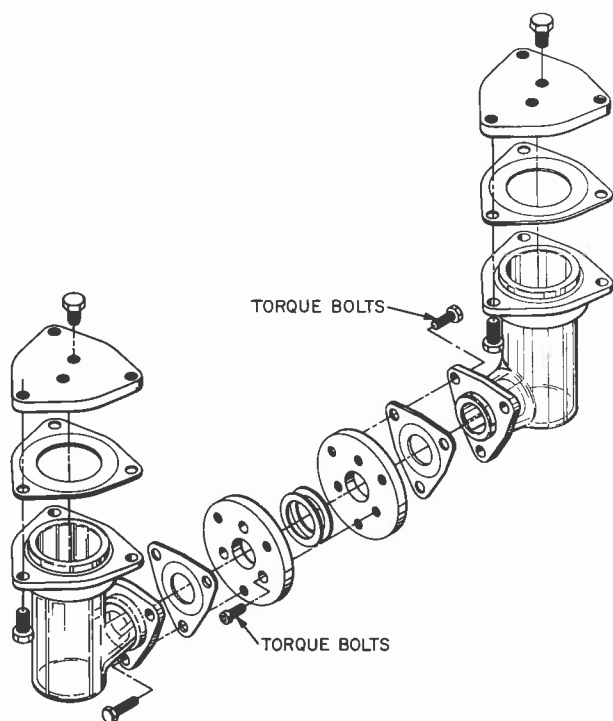


Fig. 1.

Permeation cell used to measure protective garment material breakthrough times.

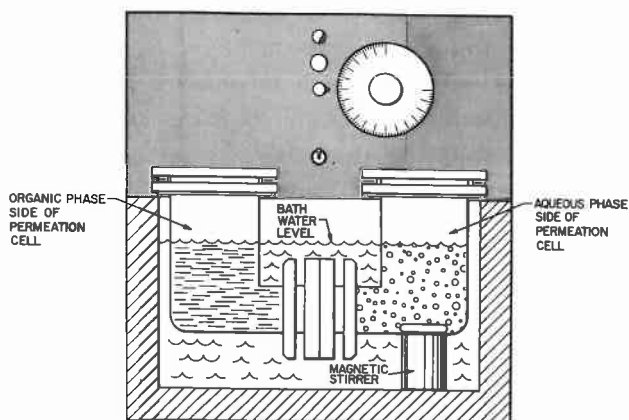


Fig. 2.

Cross-sectional drawing of water bath, magnetic stirrer, and permeation cell.

test temperature equilibrium in the bottle in which it came from the manufacturer. When it was desired to begin a study, 100 mL of the thermally equilibrated organic was poured rapidly into the permeation cell and this was defined as the zero point in time for a given study. Samples (3 mL for 1,1,2- and 1,1,1-trichloroethane and 5 mL for 1,2-dichloroethane) were taken via pipet from the aqueous phase of the permeation cell at predetermined times. Each sample was placed in a 5-mL Mini-Vial (Applied Science Laboratories, State College, PA) and capped with a Teflon-faced silicone rubber septum screw cap (Teflon toward solution).

The halogenated ethane concentration in the aqueous phase of the permeation cell was obtained using a gas chromatograph (GC) (Perkin-Elmer Model 900 (Norwalk, CN) equipped with a Tracor (Austin, TX) linearized Ni-63 electron capture detector) following solvent extraction. Particularly, the water aliquot from 1,2-dichloroethane was extracted with 2 mL of n-hexane and the trichloroethanes were extracted with 3 mL of n-hexane to collect the halogenated ethanes. The hexane was then analyzed by GC in a manner similar to that reported by Reding, et al.¹² for halogenated methanes. Each water aliquot removed was replaced with an equal amount of water. Calibration curves were prepared daily and calibration standards were prepared at appropriate intervals. Numerical integration of peak areas was performed using a Spectra-Physics (Santa Clara, CA) Minigrator electronic integrator. The conditions for these determinations are given in Table I.

The determination of the breakthrough time and the rate at which the particular PCB of this study permeated the various garment materials was performed by placing 110 mL of PCB ($T=25^{\circ}\text{C}$) in the organic phase side of the permeation cell with the test material in place and with 120 mL of water and 40 mL of n-heptane atop the water in the cells' aqueous phase side. The aqueous phase was stirred vigorously to allow the heptane to continuously extract the PCB from the water. This procedure was necessary because of the limited solubility of PCB constituents in water. Five

TABLE I
GAS CHROMATOGRAPHIC ANALYSIS^a
CONDITION FOR HALOGENATED ETHANES

| | Analyte | | |
|--|--------------------|-----------------------|-----------------------|
| | 1,2-Dichloroethane | 1,1,1-Trichloroethane | 1,1,2-Trichloroethane |
| Injector temperature, °C | 300 | 200 | 200 |
| Column temperature, °C | 150 | 150 | 180 |
| Detector temperature, °C | 300 | 300 | 300 |
| Lower limit of quantitation (ppm) ^b | 50 | 10 | 10 |
| Lower limit of detection (ppm) ^b | 8 | 2 | 1 |

^aPerkin-Elmer Model 900 gas chromatograph equipped with a Tracor linearized Ni-63 electron capture detector and using a 2-ft. by 1/8-in. o.d. stainless-steel Chromosorb 107 column.

^bPer injection of 0.2 μ L.

mL heptane aliquots were used for each determination and after each sample withdrawal n-heptane was added to replace that which had been removed and to thus maintain constant heptane volume.

Determinations of PCB concentrations in the n-heptane were performed using either a 1 or a 10-cm far UV quartz cell in conjunction with a DK-2A UV-visible-near IR range scanning spectrophotometer (Beckmann Instruments Co., Fullerton, CA). Quantitation was effected using the 288 nm peak of the mixture.

For both the halogenated ethanes and the PCBs, in those cases where a positive organic concentration value was obtained, i.e., after breakthrough, it was necessary to mathematically correct the observed concentration to compensate for dilution effects. Because of sequential dilutions during sampling, the true organic concentration for each discrete sample was calculated from the formula:¹²

$$C_n = c_n + (V_s)/(V_p) \sum_{i=1}^{n-1} c_i ,$$

where

- i = an indexing number for each discrete sample,
- c_i = the organic concentration in discrete sample number i, (ppm),
- n = the number of the most recent discrete sample taken,
- c_n = the organic concentration in sample n, (ppm),
- C_n = the organic concentration in the aqueous phase at the time of sample number n, (ppm),
- V_s = volume of sample, (mL), and
- V_p = volume of fluid from which sample was removed (mL).

III. RESULTS AND DISCUSSIONS

Because of their widespread use in the American workplace, butyl rubber, nitrile latex, neoprene latex, poly(vinyl alcohol), surgical rubber latex, and Viton elastomer were chosen for the present studies. The composite/bonded substances of this study were not in all cases presently available as commercial material for protective garments, but rather were chosen to determine their potential for resistance to solvent permeation. Likewise, Teflon gloves were included in these studies simply because they are commercially available.

In studies involving protective garments constructed of neoprene, nitrile, natural or surgical rubber, one must note that giving a particular composition is not sufficient, by itself, to describe the materials. In addition to its composition *per se*, one must state whether the material was prepared as a latex, i.e., colloidal material deposited from an aqueous suspension or was a so-called solvent/cement dipped or milled material¹³ which denotes production by a molecular layering from an organic solvent. This industry jargon is further complicated by the fact that a "milled" material may mean either that the material was prepared from an organic solvent or that at some stage in processing the raw material was actually subjected to physical milling by a crushing/abrading type operation, but this meaning will not be used in this report. An exaggerated illustration of the "latex" and the "solvent dipped" forms is given in Fig. 3.

In general, the conditions of the present study did not show that the latex materials were more porous than the "milled" or "cement dipped" materials for a given chemical composition, but as shown in Table II, the percent weight change of milled nitrile immersed in 1,2-dichloroethane was much less than that of nitrile latex immersed in this same solvent. This would be expected from physical forms such as those of Fig. 3 wherein there is less surface area for sorption to occur in the cement dipped material than with the colloidal particles of the latex. As will be discussed later in this section, there was a correlation between permeation and weight or volume gain. This leads to the possibility that permeation occurred more rapidly through the latex, but as mentioned above, the experimental conditions of the present work coupled with the relatively rapid 1,2-dichloroethane breakthrough would not allow definite differentiation of the breakthrough times for the latex as opposed to the milled nitrile. Further work is necessary to better define the general case of permeation being a function of method of preparation of material.

A. Protective Garment Material Weight Change Following Immersion in Organics

Because of the known relationship between permeation and equilibrium solubility,¹⁴⁻¹⁶ studies were performed to note any correlation which existed between weight gain of material following immersion and the breakthrough time at which the material was permeated by organic solvent. For such studies to allow comparisons among the samples, results were normalized to breakthrough time per unit thickness of test material. The so-called equilibrium or steady-state weight change for each material was determined by measuring the weight change at 24 and 168 h following immersion and is discussed in Sec. III.C.3. As may be noted in Table II, of the homogeneous, nonbonded materials of this study, only PVA, surgical rubber latex, and Viton reached weight equilibrium for all the solvents before 24 h. Typical examples of this are given in Figs. 4, 5, and 6. These show that following immersion in 1,1,1-trichloroethane, neoprene rubber latex, and cement dipped butyl rubber had attained an equilibrium weight gain after 24 h immersion whereas medium density polyethylene experienced a continuing weight increase through day seven.

B. Protective Garment Material Volume Change Following Immersion in Organics

Because of the relation between weight and volume changes of given systems, studies were performed to determine the change in volume of a material as a function of time following immersion in solvent and to correlate these changes with the breakthrough time when the solvent permeates the particular material. As was the case for weight changes, equilibrium volume changes were a function of time following immersion and are presented in Table III for times of 1, 4, and 24 h of immersion. As with the situation for weight change, volume change equilibrium was not obtained immediately upon immersion, but rather was a function of time following immersion. As might have been expected, the most rapid increase in volume occurred within 1 h following immersion, but a longer time period was required for a steady-state volume to be attained. As shown in Table III for this study, in the case of all halogenated ethanes except Viton in 1,1,1-trichloroethane,

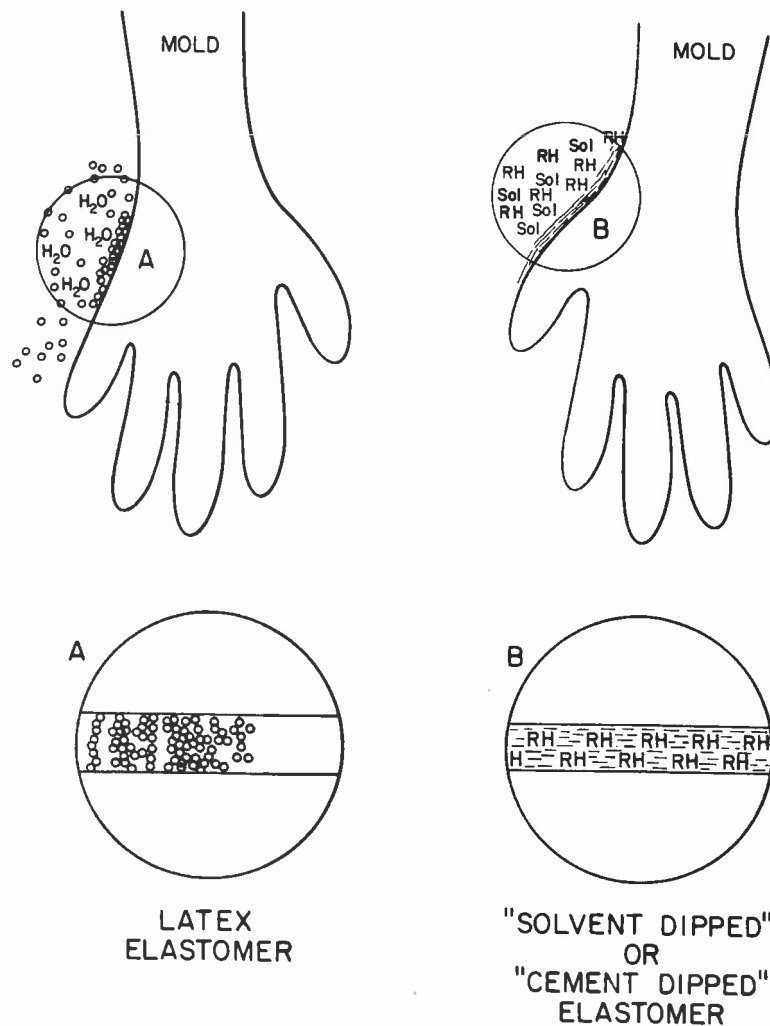


Fig. 3.

Illustration depicting the physical form of "latex" protective garment material and "cement or solvent dipped" protective garment material and showing how a latex is deposited as colloidal particles whereas the "cement dipped" materials are deposited as molecular layers.

TABLE II

WEIGHT CHANGE OF PROTECTIVE GARMENT MATERIAL
FOLLOWING IMMERSION IN VARIOUS LIQUIDS

| | Per Cent Weight Change* | | | | | | | |
|---|-------------------------|------------------|-----------------------|-------|-----------------------|--------------|--|-------|
| | 1,2-Dichloroethane | | 1,1,1-Trichloroethane | | 1,1,2-Trichloroethane | | Polychlorinated Biphenyl (Aroclor 1254) | |
| | 24 h | 168 h | 24 h | 168 h | 24 h | 168 h | 24 h | 168 h |
| A. Homogeneous, Nonbonded Material | | | | | | | | |
| Butyl rubber | 34 | 34 | 319 | 328 | 80 | 80 | 48 | 176 |
| Neoprene rubber latex | 182 | 190 | 230 | 241 | 290 | 291 | 170 | 287 |
| Nitrile rubber latex | 655 ^b | ^b | 237 | 263 | ^b | ^b | 112 | 208 |
| Nitrile rubber milled | 340 | 440 ^b | --- | --- | --- | --- | --- | --- |
| Polyethylene (medium density) | 0.2 | 16 | 8.2 | 21 | 5 | 16 | 46 | 66 |
| Poly(vinyl alcohol), unsupported | 0.3 | 0.4 | 0.2 | 0.2 | 0.8 | 0.9 | 2 | 2 |
| Surgical rubber latex | 211 | 226 | 550 | 564 | 464 | 473 | 519 | 513 |
| Teflon | 0.2 | 1 | 0.0 | 0.1 | 0.3 | 0.4 | -0.3 | -0.2 |
| Viton elastomer | 6 | 6 | 12.8 | 13.5 | 4 | 5 | 0.6 | 0.8 |
| B. Coated/Bonded Materials | | | | | | | | |
| Butyl-coated nylon | 24 | 27 | 121 | 143 | 47 | 49 | 77 | 90 |
| Polyethylene-coated Tyvek | 74 | 100 | 47 | 75 | 131 | 147 | 171 | 190 |
| Polyurethane-coated nylon | 26 | 86 | 49 | 55 | 58 | 79 | 92 | 89 |
| Poly(vinyl chloride)-coated nylon | 251 ^b | 265 ^b | 11 | 15 | 227 | 273 | 18 | 16 |

*Arithmetic mean of two samples. Duplicate samples evidenced 168-h weight change which did not differ by more than 15% relative in any of the samples whose weight gain was more than 2%.

^bSample disintegrated.

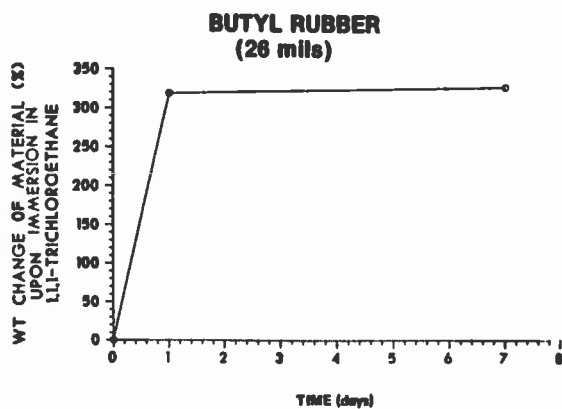


Fig. 4.

Weight change of butyl rubber as a function of time following immersion in 1,1,1-trichloroethane.

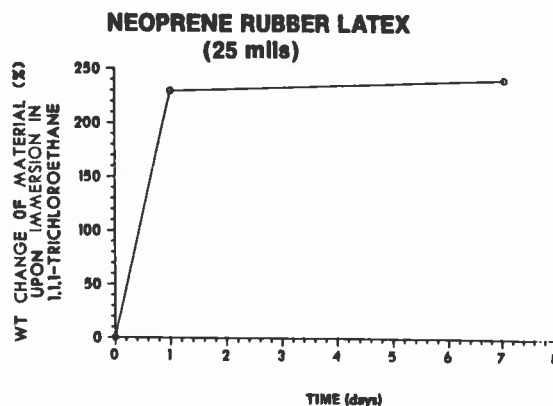


Fig. 5.

Weight change of neoprene rubber latex as a function of time following immersion in 1,1,1-trichloroethane.

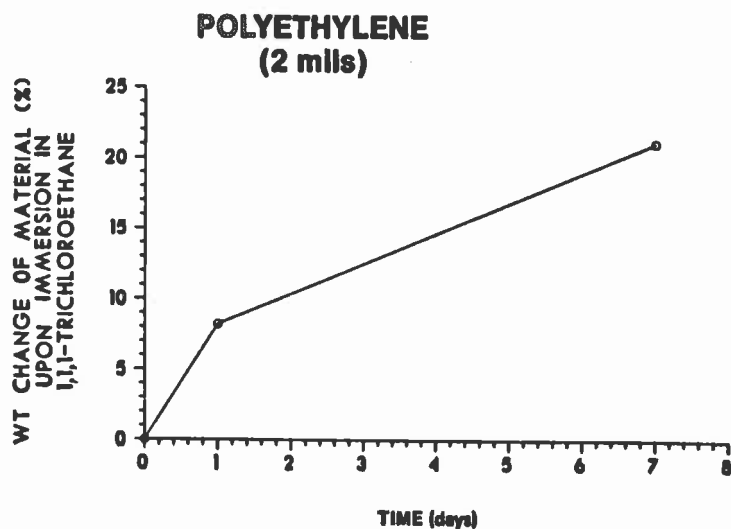


Fig. 6.
Weight change of medium density polyethylene as a function of time following immersion in 1,1,1-trichloroethane.

TABLE III

**VOLUME CHANGE OF PROTECTIVE GARMENT MATERIAL
FOLLOWING IMMERSION IN VARIOUS LIQUIDS**

Per Cent Volume Changes^a

| | 1,2-Dichloroethane | | | 1,1,1-Trichloroethane | | | 1,1,2-Trichloroethane | | | Polychlorinated Biphenyl (Aroclor 1254) | | |
|--|--------------------|-----|------|-----------------------|------|------|-----------------------|-----|------|--|------|-------|
| | 1 h | 4 h | 24 h | 1 h | 4 h | 24 h | 1 h | 4 h | 24 h | 1 h | 4 h | 24 h |
| A. Homogeneous, Nonbonded Materials | | | | | | | | | | | | |
| Butyl rubber | 19 | 19 | 19 | 249 | 260 | 263 | 10 | 7 | -1 | -2.6 | -2.6 | 22.5 |
| Neoprene rubber latex | 123 | 141 | 142 | 213 | 239 | 246 | 158 | 140 | 158 | 32 | 69 | 192 |
| Nitrile rubber latex | 259 | 275 | 286 | 182 | 208 | 214 | 277 | 339 | 355 | 31 | 41 | 138 |
| Nitrile rubber milled | 252 | 252 | 254 | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Polyethylene (medium density) | 8 | 20 | 20 | 9.6 | 9.6 | 9.6 | -23 | -16 | -20 | 9.6 | -4.1 | 2.7 |
| Poly(vinyl alcohol), unsupported | 0.3 | 1.5 | 1 | 0 | 3 | 4 | 0 | 5 | 5 | 0 | 4.4 | 5.3 |
| Surgical rubber latex | 118 | 118 | 124 | 334 | 429 | 425 | 146 | 154 | 154 | 203 | 276 | 297 |
| Teflon | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Viton elastomer | 0 | 9 | 11 | 0 | 8.6 | 20.5 | 16 | 16 | 19 | 0 | -12 | -21 |
| B. Coated/Bonded Materials | | | | | | | | | | | | |
| Butyl-coated nylon | 25 | 25 | 25 | 11 | 153 | 181 | 42 | 44 | 44 | 18 | 26 | 71 |
| Polyethylene-coated Tyvek | 4.3 | 9 | 9 | -5 | 13.3 | 12.3 | 14 | 4 | -1 | 27 | 14 | 16 |
| Polyurethane-coated nylon | -3 | 1.5 | 0 | 14.3 | 15.7 | 13.7 | -5 | -5 | -5 | -2 | 0.6 | 1 |
| Poly(vinyl chloride)-coated nylon | b | b | b | 0 | 0 | 22 | b | b | b | -5.5 | -5.5 | -11.8 |

^aArithmetic mean of two samples. Duplicate samples evidenced 24-h volume changes which did not differ by more than 15% relative in any of the samples whose volume gain was more than 5%.

^bSample disintegrated.

there was little change in volume between 4 and 24 h. However, for the Aroclor 1254 there was a noticeable change in volume between 4 and 24-h immersion, and this points out that care must be taken in defining an equilibrium volume change. Examples of volume change following immersion are given in Figs. 7 and 8. Figure 7 illustrates the volume change of Viton elastomer following immersion in 1,1,2-trichloroethane. The relatively small 24-h volume change (<20%) for Viton is in agreement with its relatively long breakthrough time as evidenced against this solvent, i.e., even at 24 h past challenge there was no 1,1,2-trichloroethane found in the aqueous phase of the permeation cell. At the other extreme in the relationship between volume change and permeability, Fig. 8 shows that for surgical rubber latex there was a volume change of ~150% following 24-h immersion in 1,1,2-trichloroethane, and this correlates well with the fact that 1,1,2-trichloroethane was observed in the aqueous phase of the permeation cell within minutes following challenge, i.e., the breakthrough time was inversely related to the equilibrium volume change for the homogeneous, nonbonded materials.

C. Permeation of Organics Through Protective Garment Material

Most of the homogeneous, nonbonded protective garment materials chosen for these studies were obtained from commercial sources and were thus representative of materials available to workers in the U. S. The composite materials were not generally used as glove materials, but rather were chosen as being representative of material available for use in coats or aprons or were experimental or prototype materials. In the present work, the results of these permeation studies are presented in three ways:

1. The time required for the first detectable quantity of organic to permeate the given material into the aqueous phase, i.e., the so-called breakthrough time (T_B).
2. A normalized breakthrough time in which the breakthrough time per unit thickness of the subject material is reported (T_B/x).
3. The diffusivity, D , i.e., the diffusion coefficient for each material is presented.

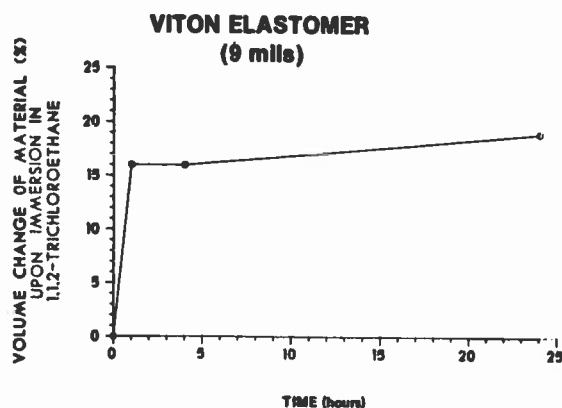


Fig. 7.

Volume change of Viton elastomer as a function of time following immersion in 1,1,2-trichloroethane.

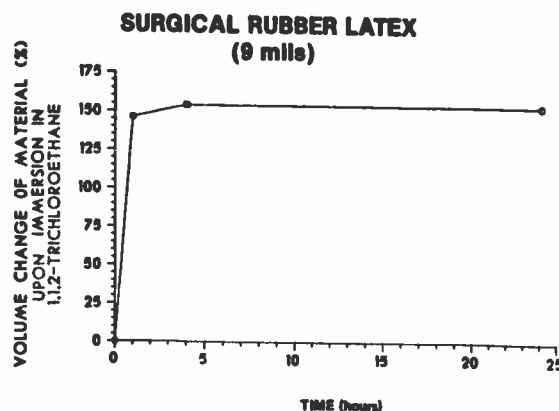


Fig. 8.

Volume change of surgical rubber latex as a function of time following immersion in 1,1,2-trichloroethane.

Each of the above is of value for determining the relative efficacy of a given material in protecting the worker against exposure to the particular chemical being studied. The breakthrough time (T_B) gives the "bottom line" for the particular materials included in this study. It represents the combined effects of material imperviousness and material thickness and, thus, the relative degree of protection a worker is afforded by those materials of this study. Likewise, the diffusivity is defined^{11,17-19} as the thickness squared, divided by 6 times the (breakthrough time):

$$D = (x^2)/(6 T_B),$$

D = diffusion coefficient or diffusivity,

x = thickness of membrane, cm, and

T_B = breakthrough time, minutes.

Both the normalized breakthrough time and the diffusivity values provide information which eliminates the thickness constraint and which concern the analytes' permeation rate as a function of the material *per se*. In those cases in which the first measured organic concentration (following zero concentration values) was considerably higher than the lower limit of detection values, the breakthrough time was estimated by an extrapolation to zero concentration of a plot aqueous phase permeation cell concentrations vs time following challenge. This provided the short-term diffusion coefficient¹¹ whose values would be slightly larger than the steady-state diffusion coefficient obtained through the time lag method. Because of the nature of these experiments and the fact that T_B was determined in terms of minutes at best, the short-term diffusion coefficient is reported in terms of $\text{cm}^2 \text{min}^{-1}$ rather than $\text{cm}^2 \text{s}^{-1}$, its standard dimensions. The resulting value, D, will in terms of diffusion theory, allow a calculation of permeant flux when the concentration of the permeant is known.¹⁸⁻¹⁹

As may be seen in Tables IV, V, VI, and VII, the normalized breakthrough times for the materials and permeants studied varied from a low value of 0.04 min/mil of thickness for the permeation of Aroclor 1254 through surgical rubber latex to a high value of >720 min/mil for the permeation of 1,1,2-trichloroethane through uncrumpled Teflon. These values illustrate the rate of permeation per unit thickness and show how with common protective garment materials it was possible to observe permeation rates and hence degrees of worker protection, which varied by several orders of magnitude. From these values and as mentioned above, for the systems of this study, one may see that the amount of a given analyte permeating the various membranes in a given time period will vary by several orders of magnitude.

1. Protective Garment Material Permeation by Halogenated Ethanes (1,2-Dichloroethane; 1,1,1-Trichloroethane; and 1,1,2-Trichloroethane). Tables IV, V, and VI present the protective garment breakthrough times for 1,2-dichloroethane; 1,1,1-trichloroethane; and 1,1,2-trichloroethane for both the homogeneous, nonbonded materials and for the coated/bonded composite materials. For these compounds the breakthrough time was defined as that time at which the aqueous phase organic concentrations exceeded the lower limit of detection (LLD) values listed in Table I or was extrapolated to zero concentration as mentioned above for those cases in which the first measured organic concentration was considerably higher than the LLD. For 1,2-dichloroethane the breakthrough time was defined as that time at which its aqueous phase concentration exceeded 8 ppm. Likewise, the breakthrough times for 1,1,1-trichloroethane and 1,1,2-trichloroethane were defined as those times wherein their aqueous phase concentrations exceeded 2 and 1 ppm, respectively.

As may be seen in Table IV and Figs. 9-18, the, apparent breakthrough times for 1,2-dichloroethane varied from less than 2 min for surgical rubber latex to more than 24 h (1440 min)

TABLE IV
1,2-DICHLOROETHANE PERMEATION RATE
PROPERTIES OF PROTECTIVE GARMENT MATERIALS

| | <u>Thickness</u> (mils mm) | <u>Breakthrough^a</u> <u>Time (min)</u> | <u>Normalized</u> <u>Breakthrough Time</u> (min mil ⁻¹) | <u>Diffusivity</u> (cm ² /min ⁻¹) |
|--|-------------------------------|--|---|---|
| A. Homogeneous, Nonbonded Materials | | | | |
| Butyl rubber | (22 0.56) | 140 | 6.36 | 3.74 × 10 ⁻⁶ |
| Neoprene rubber latex | (23 0.58) | 20 | 0.87 | 28 × 10 ⁻⁶ |
| Nitrile rubber latex | (8 0.20) | 2.5 | 0.31 | 27 × 10 ⁻⁶ |
| Nitrile rubber, milled | (12 0.30) | 2.5 | 0.21 | 60 × 10 ⁻⁶ |
| Polyethylene (medium density) | (2 0.05) | 2.3 | 1.15 | 2 × 10 ⁻⁶ |
| Poly(vinyl alcohol) unsupported | (15 0.38) | 22 | 1.47 | 11 × 10 ⁻⁶ |
| Surgical rubber latex | (8 0.20) | 1.5 | 0.19 | 45 × 10 ⁻⁶ |
| Teflon | (2 0.05) | --- | --- | --- |
| Crumpled | --- | 90 | 45 | 0.05 × 10 ⁻⁶ |
| Unwrinkled | --- | >1440 | >720 | <3 × 10 ⁻⁹ |
| Viton | (10 0.254) | 820 | 82 | <0.005 × 10 ⁻⁶ |
| B. Coated/Bonded Materials | | | | |
| Butyl-coated nylon (Mil C-12189) | (15 0.38) | 70 | 4.7 | 3.5 × 10 ⁻⁶ |

^aBreakthrough time defined as that time following challenge when the permeation cells aqueous phase concentration reached 8 ppm.

for noncrumpled Teflon. However, for this same Teflon which had been crumpled, breakthrough occurred at 90 min. Because in an actual work situation a crumpling of the Teflon would likely occur to an extent greater than that of these tests, the Teflon should be used with caution for most work situations.

Of the remaining materials in Table IV, only Viton, neoprene rubber latex, poly(vinyl alcohol), butyl rubber, and butyl-coated nylon exhibited at least a 20-min breakthrough time for 1,2-dichloroethane permeation to occur. The nitrile rubber latex, cement dipped nitrile rubber, polyethylene (medium density), and surgical rubber latex were all penetrated by 1,2-dichloroethane in less than 3 min and would be of little use in situations requiring the garment to be in constant contact with 1,2-dichloroethane. From the above, butyl rubber or Viton appear to be the best materials to protect the worker against 1,2-dichloroethane, but because of apparent lot-to-lot variations²⁰ in butyl properties, Viton appears to be the best suited material of these studies to protect the worker from this chemical.

The results for the permeation of 1,1,1-trichloroethane through the subject protective garment materials are presented in Table V and Figs. 19-28. Of the homogeneous, nonbonded materials of this study, only medium density polyethylene and surgical rubber latex gave breakthrough times less than 10 min. Similarly, the composite/bonded materials polyurethane-coated nylon, poly(vinyl chloride)-coated nylon, and polyethylene-coated Tyvek all gave breakthrough times of 12 min or less. Butyl-coated nylon (Mil C-12189) gave the longest 1,1,1-trichloroethane breakthrough time (25 min) of the composite/bonded materials of this study. Somewhat intermediate in breakthrough time for the homogeneous, nonbonded materials were butyl rubber (60

TABLE V
1,1,1-TRICHLOROETHANE PERMEATION RATE
PROPERTIES FOR PROTECTIVE GARMENT MATERIALS

| | <u>Thickness</u> (mils mm) | <u>Breakthrough^a</u> <u>Time (min)</u> | <u>Normalized</u> <u>Breakthrough Time</u> (min mil ⁻¹) | <u>Diffusivity</u> (cm ² min ⁻¹) |
|--|-------------------------------|--|---|--|
| A. Homogeneous, Nonbonded Materials | | | | |
| Butyl rubber | (22 0.56) | 60 | 2.72 | 8.71 × 10 ⁻⁶ |
| Neoprene rubber latex | 23 0.58) | 45 | 1.96 | 12.5 × 10 ⁻⁶ |
| Nitrile rubber latex | (8 0.20) | 30 | 3.75 | 2.2 × 10 ⁻⁶ |
| Polyethylene (medium density) | (2.0 0.05) | 3 | 1.5 | 1.4 × 10 ⁻⁶ |
| Surgical rubber latex | (8 0.20) | 4 | 0.50 | 16.7 × 10 ⁻⁶ |
| Viton | (10 0.25) | >1440 | >144 | <0.07 × 10 ⁻⁶ |
| B. Coated/Bonded Materials | | | | |
| Butyl-coated nylon (Mil C-12189) | 15 0.38) | 25 | 1.67 | 10 × 10 ⁻⁶ |
| Polyethylene-coated Tyvek | (5 0.13) | --- | --- | --- |
| Tyvek toward water | --- | 10 | 2.0 | 2.8 × 10 ⁻⁶ |
| Polyethylene toward water | --- | 12 | 2.4 | 2.3 × 10 ⁻⁶ |
| Polyurethane-coated nylon | (4 0.10) | 2 | 0.5 | 8.3 × 10 ⁻⁶ |
| Poly(vinyl chloride)-coated nylon | (10 0.26) | 3 | 0.3 | 38 × 10 ⁻⁶ |

^aThat time at which the aqueous phase 1,1,1-trichloroethane concentration exceeded 2 ppm.

TABLE VI
1,1,2-TRICHLOROETHANE PERMEATION RATE
PROPERTIES FOR PROTECTIVE GARMENT MATERIALS

| | <u>Thickness</u> (mils mm) | <u>Breakthrough^a</u> <u>Time (min)</u> | <u>Normalized</u> <u>Breakthrough Time^a</u> (min mil ⁻¹) | <u>Diffusivity</u> (cm ² min ⁻¹) |
|---|-------------------------------|--|---|--|
| A. Homogeneous, Nonbonded Material | | | | |
| Butyl rubber | (22 0.56) | 50 | 2.27 | 10 × 10 ⁻⁶ |
| Neoprene rubber latex | (23 0.58) | 7 | 0.30 | 80 × 10 ⁻⁶ |
| Nitrile rubber latex | (8 0.20) | 2 | 0.25 | 33 × 10 ⁻⁶ |
| Polyethylene (medium density) | (2 0.05) | 3.5 | 1.8 | 1.2 × 10 ⁻⁶ |
| Poly(vinyl alcohol), unsupported | (15 0.38) | 15 | 1.0 | 16 × 10 ⁻⁶ |
| Surgical rubber latex | (9 0.23) | 1 | 0.11 | 88 × 10 ⁻⁶ |
| Teflon | (2 0.05) | --- | --- | --- |
| Crumpled | --- | 175 | 87 | 0.024 × 10 ⁻⁶ |
| Unwrinkled | --- | >1440 | >720 | <0.0029 × 10 ⁻⁶ |
| Viton | (10 0.25) | >1440 | >144 | <0.072 × 10 ⁻⁶ |
| B. Coated/Bonded Materials | | | | |
| Butyl-coated nylon (Mil C-12189) | (15 0.38) | 45 | 3 | 5 × 10 ⁻⁶ |
| Polyurethane-coated nylon | (4 0.10) | <1 | <0.25 | >17 × 10 ⁻⁶ |

^aThat time following test initiation when 1,1,2-trichloroethane was observed at a concentration of 1 ppm in the aqueous phase of the permeation cell.

TABLE VII

POLYCHLORINATED BIPHENYL (PCB)^a
PERMEATION RATE PROPERTIES FOR PROTECTIVE GARMENT MATERIALS

| | Thickness (mils mm) | Breakthrough ^b Time (min) | Normalized Breakthrough Time (min mil ⁻¹) | Diffusivity (cm ² min ⁻¹) |
|--|------------------------|---|---|---|
| A. Homogeneous, Nonbonded Materials | | | | |
| Butyl rubber | (22 0.56) | 2.5 | 0.114 | 209 × 10 ⁻⁶ |
| Neoprene rubber latex | (23 0.58) | 0.5 | 0.022 | 1121 × 10 ⁻⁶ |
| Nitrile rubber latex | (8 0.20) | 1 | 0.125 | 67 × 10 ⁻⁶ |
| Polyethylene (medium density) | (2 0.05) | 0.8 | 0.40 | 5 × 10 ⁻⁶ |
| Poly(vinyl alcohol), unsupported | (11 0.28) | 0.6 | 0.05 | 218 × 10 ⁻⁶ |
| Surgical rubber latex | (8 0.20) | 0.3 | 0.0375 | 222 × 10 ⁻⁶ |
| Viton | (10 0.254) | 60 | 6.0 | 2 × 10 ⁻⁶ |
| B. Coated/Bonded Materials | | | | |
| Butyl-coated nylon (Mil C-12189) | (15 0.38) | 3 | 0.20 | 80 × 10 ⁻⁶ |
| Polyurethane-coated nylon | (4 0.10) | 0.5 | 0.125 | 33 × 10 ⁻⁶ |
| Poly(vinyl chloride)-coated nylon | (10 0.25) | 0.5 | 0.05 | 208 × 10 ⁻⁶ |

^a Aroclor 1254.

^b That time following test initiation when a PCB concentration of 1 ppm was observed present in the aqueous phase of the permeation cell.

min), neoprene rubber latex (45 min), and nitrile rubber latex (30 min). The longest breakthrough time of the materials studied was Viton elastomer whose 1,1,1-trichloroethane breakthrough time was in excess of 24 h.

The breakthrough times of Table VI and Figs. 29-38 present information concerning the breakthrough of 1,1,2-trichloroethane. There was a greater range in breakthrough times for this halogenated ethane than there was for 1,1,1-trichloroethane. Although unsupported poly(vinyl alcohol) showed a breakthrough time of 15 min, neoprene rubber latex, nitrile rubber latex, medium density polyethylene and surgical rubber latex all had breakthrough times of 7 min or less as did polyurethane-coated nylon. Both the crumpled ($T_B = 175$ min) and the uncrumpled ($T_B > 1440$ min) Teflon, the butyl rubber ($T_B = 50$ min), and the butyl-coated nylon ($T_B = 45$ min) had relatively long breakthrough times, but with the exception of uncrumpled Teflon, Viton again had the longest breakthrough time of the materials tested.

2. Protective Garment Material Permeation by Aroclor 1254. Because the PCB sample of this study was actually a complex mixture of chlorinated aromatics, that constituent which permeated the garment first could not be designated by the particular analytical procedure used here. For most of the materials of this study the PCB breakthrough was so quick that it is unlikely a molecular permeation differential occurred to any appreciable extent for the different constituents of this PCB mixture. As presented in Table VII and Figs. 39-48, the breakthrough times were quite rapid for all materials except Viton. Butyl rubber, neoprene rubber latex, nitrile rubber latex, polyethylene, poly(vinyl alcohol), butyl-coated nylon, polyurethane-coated nylon, and poly(vinyl chloride)-coated nylon all had Aroclor 1254 breakthrough times of 3 min or less.

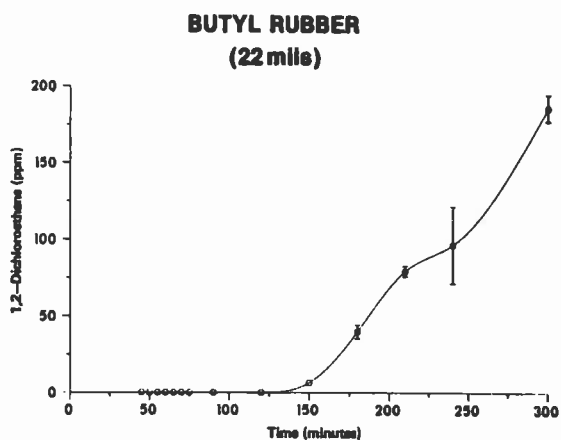


Fig. 9.

Aqueous phase concentration (\pm one σ) of 1,2-dichloroethane as a function of time following challenge to butyl rubber.

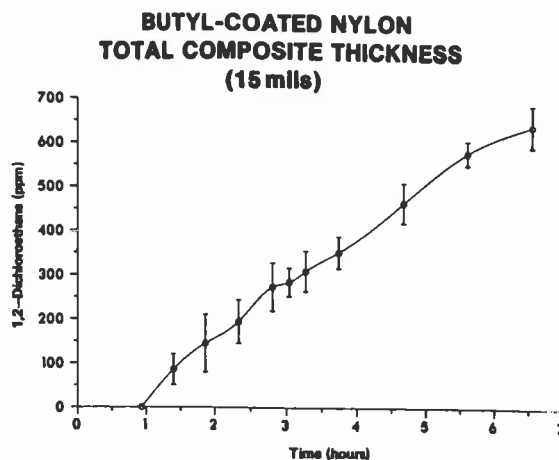


Fig. 10.

Aqueous phase concentration (\pm one σ) of 1,2-dichloroethane as a function of time following challenge to butyl-coated nylon composite material.

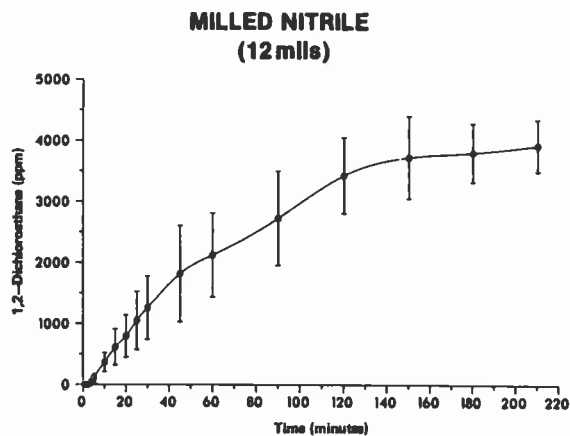


Fig. 11.

Aqueous phase concentration (\pm one σ) of 1,2-dichloroethane as a function of time following challenge to milled nitrile material.

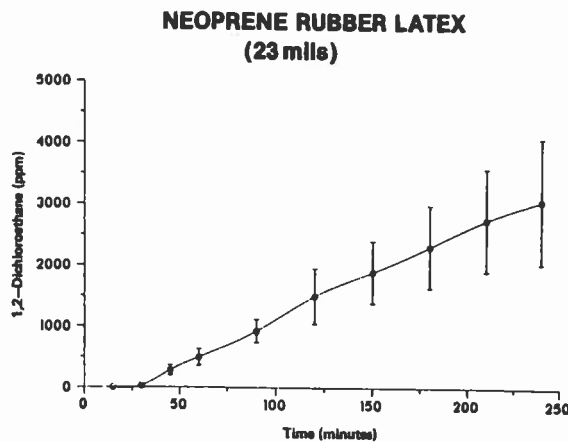


Fig. 12.

Aqueous phase concentration (\pm one σ) of 1,2-dichloroethane as a function of time following challenge to neoprene latex.

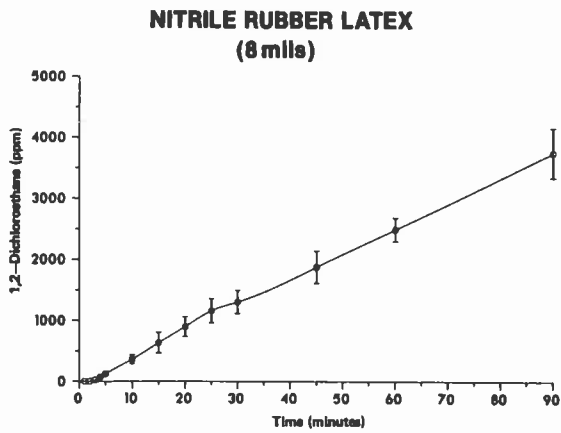


Fig. 13.

Concentration (\pm one σ) of 1,2-dichloroethane in aqueous phase of cell as a function of time following challenge to nitrile rubber latex.

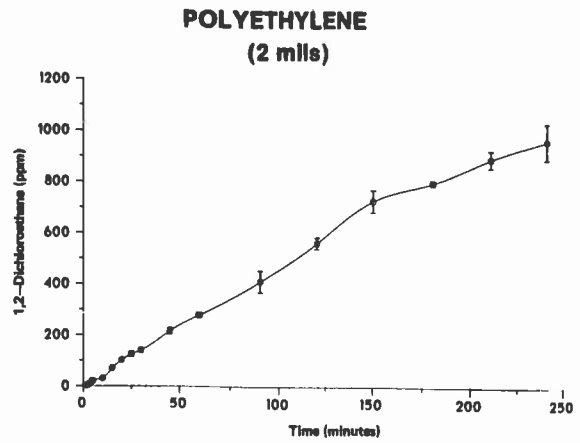


Fig. 14.

Concentration (\pm one σ) of 1,2-dichloroethane in aqueous phase of cell as a function of time following challenge to medium density polyethylene.

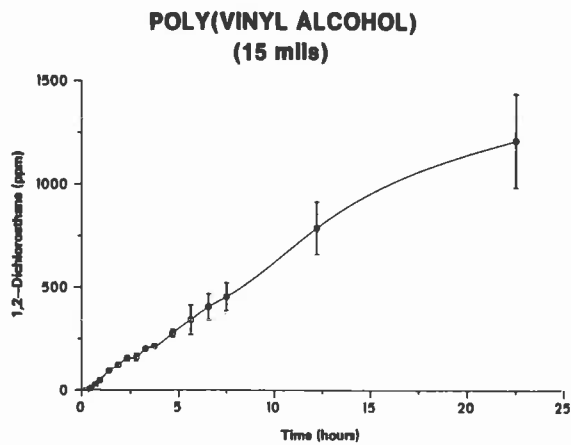


Fig. 15.

Concentration (\pm one σ) of 1,2-dichloroethane in aqueous phase of cell as a function of time following challenge to poly(vinyl alcohol).

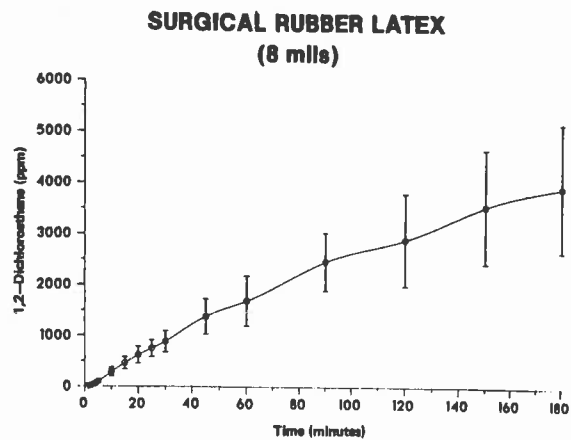


Fig. 16.

Concentration (\pm one σ) of 1,2-dichloroethane in aqueous phase of cell as a function of time following challenge to surgical rubber latex.

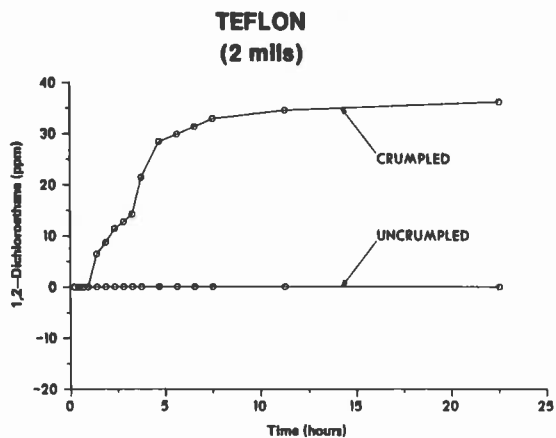


Fig. 17.

Concentration of 1,2-dichloroethane in aqueous phase of permeation cell following challenge to Teflon.

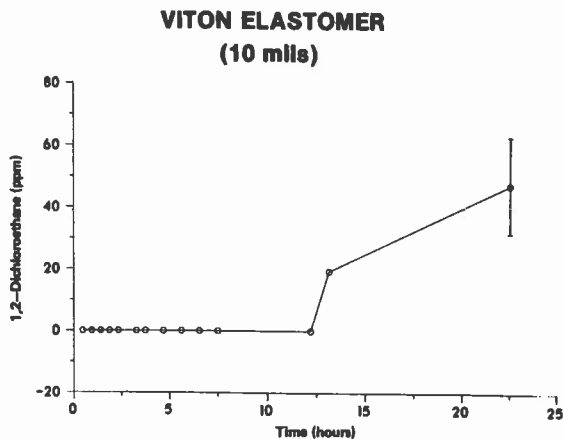


Fig. 18.

Concentration of 1,2-dichloroethane in aqueous phase of permeation cell following challenge to Viton.

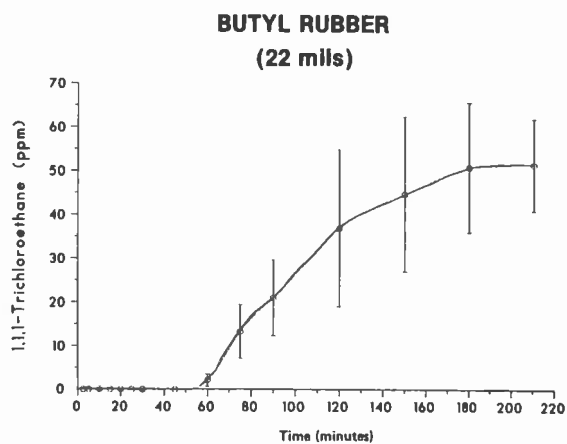


Fig. 19.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge of butyl rubber.

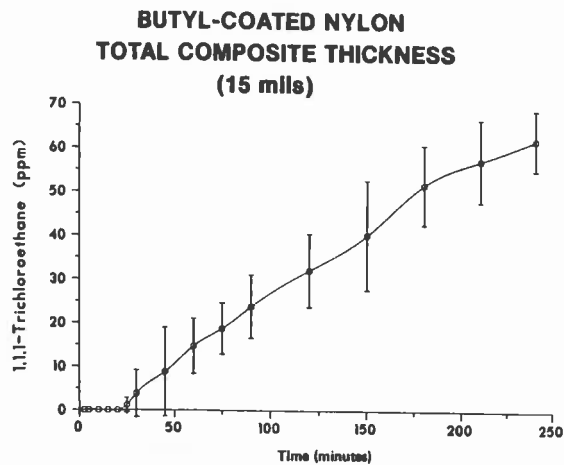


Fig. 20.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to butyl-coated nylon.

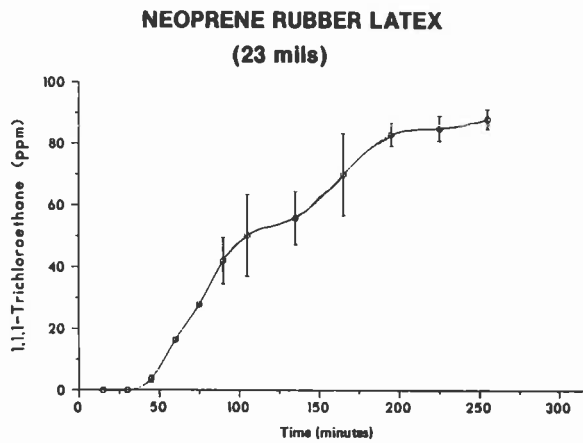


Fig. 21.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to neoprene rubber latex.

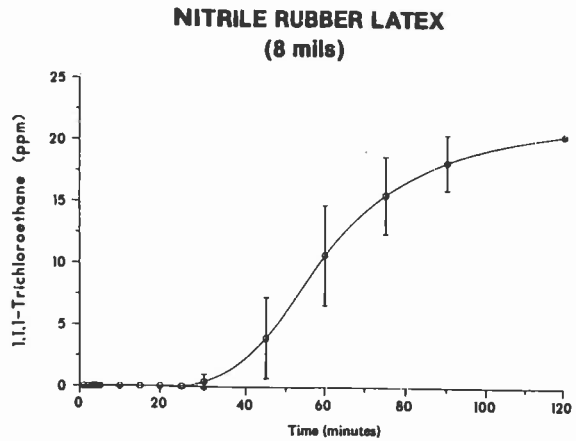


Fig. 22.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to nitrile rubber latex.

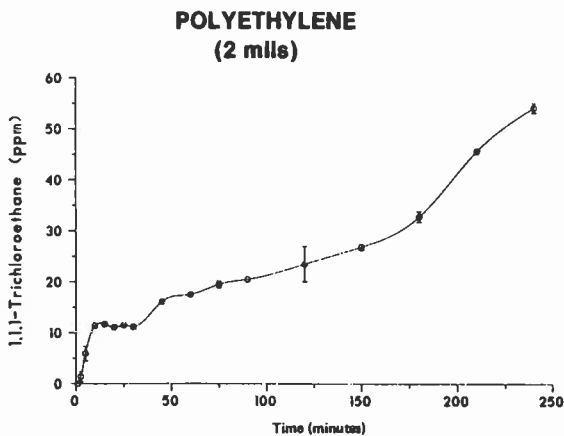


Fig. 23.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to medium density polyethylene.

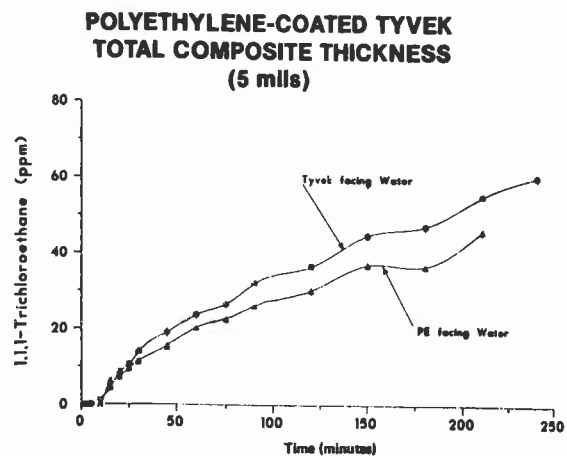


Fig. 24.

Concentration of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to polyethylene-coated Tyvek.

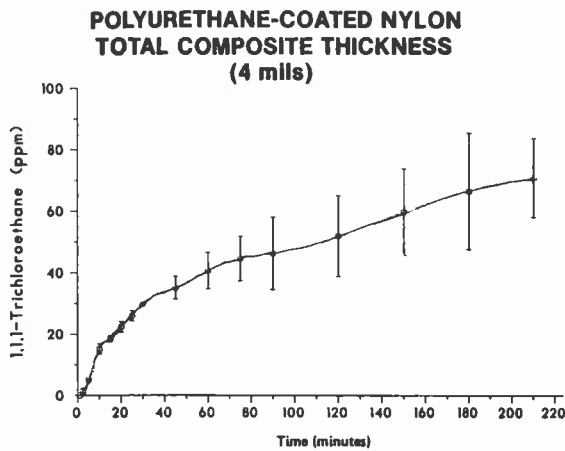


Fig. 25.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge of polyurethane-coated nylon.

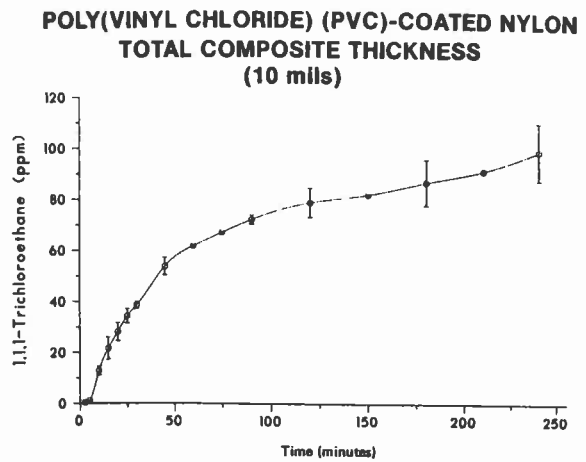


Fig. 26.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to poly(vinyl chloride)-coated nylon.

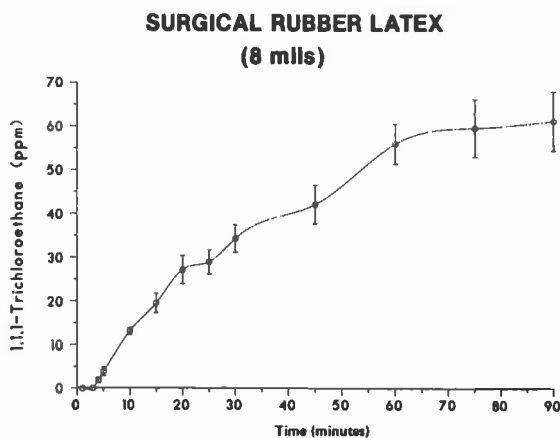


Fig. 27.

Concentration (\pm one σ) of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to surgical rubber latex.

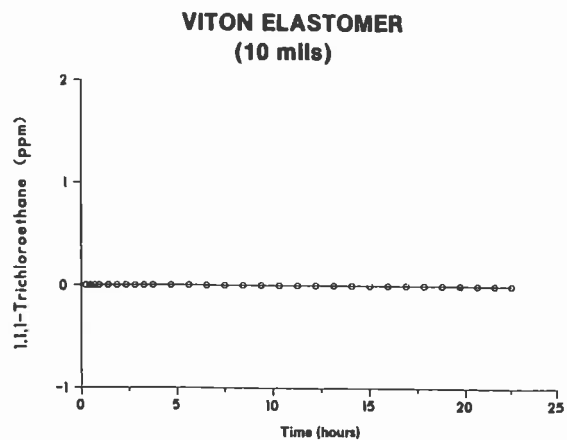


Fig. 28.

Concentration of 1,1,1-trichloroethane in aqueous phase of permeation cell following challenge to Viton elastomer.

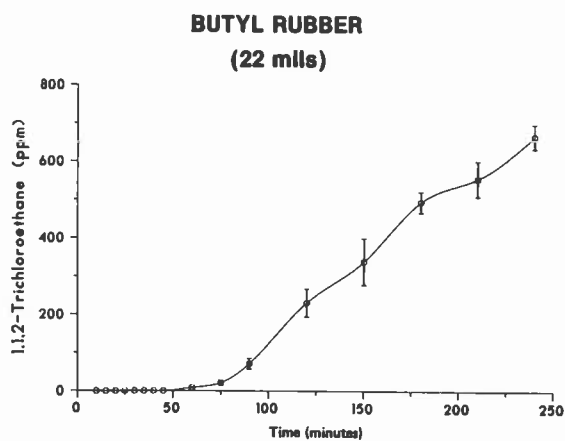


Fig. 29.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to butyl rubber.

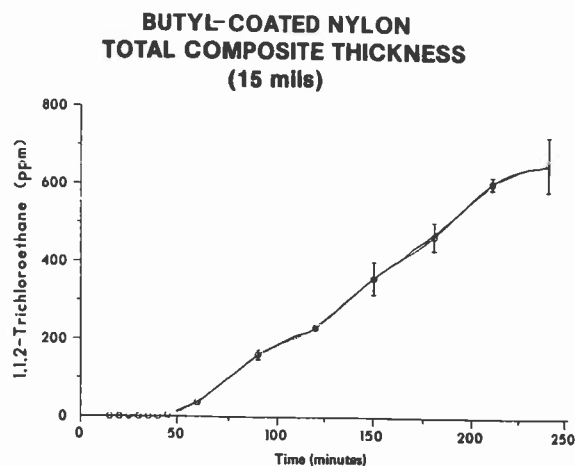


Fig. 30.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to butyl-coated nylon.

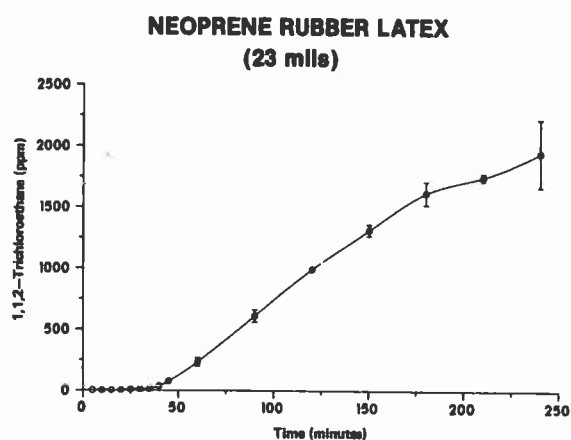


Fig. 31.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to neoprene rubber latex.

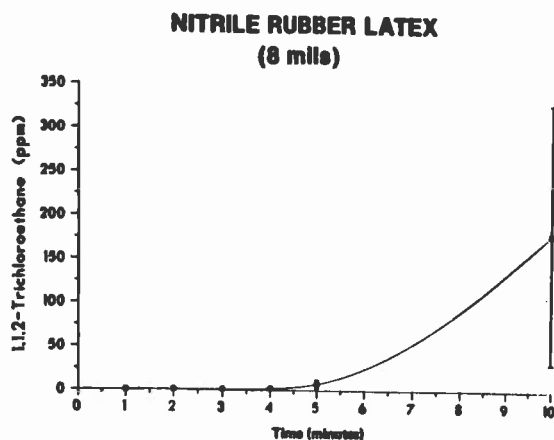


Fig. 32.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to nitrile rubber latex.

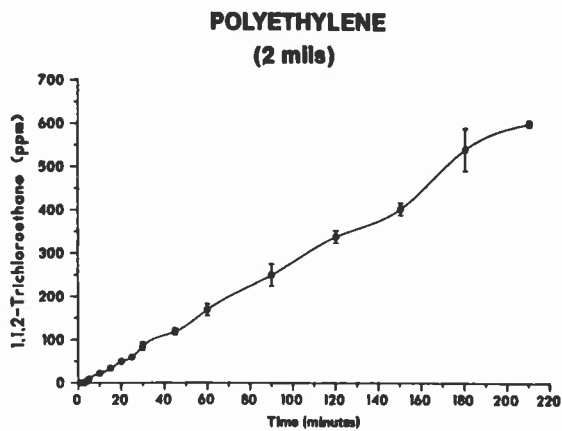


Fig. 33.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to medium density polyethylene.

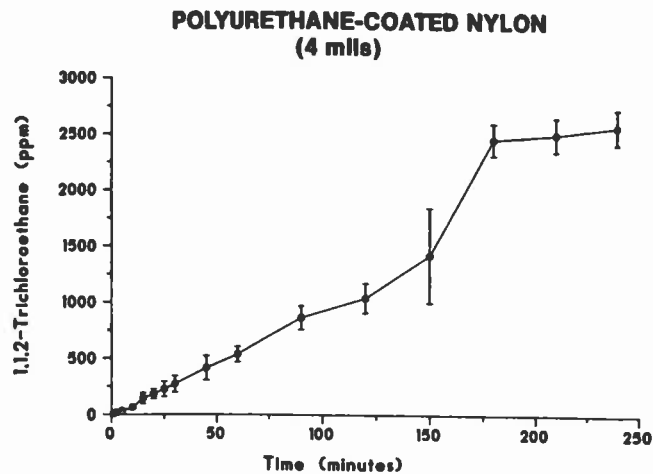


Fig. 34.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to polyurethane-coated nylon.

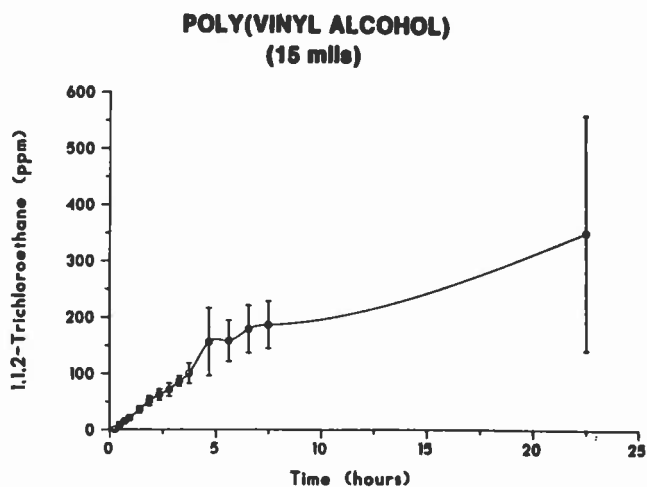


Fig. 35.

Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to poly(vinyl alcohol).

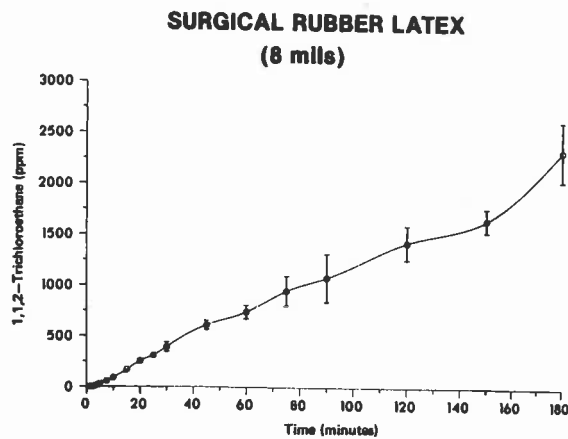
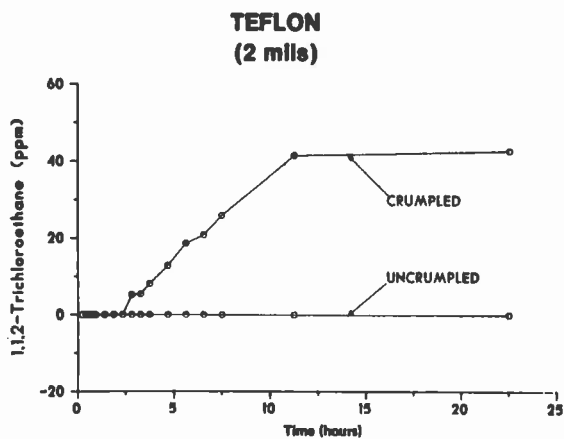


Fig. 36.

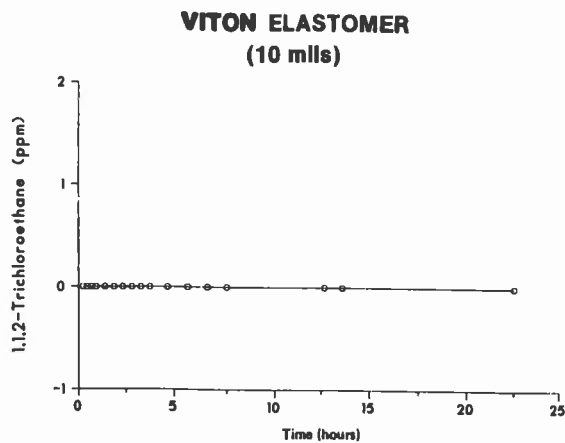
Concentration (\pm one σ) of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to surgical rubber latex.



TEFLON
(2 mils)

Fig. 37.

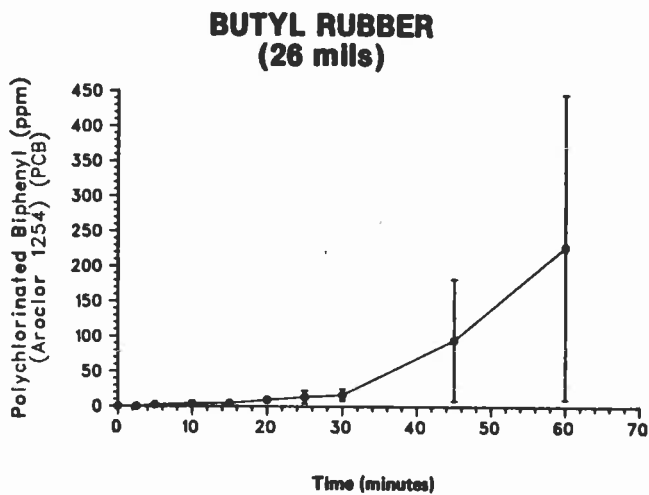
Concentration of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to Teflon.



VITON ELASTOMER
(10 mils)

Fig. 38.

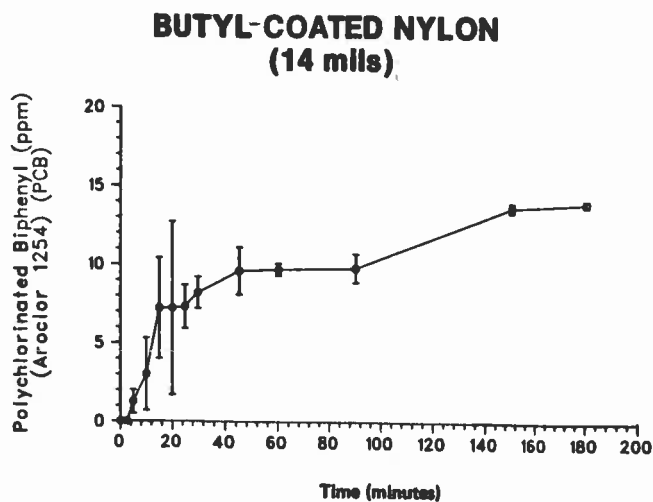
Concentration of 1,1,2-trichloroethane in aqueous phase of permeation cell following challenge to Viton elastomer.



BUTYL RUBBER
(26 mils)

Fig. 39.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to butyl rubber.



BUTYL-COATED NYLON
(14 mils)

Fig. 40.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to butyl-coated nylon.

**NEOPRENE RUBBER LATEX
(23 mls)**

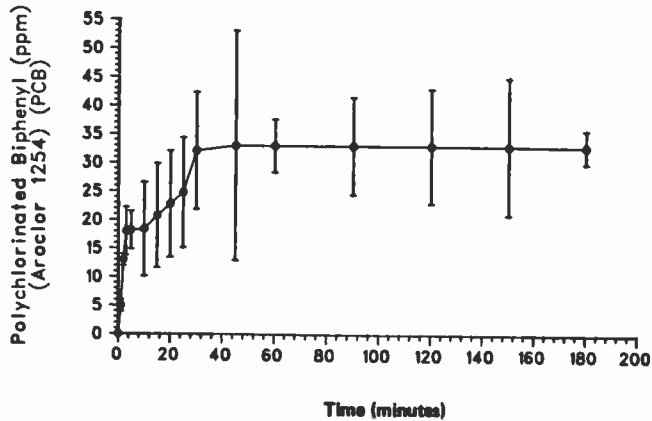


Fig. 41.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to neoprene rubber latex.

**NITRILE RUBBER LATEX
(8 mls)**

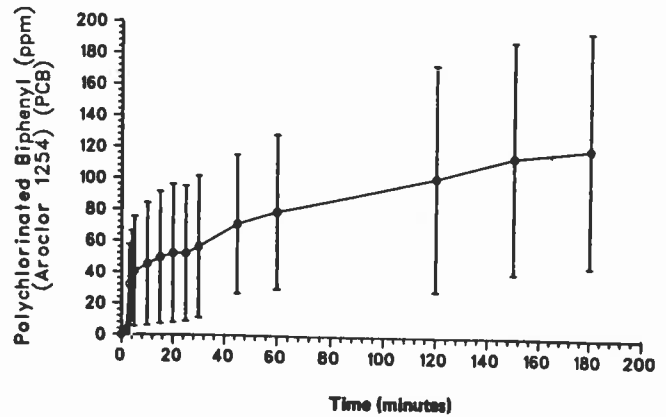


Fig. 42.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to nitrile rubber latex.

**POLYETHYLENE
(2 mls)**

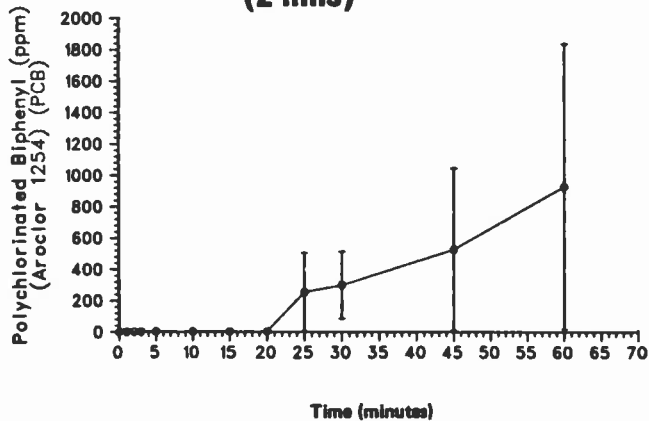


Fig. 43.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to polyethylene.

**POLYURETHANE-COATED NYLON
(4 mls)**

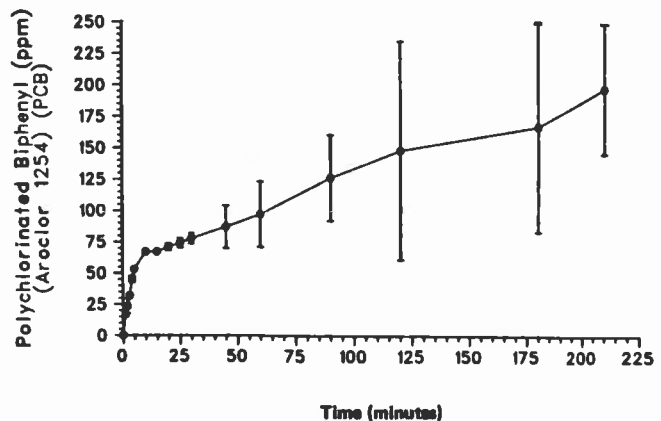


Fig. 44.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to polyurethane-coated nylon.

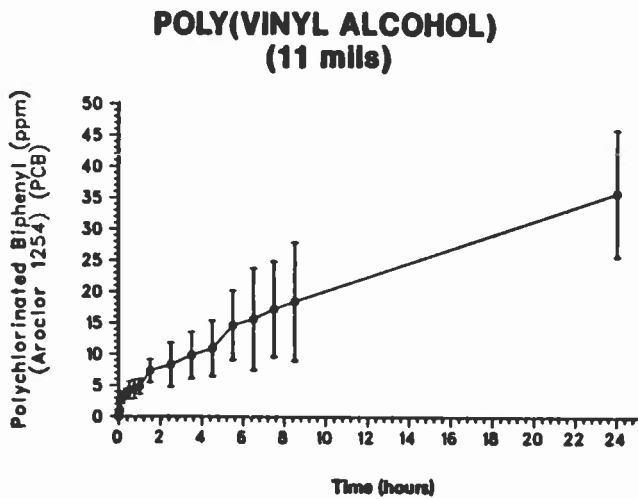


Fig. 45.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to poly(vinyl alcohol).

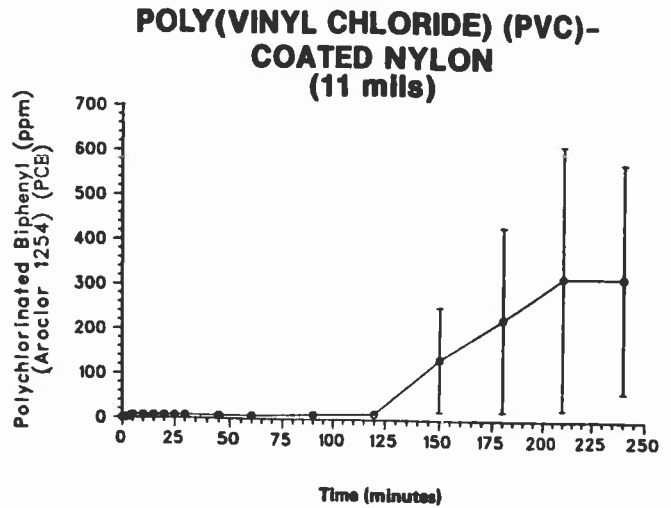


Fig. 46.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to poly(vinyl chloride)-coated nylon.

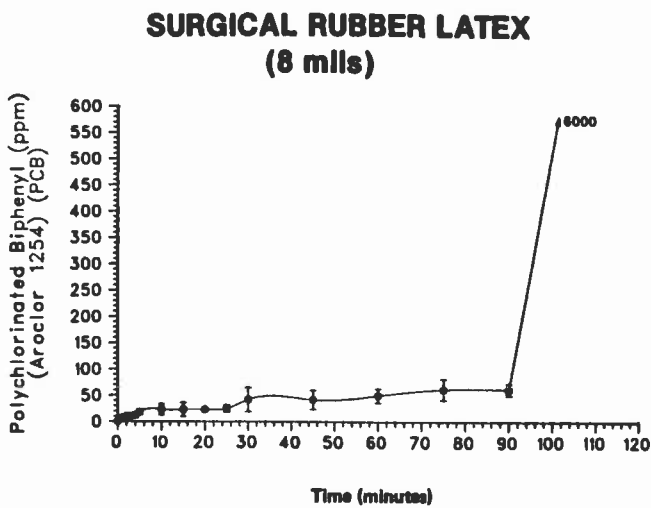


Fig. 47.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to surgical rubber latex.

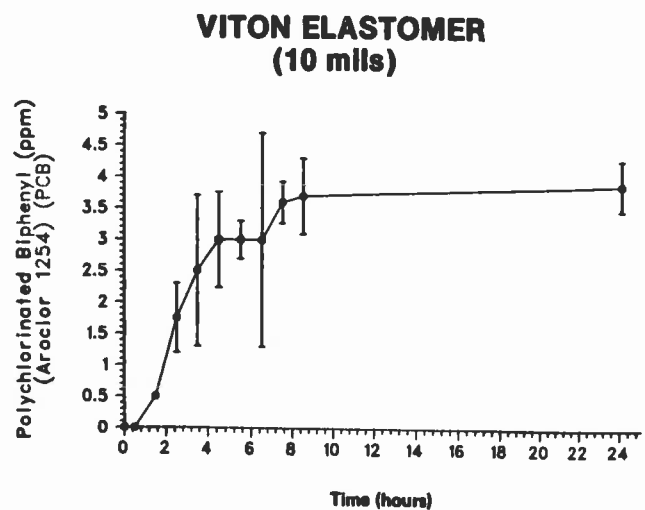


Fig. 48.

Concentration (\pm one σ) of polychlorinated biphenyl (Aroclor 1254) in aqueous phase of permeation cell following challenge to Viton elastomer.

Viton's 60-min breakthrough was the only material tested that would afford an appreciable degree of worker protection against Aroclor 1254.

As has been noted in other studies,^{21,22} a double or multi-S shaped curve resulted in many cases when the concentration of analyte which had permeated the garment material was plotted as a function of time. Of the homogeneous, nonbonded materials of this study only noncrumpled Teflon did not evidence this non-Fickian behavior to at least some degree. The reason for not observing the phenomenon in the case of noncrumpled Teflon was likely that the organics did not permeate it to a degree such that this behavior could be observed with the analytical techniques employed here.

3. Correlation of Weight Change With Material Breakthrough Time. As may be expected from theoretical considerations¹⁴⁻¹⁶ there was a correlation between the solubility of a permeant in a test material and the rate at which the permeant permeated the test material. Such cases have been identified previously.^{14,15,21} Further examples of this correlation are presented in Figs. 49 through 52 in which the equilibrium weight change of protective garment materials following immersion in 1,2-dichloroethane; 1,1,1-trichloroethane; 1,1,2-trichloroethane; and Aroclor 1254 respectively are plotted vs the normalized breakthrough time (minutes per unit thickness of protective garment material). For the homogeneous, nonbonded materials evaluated in these studies (butyl rubber, neoprene latex, nitrile latex, polyethylene, poly(vinyl alcohol), surgical rubber latex, and Viton elastomer), only the poly(vinyl alcohol) did not correlate well in this relationship. As has been shown in Fig. 6, most likely the polyethylene (PE) did not reach equilibrium weight following 7-day immersion in 1,1,1-trichloroethane. If this were also the situation for the 1,2-dichloroethane and the 1,1,2-trichloroethane, then upon attaining weight equilibrium, the PE percent weight increase would be shifted to a higher value and thus fall closer to the trend lines for the other halogenated ethanes. Because the permeation test method used in these studies required an aqueous media in contact with the test material, the PVA would not have been expected to respond as did the other test materials. Particularly, since PVA is known to chemically react with water (whereas none of the other test materials did) the organic permeation rate would not have been expected to respond in the same fashion as was observed for those garment materials showing no reaction with water.

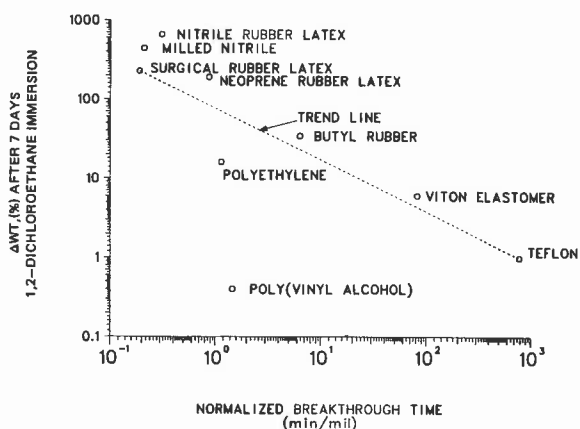


Fig. 49.

Log-log plot of equilibrium weight change of homogeneous nonbonded protective garment material following immersion in 1,2-dichloroethane.

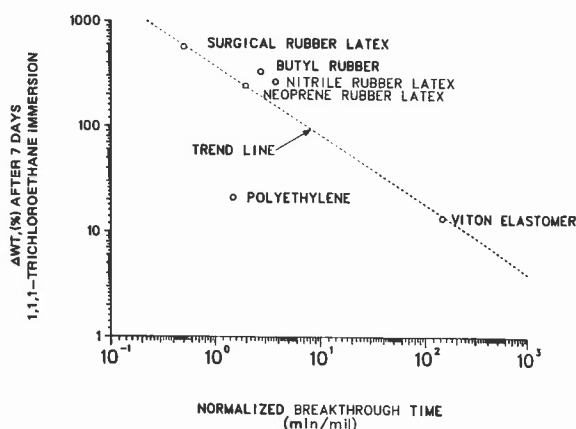


Fig. 50.

Log-log plot of equilibrium weight change of homogeneous nonbonded protective garment material following immersion in 1,1,1-trichloroethane.

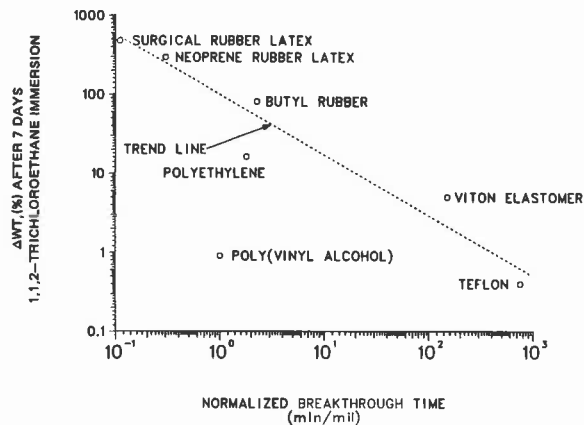


Fig. 51.

Log-log plot of equilibrium weight change of homogeneous nonbonded protective garment material following immersion in 1,1,2-trichloroethane.

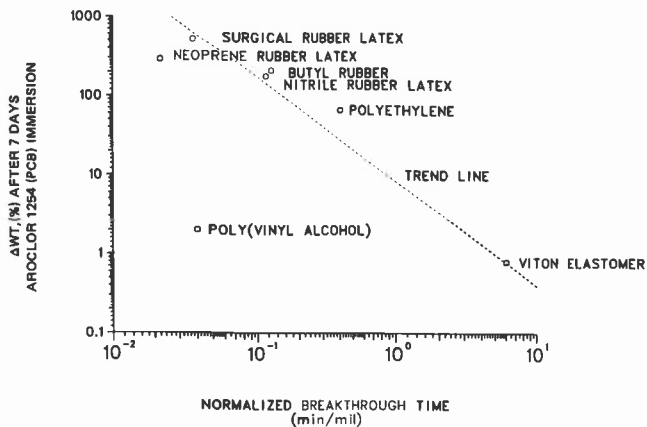


Fig. 52.

Log-log plot of equilibrium weight change of homogeneous nonbonded protective garment material following immersion in a polychlorinated biphenyl (Aroclor 1254).

4. Correlation of Volume Change With Material Breakthrough Time. Intuitively one would expect a direct relationship to exist between weight changes and volume changes for elastomeric materials such as the homogeneous, nonbonded materials of the present study. Such is the general case in these investigations as may be seen by comparing trends in weight (Table II) and volume (Table III) changes for given materials with specific solvents. In view of this and from theoretical considerations,¹⁴⁻¹⁶ the same type of inverse relationship might be expected to exist between volume change and normalized breakthrough time as existed with weight change and normalized breakthrough time. That this was the case is shown in Figs. 53 through 56 in which the logarithm of the 24-h volume change of the materials is plotted against the log of their normalized breakthrough times. As with the equilibrium weight changes with the exception of PVA, good correlation exists in these plots for the homogeneous, nonbonded materials in these studies.

As shown above, the normalized breakthrough time vs weight or volume change correlations do allow insight into how the homogeneous materials behaved with respect to permeation. However, because the normalized breakthrough values have eliminated thickness as a variable, these correlations cannot be applied as a universal rule concerning the individual garments because garments constructed from given materials are often found to be of different thicknesses.

IV. CONCLUSIONS AND RECOMMENDATIONS

The present work has shown that for a homogeneous, nonbonded material, an inverse relationship exists between the weight change the materials will experience upon immersion in a given solvent and the rate at which this solvent will break through a material. Such was not the case for the bonded composite materials and from theoretical considerations¹⁴⁻¹⁶ would not necessarily have been expected. From these observations one can conclude that a nonironclad rule-of-thumb for the relative rate of permeation of given solvents through given materials is, "The more the material swells (gains weight) in a given solvent, the greater the rate of permeation of the solvent through the material." Application of this rule will allow the industrial hygienist to make screening test recommendations in the field in situations which do not allow a detailed set of permeation studies to be performed.

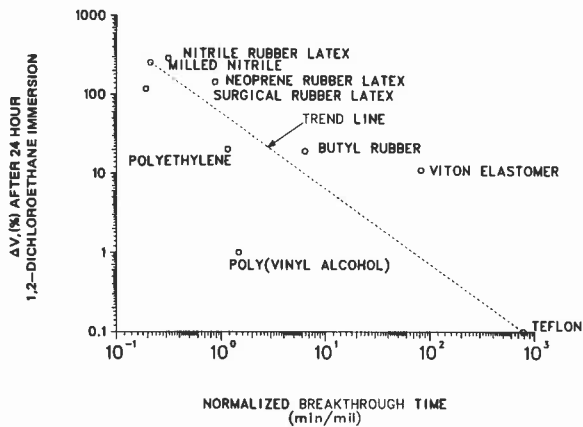


Fig. 53.

Log-log plot of equilibrium volume change of homogeneous nonbonded protective garment material following immersion in 1,2-dichloroethane.

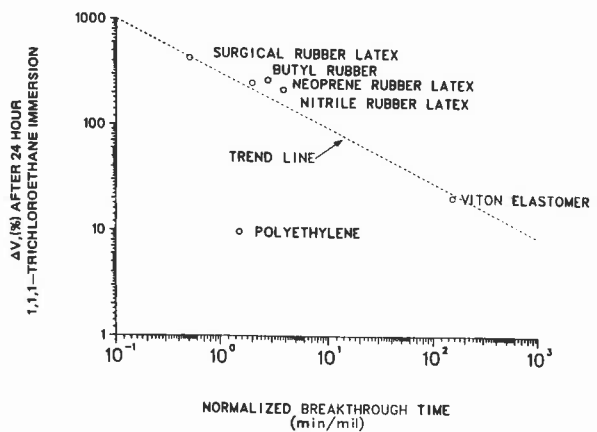


Fig. 54.

Log-log plot of equilibrium volume change of homogeneous nonbonded protective garment material following immersion in 1,1,1-trichloroethane.

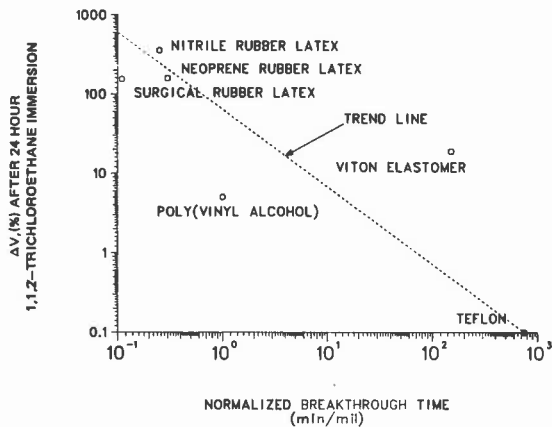


Fig. 55.

Log-log plot of equilibrium volume change of homogeneous nonbonded protective garment material following immersion in 1,1,2-trichloroethane.

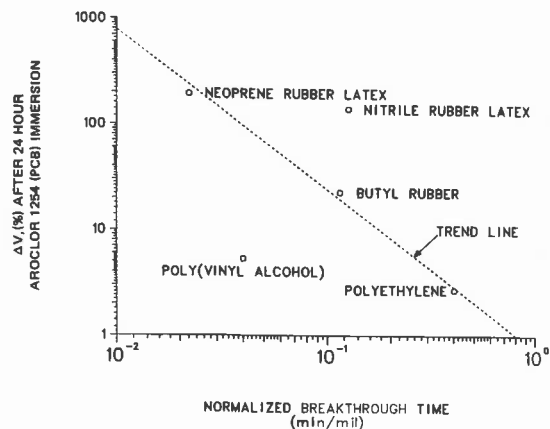


Fig. 56.

Log-log plot of equilibrium volume change of homogeneous nonbonded protective garment material following immersion in a polychlorinated biphenyl (Aroclor 1254).

Another important point which may be inferred from the limited data of Tables IV, V, and VI is that for compounds which are chemically similar, i.e., congeners or isomers as was the case for the halogenated ethanes, there may be appreciable differences in the rate at which they permeate given materials, and in many cases will show non-Fickian behavior as shown in the graphs of Figs. 9-48.

This study has also shown that protective garment material which is commercially available in the United States is, generally speaking, not satisfactory for worker protection against 1,2-dichloroethane, 1,1,1-trichloroethane; 1,1,2-trichloroethane; or Aroclor 1254 (PCB). This situation was observed for both homogeneous, nonbonded protective garment materials and also for those materials tested which were either coated or bonded composite materials. Indeed, of the materials studied only PVA, Teflon, and Viton elastomer showed an appreciable resistance to permeation against those chemicals for which they were tested. Because PVA reacts with moisture and Teflon (in a thickness conducive to manual dexterity) mechanically degrades rather readily, of the materials studied in this work only Viton can be recommended as being capable of affording adequate worker protection under the conditions of these tests. The fact that gloves constructed from Viton are expensive relative to gloves constructed from other elastomers is a negative factor, but one which employers must face to protect their workers.

Clearly there is much work to be done by the American protective garment industry in order to provide the worker protective equipment which is adequate, yet of reasonable price and the successful meeting of this challenge will afford a safer workplace for the worker and a better worker health record for his employer. To help meet this challenge, the establishment of a standard method for the evaluation of permeation through protective garment material is currently being pursued by ASTM Committee F-23²³ with the goal of publishing such a method during calendar year 1981.

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APPENDIX A

1,2-DICHLOROETHANE: AN OVERVIEW OF OCCUPATIONAL EXPOSURES AND HAZARDS

I. SUMMARY

1,2-Dichloroethane (ethylene dichloride) is a water white organic liquid with a melting point of -35.36°C , and boiling point at 760 mm of 83.47°C .¹ It has been used as a solvent for metal cleaning, a component in fumigant mixtures for the control of insects, bacteria, and fungi, and in solvent-dewaxing processes by the oil industry.² The most important end product manufactured from 1,2-dichloroethane is, however, vinyl chloride monomer used in the production of poly(vinyl chloride) (PVC) plastics and resins.³ It has been estimated that in the United States, 1,900,000 people are exposed annually to 1,2-dichloroethane.⁴

II. SELECTED PROPERTIES

Table A-I presents data describing physical and chemical properties of 1,2-dichloroethane and a brief statement of its carcinogenicity.

III. SOURCES

In the United States, 1,2-dichloroethane is manufactured by Conoco Chemicals, Diamond Shamrock Chemical Co., Dow Chemical Co., Eastman Ethyl Corporation, Goodrich Chemical Co., PPG Industries, Inc., Shell Chemical Co., Stauffer Chemical Co., Union Carbide Corporation, and Vulcan Materials Company,⁵ and the 1978 production was 10.5 billion pounds.⁶ The environment is exposed to this compound primarily through manufacturing losses.⁸ In the environment the primary degradation mode of 1,2-dichloroethane is photooxidation in the atmosphere and one of its photooxidation products, chloroacetyl chloride, may interact destructively with the earth's ozone layer.³

TABLE A-I

PROPERTIES OF 1,2-DICHLOROETHANE

| | |
|-------------------------------------|----------------------------------|
| Molecular weight ¹ | 98.96 a.m.u. |
| Melting point ¹ | -35.36°C |
| Boiling point (760 mm) ¹ | 83.47°C |
| Density ¹ | 1.235 ²⁰ ₄ |
| Solubility | |
| Water ⁷ | 0.81 % W. 20°C |
| Ethanol ¹ | Very soluble |
| Benzene ¹ | Miscible |

Statement of Carcinogenicity:

The National Institute for Occupational Safety and Health recommends that 1,2-dichloroethane be handled in the workplace as if it were a human carcinogen.⁴

IV. USES

By far the largest quantities of 1,2-dichloroethane are used in the manufacturing of vinyl chloride monomer for production of vinyl plastics. Smaller quantities are used for the production of several other chlorinated hydrocarbons and as solvents.

V. TRANSPORTATION

Uninhibited 1,2-dichloroethane (DCE) decomposes yielding corrosion products which attack iron. Commercial grade DCE contains alkylamines (~0.1 %) which inhibit this degradation. Uninhibited DCE should be stored or transported only in plain, galvanized or lead-lined mild steel. Because of its ability to decompose rapidly with the evolution of phosgene, HCl, and carbon monoxide when subjected to ultraviolet light, air, moisture, open flames, or hot surfaces, 1,2-dichloroethane should be stored in cool, dry, well-ventilated areas away from direct sunlight.³ In addition to transportation in tank cars, trucks, or barrels of appropriate metal, this material may be transported in actinic bottles properly protected against breakage.

VI. NUMBER OF AFFECTED WORKERS

The National Occupational Hazards Survey (NOHS) conducted by the National Institute for Occupational Safety and Health (NIOSH) has used appropriate algorithms to estimate that 1,900,000 United States workers are exposed to 1,2-dichloroethane each year.^{4,8}

VII. RECOMMENDED PROTECTIVE CLOTHING MATERIAL

Protective garment material (gloves, aprons, etc.) constructed from butyl rubber or Viton elastomer afford the best protection, but in cases of limited contact butyl-coated nylon, neoprene rubber latex, or poly(vinyl alcohol) will afford some protection.

VIII. CURRENT PRACTICES IN WORKER PROTECTION

Upon eye or skin contact flush/irrigate with flowing water immediately and continuously for 15 min and consult a physician. Remove contaminated clothing.⁹

Upon inhalation, remove to fresh air if effects occur. If respiration stops, give mouth-to-mouth resuscitation and consult a physician.⁹

Upon oral ingestion, induce vomiting. However, because DCE may cause chemical pneumonia, this danger must be weighed against the compounds's toxicity when considering emptying the stomach.

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APPENDIX B

1,1,1-TRICHLOROETHANE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

I. SUMMARY

1,1,1-Trichloroethane (methyl chloroform) is a water-white organic liquid with a melting point of -30.4°C and boiling point of 74.1°C at 760 mm.¹ The material is widely used as a solvent and as a cleaning material in metal finishing operations. Excess exposure to the compound can damage the central nervous system, liver, gastrointestinal system, cardiovascular system, hematological system, and the skin. It has been estimated that 2,900,000² workers in the United States are exposed annually to the compound.

II. SELECTED PROPERTIES

Table B-I presents data describing physical and chemical properties of 1,1,1-trichloroethane and a brief characterization of its carcinogenicity.

III. SOURCES

In the United States, 1,1,1-trichloroethane is produced by the Dow Chemical Company, PPG Industries, and Vulcan Materials and the 1980 estimated production is in the vicinity of 625 million pounds.³ The compound is considered nonflammable and is thought to have little effect on the environment although its effect on the earth's ozone layer has not been established.

TABLE B-I

PROPERTIES OF 1,1,1-TRICHLOROETHANE

| | |
|-------------------------------|----------------------------------|
| Molecular weight ¹ | 133.41 a.m.u. |
| Melting point ¹ | -30.41°C |
| Boiling point (760 mm) | 74.1°C |
| Density ¹ | 1.339^{20}_4 |
| Solubility | |
| Water ⁴ | 0.132 % wt, 20°C |
| Ethanol ¹ | Miscible |
| Benzene ¹ | Miscible |

Statement of Carcinogenicity:

Because of its chemical relationship to halogenated ethanes which have been shown to induce a statistically significant excess of cancer in animals, the National Institute for Occupational Safety and Health recommends caution when handling this compound in the workplace.²

IV. USES

1,1,1-Trichloroethane is used in degreasing and metal finishing operations. The compound is currently being studied as a replacement compound for aromatic solvents used in adhesives and glues. Because 1979 U.S. production was roughly 50%⁸ of capacity, manufacturers are currently placing heavy emphasis on discovering new high volume uses for the compound.

V. TRANSPORTATION

1,1,1-Trichloroethane is transported in tank trucks, railroad tank cars, 55-gallon drums, metal cans, and in well-sealed glass bottles appropriately protected against breakage. Shipping of the compound does not normally cause problems in terms of worker exposure.

VI. NUMBER OF AFFECTED WORKERS

The National Occupational Hazards Survey (NOHS) conducted by the National Institute for Occupational Safety and Health (NIOSH) has used appropriate algorithms to estimate that 2,-900,000 United States workers are exposed to 1,1,1-trichloroethane each year.⁴

VII. RECOMMENDED PROTECTIVE CLOTHING MATERIALS

Butyl rubber or Viton elastomer gloves, aprons, or other protective garments are recommended for use to protect against exposure to liquid phase 1,1,1-trichloroethane.⁵ Neoprene rubber latex or nitrile rubber latex may be used in cases where the protective garment will not be in contact with either the liquid or saturated vapor of 1,1,1-trichloroethane.

VIII. CURRENT PRACTICES IN WORKER PROTECTION

Upon eye exposure, immediate irrigation is recommended and upon skin exposure the exposed area should be washed promptly with soapy water. If 1,1,1-trichloroethane has been swallowed salt water should be taken until vomiting is induced.⁶

Respiratory protection is not required if the time-weighted average exposure limit of 350 ppm is not exceeded.

If exposures above 500 ppm occur, a chemical cartridge with organic vapor cartridge respirator, supplied air, or self-contained breathing apparatus (SCBA) unit is recommended. Exposures above 1000 ppm require an SCBA with full face piece, supplied-air suit with full face piece, or gas mask with organic vapor canister.⁷

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APPENDIX C

1,1,2-TRICHLOROETHANE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

I. SUMMARY

1,1,2-Trichloroethane is a colorless liquid with a chloroform-like odor, whose melting point is -35.5°C and whose boiling point is 113.77°C at 760 mm. It is moderately reactive and the National Institute for Occupational Safety and Health (NIOSH) has recommended that it be handled in the workplace as if it were a human chemical carcinogen.^{2,3} 1,1,2-Trichloroethane is considered more toxic than 1,1,1-trichloroethane and should be handled more cautiously.

II. SELECTED PROPERTIES

Table C-I presents data describing certain physical and chemical properties of 1,1,2-trichloroethane and a brief statement of its carcinogenicity.

III. SOURCES

In the United States, 1,1,2-trichloroethane is produced by the Dow Chemical Company and the RSA Corporation.⁴ Approximately 124,000,000 lbs. of 1,1,2-trichloroethane was produced in the United States in 1974.⁵

TABLE C-I

PROPERTIES OF 1,1,2-TRICHLOROETHANE

| | |
|-------------------------------------|----------------------|
| Molecular weight ¹ | 133.41 a.m.u. |
| Melting point ¹ | -36.5°C |
| Boiling point ¹ (760 mm) | 113.8°C |
| Density ¹ | 1.4397 ²⁰ |
| Solubility | |
| Water ² | 0.45 g/100 at 25°C |
| Ethanol ¹ | Soluble |
| Diethyl ether ¹ | Miscible |

Statement of Carcinogenicity:

The National Cancer Institute⁸ has concluded that under certain conditions 1,1,2-trichloroethane has induced liver cancer in both male and female mice. Also, 1,1,2-trichloroethane has been implicated as causing adrenal pheochromocytoma, a tumor which gives rise to high blood pressure and hyperglycemia. The National Institute for Occupational Safety and Health⁹ recommends that occupational exposure to 1,1,2-trichloroethane be minimized while the carcinogenicity of haloethanes is being studied further and that this compound be handled in the workplace as if it were a human carcinogen.

IV. USES

1,1,2-Trichloroethane is used in primary metal industries and in certain operations requiring very strong and unique solvent properties. It has also been used in certain cases for organic syntheses including its use as an intermediate in the production of copolymer vinylidene chloride thermoplastic resins.⁶ Where possible 1,2-dichloroethane is recommended for use rather than 1,1,2-trichloroethane,⁷ because of the more hazardous nature of the latter.

V. TRANSPORTATION

1,1,2-Trichloroethane is transported in tank trucks, railroad tank cars, 55-gallon drums, metal cans, and in well-sealed glass bottles appropriately protected against breakage. Because of the carcinogenic nature of this compound, care should be taken to avoid eye and skin contact and the breathing of its vapors.

VI. NUMBER OF AFFECTED WORKERS

The National Occupational Hazards Survey (NOHS) conducted by the National Institute for Occupational Safety and Health has used appropriate algorithms to estimate that 112,000 United States workers are exposed to 1,1,2-trichloroethane per year.⁹

VII. RECOMMENDED PROTECTIVE CLOTHING MATERIALS

Because of the carcinogenic nature of 1,1,2-trichloroethane, one should not allow contact of the skin by this material. Protective garments constructed from butyl rubber or Viton elastomer have been shown⁸ to afford penetration resistance to 1,1,2-trichloroethane and are recommended for use with this compound.

VIII. CURRENT PRACTICES IN WORKER PROTECTION²

Upon skin or eye exposure to 1,1,2-trichloroethane the contacted region should be irrigated with flowing water immediately and continuously for 15 min and a physician consulted. Effected clothing should be washed before reuse.

Upon inhalation, the exposed person should be taken to a region of fresh air and if breathing has stopped, given mouth-to-mouth resuscitation.

If 1,1,2-trichloroethane has been ingested, vomiting should immediately be induced and a physician consulted.

NIOSH-approved respiratory protection is required in instances wherein the 1,1,2-trichloroethane concentration exceeds 10 ppm.

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APPENDIX D

POLYCHLORINATED BIPHENYLS (PCBs): AN OVERVIEW OF OCCUPATIONAL EXPOSURES AND HAZARDS

I. SUMMARY

Polychlorinated biphenyls (PCBs) constitute a class of chemical compounds of general formula $C_{12}H_{10-Y}Cl_Y$ ($2 \leq Y \leq 10$) in which the carbon atoms form the biphenyl structure. As commercial products they are a mixture of isomers and sometimes contain chlorinated benzenes as diluents. They have been shown to contain small quantities of polychlorinated dibenzofurans and may contain polychlorinated dibenzo-p-dioxins (PCDDs),^{1,2} both dibenzo compound classes being themselves of a hazardous nature. The range of melting and boiling points which PCBs have varies from 19 and 322°C, respectively for 3,3'-dichlorobiphenyl to 179 and ~210°C (10 mm) for 2,4,5,3',4'-pentachlorobiphenyl¹ with likely higher values for the higher halogenated homologues. Because of the carcinogenic effects of PCBs in animals and adverse health effects in humans,^{1,2} direct skin contact, inhalation, or ingestion of PCBs should be avoided.

II. SELECTED PROPERTIES

Table D-I presents data describing certain representative physical and chemical properties of the generic class of chemical compounds known as PCBs and also presents a brief statement of carcinogenicity of these compounds.

TABLE D-I

POLYCHLORINATED BIPHENYLS (PCBs)

| | |
|--|------------------------------------|
| Molecular weight range | |
| 1-Chlorobiphenyl | 164 a.m.u. |
| Decachlorobiphenyl | 470 a.m.u. |
| Representative melting points | |
| 3,3'-Dichlorobiphenyl | 29°C |
| 2,4,5,3',4'-Pentachlorobiphenyl ¹ | 179°C |
| Representative boiling points | |
| 3,3'-Dichlorobiphenyl ¹ | 322°C |
| 2,4,5,3',4'-Pentachlorobiphenyl ¹ | 210°C (10 mm) |
| Representative densities | |
| Aroclor 1221 ¹ | 1.19 _{18.5} ²⁵ |
| Aroclor 1270 ¹ | 1.95 ₂₆ ²⁵ |
| Representative Solubilities in Water | |
| Aroclor 1241 ¹ | 0.24 ppm |
| Aroclor 1260 ¹ | 2.7 x 10 ⁻² ppm |

Statement of Carcinogenicity:

Because of the toxic and potentially carcinogenic nature of PCBs *per se* in humans, and also because of the hazardous nature of compounds such as dibenzofurans which are associated with PCBs, care should be taken to avoid exposure.³

III. SOURCES

In the United States, there are currently no firms manufacturing PCBs. Past United States manufacturers and their PCB trade names are:⁴

| <u>Trade Name</u> | <u>Trade Name Owner</u> |
|-------------------|------------------------------|
| Aroclor | Monsanto Co. |
| Chlorextal | Allis-Chalmers |
| Dykanol | Federal Pacific Electric Co. |
| Inerteen | Westinghouse Electric Corp. |
| Noflamol | Wagner Electric Corp. |
| Pyranol | General Electric Co. |
| Therminol* | Monsanto Co. |

**Therminol products formulated after 1976 do not contain PCBs.*

From their introduction to industry in 1929-30, roughly 1.25 billion pounds of PCBs have been purchased by United States industry and about 60% of this total domestic consumption is still in service. It has been estimated that 194 million pounds of PCBs are in the environment and 290 million pounds are in landfills or dumps.⁵

IV. USES

Prior to the widespread concern about the persistence of PCBs in the environment, they were used in industry as fluids for heat transfer systems, hydraulic systems, gas turbines, and vacuum pumps and as fire retardants and plasticizers. These compounds were also used in carbonless copy paper, but by far their widest use was as dielectric fluids in capacitors and transformers.

V. TRANSPORTATION

Commercial quantities of PCBs are transported in tank trucks, railroad tank cars, or 55-gallon drums.⁶ Laboratory quantities (i.e., gram quantities) of PCBs are shipped in small glass vials with screw type lids. During late 1972, standards and guidelines for handling and disposal of PCBs were issued under the aegis of the American National Standards Institute as ANSI-C107-1-1974.⁸

VI. NUMBER OF AFFECTED WORKERS

Twelve thousand people were estimated⁷ to have a potential for occupational exposure to PCBs in the United States during the mid-1970s. Because of the ubiquitous and persistent nature of PCBs, quite likely anyone in any industrialized country has been exposed to PCBs and PCBs are, along with dichlorodiphenyldichloroethylene (DDE), a degradation product of DDT, the most abundant of the chlorinated aromatic pollutants in the earth's ecosystem.⁸

VII. RECOMMENDED PROTECTIVE CLOTHING MATERIALS

Because of the toxic and potentially carcinogenic nature of polychlorinated biphenyls, they should not be allowed to contact the skin. Viton elastomer has been shown earlier in this report⁹ to afford penetration resistance to Aroclor 1254 and protective garment materials of Viton are recommended.

VIII. CURRENT PRACTICES IN WORKER PROTECTION

The Occupational Safety and Health Administration standards for PCBs in the air are 1 mg/m³ for 42% chlorine mixtures and 0.5 mg/m³ for 54% chlorine mixtures.¹⁰ Exposure to PCBs should be minimized and the U. S. Government Code of Federal Regulations¹¹ states that "employees shall wear equipment adequate to prevent exposure to a carcinogen," but makes no specific recommendations as to what this equipment might be. At the end of the work day, workers are required to remove their protective clothing and equipment and take a shower.⁹

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