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Permeation of Eleven Protective Garment Materials By Four Organic Solvents*

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The resistance of 11 different protective garment materials to permeation by epichlorohydrin, perchloroethylene, trichloroethylene, and 1,2-dibromoethane were determined. Water was the collection medium in the epichlorohydrin tests with samples taken periodically and analyzed by gas chromatography. Because of the relatively low solubilities of the other three challenge liquids in water, air was used as the collection medium. The concentrations of the permeant vapors in an airstream which passed across the downstream sides of the membranes were determined automatically every 2 min with a flame ionization detector. Butyl rubber offers good protection against epichlorohydrin, with breakthrough occurring after 8 hrs. With the halogenated hydrocarbons, Viton and Vitrile provide protection for at least 12 and 24 hrs, respectively, while PVA showed no breakthrough in 24 hrs¹ with trichloroethylene and dibromoethane. With perchloroethylene, nitrile breakthrough occurred in 5 hrs. The weight and volume changes which occurred when the materials were soaked in each of the challenge liquids were also determined. The log of these changes correlated moderately well with the log of the breakthrough time normalized by the square of the material thickness.

Introduction

The permeation resistance of 11 different protective garment materials to four liquid, organic compounds was determined. These compounds, epichlorohydrin (EPI), perchloroethylene (PCE), trichloroethylene (TCE), and 1,2-dibromoethane (DBE), are all extensively used in industry with United States production reaching 10⁸ to 10⁹ kg/yr of each.⁽¹⁻⁴⁾ The primary uses of these materials are: (1) EPI — manufacture of glycerin and epoxy resins; (2) PCE — dry-cleaning, processing and finishing in the textile industry, and cold cleaning and vapor degreasing; (3) TCE — vapor degreasing; and (4) DBE — lead scavenger in gasoline, and as a soil and grain fumigant.⁽⁴⁾

Both EPI⁽¹⁾ and DBE⁽⁴⁾ have been shown to be carcinogenic in mice, while TCE⁽⁵⁾ is a suspect carcinogen. EPI and DBE have also been implicated in cases of sterility⁽⁵⁾ and can cause kidney damage. With PCE there is limited evidence for carcinogenicity⁽²⁾ in mice and it can cause dermatitis.

Because of the widespread industrial use of these compounds and their possible carcinogenic potential and other toxic properties, there is a need for garment materials which will protect the worker. Eleven materials were tested for permeation resistance to these four compounds. Breakthrough time and steady-state permeation rate were determined. The changes in weight and volume which occurred when 10 of these materials were soaked in the challenge liquids were measured to determine whether there was a correlation between these changes and permeation performance.

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Mention of a company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH)

Experimental

Materials

The garment materials, manufacturers, and nominal thicknesses are shown in Table I. Samples were usually cut from the palm or gauntlet of a glove except the Saranex-laminated Tyvek (SLT) samples were cut from a sheet of the material. The Viton SF and Vitrile gloves were prototypes supplied by the manufacturer. The challenge compounds, all from Aldrich Chemical Co., were used without additional purification. Listed purities were at least 99 percent for the EPI, PCE, and DBE, and 98 percent for the TCE.

Permeation Testing — General

All permeation testing used the standard American Society for Testing and Materials (ASTM) permeation cell.^(6,7) Two different collection media were used: water for epichlorohydrin, and a flowing airstream for the other three challenge liquids. To conduct the experiments, a material sample was clamped in the middle of the cell, which was then placed in a

TABLE I
Materials Tested

Material	Approximate Thickness (cm)	Supplier
Surgical Rubber	0.023	Los Alamos National Laboratory Stock
Butyl Rubber	0.038	Norton Company
Polyethylene	0.003	Edmont
Polyvinyl Alcohol	0.046	Edmont
Saranex-laminated Tyvek	0.015	DuPont
Neoprene	0.043	Edmont
Milled Nitrile	0.038	Surety Rubber
Viton	0.023	Norton Company
Viton SF	0.023	Norton Company
Vitrile	0.020	Norton Company
Teflon (Flexed)	0.005	Clean Room Products

constant temperature bath. For all material/challenge combinations, at least two replicate experiments were conducted simultaneously. Testing lasted until a steady-state permeation rate was achieved or 24 hrs had elapsed, whichever occurred first. Two of the materials which showed the best permeation resistance were tested for reuse with each challenge liquid. This was done by air-drying the samples for 24 hrs and then retesting for permeation.

Epichlorohydrin (EPI)

To start the experiment, the collection side of the cell was filled with a measured amount of water, approximately 90 mL, and then the challenge side was filled with EPI. A magnetic stirrer kept the water in the collection side well mixed. At specific time intervals after introduction of the EPI, a 2 mL aliquot of the water was taken and sealed in a 2 mL sample bottle. Samples were taken at 1, 3, 5, 10, 15, 30, and 45 min; and, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8 and 24 hrs. Immediately after each sampling, 2 mL of water were added to the cell to maintain a constant liquid volume.

The concentration of EPI in each sample was determined by gas chromatography using an SP-1000 column operated isothermally at 110°C and an electron capture detector. The sensitivity of the detector was such that 1 ppm (v) of EPI could be readily measured. Each concentration was corrected for the dilution which took place when the 2 mL aliquots of water were replaced in the cells.⁽⁶⁾ Because EPI hydrolyzes in water, analytical standards were prepared in CS₂ as the detector sensitivity was the same for both water and CS₂ solutions.

To determine the maximum possible effect of hydrolysis on the 24-hr permeation samples, three determinations were made of the hydrolysis rate. In each case, solutions of 5, 10, 25, 50, 100, and 250 ppm in water were prepared. Twenty-four hours after making up these solutions, the concentrations had decreased by 20 ± 2 percent. Since this was the maximum amount the concentrations could have been in error, no corrections were made for hydrolysis.

The analyzed concentrations were in ppm (v) units as it was easier to make the calibration standards by volume dilution. Breakthrough time can be defined as that time after the challenge is added to the cell at which a given concentra-

tion is present in the collection side. In this case, that concentration is 1 ppm (v). Because concentrations were not determined continuously, but at periodic intervals, the listed breakthrough times are those times at which analyses first showed the 1 ppm, or higher, concentration.

When a steady-state permeation rate is reached in a closed system, such as this one, the concentration increases linearly with time. During this time, the permeation rate can be calculated by:

$$J = \frac{10^{-3} s \rho v}{A} \quad (1)$$

- Where J = permeation rate: mg/min/m²
 s = slope of linear portion of permeation range: ppm/min
 ρ = density of challenge liquid: gm/mL
 v = volume of collection media: mL
 A = area of test material contacted by challenge: m²

For epichlorohydrin and the ASTM cell, $\rho = 1.18$, $v \sim 90$, $A = 19.6 \times 10^{-4}$ and $J \sim 54.2$ s.

Perchloroethylene (PCE), Trichloroethylene (TCE), and 1,2-Dibromoethane (DBE)

For these compounds, a flowing airstream was passed through the collection side of the cell into which the permeant vaporized. The concentration of the permeant was determined with a nonspecific flame ionization detector, Beckman Model 400, Hydrocarbon Analyzer, the signal from which was recorded on a strip chart recorder.

A simplified schematic of the flow apparatus is shown in Figure 1. Compressed air was cleaned by passing it through 5A molecular sieve and then Drierite. This air was divided, each half passing through a calibrated rotameter and then into one of two cells. The exhaust from each cell could be passed through a mass flowmeter which was used to set the flows at the beginning of a test. During a test, this meter was switched out of the exhaust line and the gas vented directly to the laboratory hood.

A three-way switching valve, A, was connected between the two exhaust lines with the common side going to the hydrocarbon analyzer. A pump pulled sample air from whichever exhaust line was connected through the analyzer at about 700 mL/min. A preset timer switched valve A so that the exhausts from the two cells were sequentially connected to the analyzer for 2-min intervals. If desired, the valve could be switched at any time.

In the exhaust line from one of the cells was another automatically switched three-way valve, B. This valve disconnected the analyzer from the cell exhaust and connected it to a source of calibration gas. While this valve could be switched at any time, it normally operated once every hour for 3 min, giving an automatic calibration signal on the strip chart record.

The calibration gas was produced by injecting vapors of the challenge liquid at a known, constant rate into a metered airflow. The vapors were generated from a diffusion tube

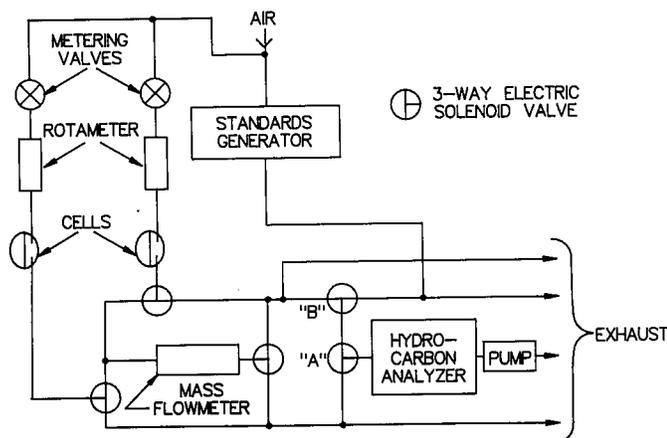


Figure 1 — Simplified schematic of gas collection apparatus.

maintained at a constant temperature in an AID Standards Generator. The rate of vaporization was determined by periodically weighing the diffusion tube. The airflow was measured with calibrated rotameters.

Calibration of the hydrocarbon analyzer was accomplished by changing the airflow through the generator, thereby changing the vapor concentration. The minimum flow was that required by the analyzer, 700 mL/min. With this concentration and the analyzer attenuator on the least sensitive setting, the span was set to give about 20 percent of full scale on the recorder. More dilute vapor concentrations

were produced by increasing the flow in steps to a maximum of about 3500 mL/min.

For an open flow system, permeation rate cannot be calculated from absolute vapor concentrations. That is, this concentration is a function of both the permeation rate and airflow. The permeation rate is given by:

$$J = \frac{FC}{A} \quad (2)$$

Where: F = airflow: mL/min

C = concentration of challenge vapor in the airstream: mg/mL

TABLE II
Permeation of Epichlorohydrin Using Water Collection Medium

Material	Breakthrough			Permeation Rate ^B	Range Over Which Rate Calculated	
	First Indication	ppm	Extrapolated ^A		min	Concentration ppm
Surgical Rubber						
Run A	3	3.7	3.9	1300	3 - 20	3.7 - 417
Run B	3-1/2	5.8	4.0	1380	3-1/2 - 20	5.8 - 453
Butyl						
Run A	1440	5.2				
Run B	1440	2.6				
Run C	1440	6.2				
Run D	1440	6.2				
Butyl - Reuse Test						
Run C	5	0.83	-70	1.31	5 - 1440	0.83 - 34
Run D	10	0.58	-26	1.23	10 - 1440	0.58 - 36
Polyethylene						
Run A	3	1.1	4.4	94.4	5 - 420	4.7 - 787
Run B	3	1.3	5.4	97.2	5 - 420	4.3 - 731
Polyvinyl Alcohol						
Run A	1	0.7	2.6	1050	5 - 120	56.2 - 2340
Run B	3	11.0	3.3	1270	5 - 120	46.8 - 3100
Saranex-laminated Tyvek						
Run A	60	1.2	61	34.3	60 - 420	1.2 - 243
Run B	60	2.8	54	33.2	60 - 360	2.8 - 179
Neoprene						
Run A	20	0.6	28	3620	30 - 60	175 - 2120
Run B	15	1.2	26	3140	30 - 60	206 - 2070
Nitrile						
Run A	20	8.8	24	11 500	25 - 45	329 - 4780
Run B	25	278	24	12 500	25 - 45	278 - 5150
Viton						
Run A	60	1.9	97	506	120 - 240	191 - 1310
Run B	60	12	67	511	60 - 300	12 - 2500
Run C	60	10	63	518	60 - 300	10 - 2530
Viton SF						
Run A	60	9.2	66	688	60 - 180	9.2 - 1430
Run B	45	3.4	47	563	45 - 120	3.4 - 823
Vitrile						
Run A	80	1.2	118	1520	130 - 240	440 - 3700
Run B	80	0.3	113	857	120 - 210	156 - 1670
Teflon						
Run A	420	0.37	258	0.12	420 - 1440	0.37 - 2.79
Run B	420	0.33	289	0.12	420 - 1440	0.33 - 2.65
Teflon - Reuse Test						
Run A	480	0.59	220	0.11	480 - 1440	0.59 - 2.74
Run B	420	0.37	234	0.09	420 - 1440	0.37 - 2.48

^ABreakthrough defined by extrapolating the steady-state permeation data to zero concentration.

^BCorrelation coefficients were 0.9823 or greater.

TABLE III
Permeation of Perchloroethylene

Material	Breakthrough Time (min) ^A	Steady-State Permeation Rate	
		Approximate Time Reached (min)	Rate mg/m ² /min
Surgical Rubber			
Run A	<1	>3	>7500
Run B	<1	>3	>7500
Butyl Rubber			
Run A	10	>13	>7500
Run B	10	>13	>7500
Polyethylene			
Run A	<1	>2	>6850
Run B	<1	>2	>6850
Polyvinyl Alcohol			
Run A	36	150	20 ^B
Run B	21	>100	116
Run C	48	>160	12
Saranex-laminated Tyvek			
Saranex to Challenge Side			
Run A	2	68	200
Run B	5	80	100
Tyvek to Challenge Side			
Run A	<2	70	73 ^C
Run B	<2	140	67 ^C
Neoprene			
Run A	6	>13	>6400
Run B	8	>13	>6400
Nitrile			
Run A	320	660 - 1180	410 ^D
Run B	435	660 - 1180	470 ^D
Viton			
Test Temperature - 23°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Reuse Test			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Test Temperature - 45°C			
Run A	180	720	42
Run B	190	720	42
Test Temperature - 10°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Viton SF			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Reuse Test			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Vitrile			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Teflon			
Run A	No breakthrough in 24 hrs		
Run B	26	300	23 ^B

^ABreakthrough defined as 5 mg/min/m².

^BRate fell to 14 mg/min/m² by 450 min.

^CTyvek to challenge side. Both rates peaked before 4 min at greater than 440 and 69, respectively. A decreased steadily to steady-state. B decreased and then rose to steady-state.

^DSteady-state reached during night and was off scale on recorder in morning.

^BRate increased to at least 43 mg/min/m² between 36 and 70 min, and then decreased.

TABLE IV
Permeation of Trichloroethylene

Material	Breakthrough Time (min) ^A	Steady-State Permeation Rate	
		Approximate Time Reached (min)	Rate mg/m ² /min
Surgical Rubber			
Run A	<1	>2	>6550
Run B	<1	>2	>6550
Butyl Rubber			
Run A	5	>7	>8250
Run B	5	>7	>8250
Polyethylene			
Run A	<1	>2	>6560
Run B	<1	>2	>6560
Polyvinyl Alcohol			
Test Temperature - 23°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Reuse - Temperature 23°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Test Temperature - 10°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Test Temperature - 45°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Saranex-laminated Tyvek			
Run A	<1	>38	>2900
Run B	<1	>38	>3100
Neoprene			
Run A	<4	>5	>5650
Run B	3	>6	>5650
Nitrile			
Run A	11	>19	>8250
Run B	<15	>21	>8250
Viton			
Test Temperature - 23°C			
Run A	720 ^B	>1440	>17
Run B	600 ^B	>1440	>16
Reuse - Temperature 23°C			
Run A	330 ^B	1020	10
Run B	330 ^B	1020	9
Test Temperature - 10°C			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Test Temperature - 45°C			
Run A	48 ^B	160	230
Run B	48 ^B	170	210
Viton SF			
Run A	340	840	30
Run B	220	840	36
Vitrile			
Run A	480	>1440	>120
Run B	500	1320	130
Teflon			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		

^ABreakthrough defined as 5 mg/min/m².

^BBreakthrough defined as 1 mg/min/m².

From the calibration data:

$$C = a (\text{Div}) + b \quad (3)$$

Where: a, b = constants
Div = recorder divisions

The slopes, A, of the calibration curves ranged from 4 to 6×10^{-6} with linear regression coefficients greater than 0.99.

For these experiments, breakthrough was defined as 5 mg/min/m². This corresponded to approximately two recorder divisions at the normal cell flow of 1300 mL/min. Full scale, 1000 divisions, corresponded to approximately

2500 mg/min/m². By increasing the flow to the maximum, full scale corresponded to greater than 6500 mg/min/m².

Results and Discussion

Epichlorohydrin (EPI)

The results of the EPI permeation tests are given in Table II. Of the materials tested, butyl rubber showed the longest breakthrough time, between 8 and 24 hrs. Teflon was the only other material which had a breakthrough time of greater than 90 min, and it subsequently exhibited a low, 0.12 mg/min/m², permeation rate. In reuse tests, breakthrough was quite rapid with the butyl rubber, less than 10

TABLE V
Permeation of 1,2-Dibromoethane

Material	Breakthrough Time (min) ^A	Steady-State Permeation Rate	
		Approximate Time Reached (min)	Rate mg/m ² /min
Surgical Rubber			
Run A	<1	>4	>7300
Run B	<1	>4	>7300
Butyl Rubber			
Run A	102	220	750
Run B	110	210	790
Polyethylene			
Run A	<2	24	1410
Run B	<2	22	1580
Polyvinyl Alcohol			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Reuse			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Saranex-laminated Tyvek			
Run A	8	240	490
Run B	10	240	490
Neoprene			
Run A	8	>16	>7300
Run B	12	>19	>7300
Nitrile			
Run A	27	>38	>7300
Run B	35	>44	>7300
Viton			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Reuse			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Viton SF			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Vitrile			
Run A	No breakthrough in 24 hrs		
Run B	No breakthrough in 24 hrs		
Teflon			
Run A	60 ^B		
Run B	No breakthrough in 24 hrs		
Run C	No breakthrough in 24 hrs		

^ABreakthrough defined as 5 mg/min/m².

^BSample replaced before steady-state reached.

min, with a subsequent low permeation rate, 1.3 mg/min/m². The behavior of the reused Teflon, on the other hand, was very similar to that of the new material.

Perchloroethylene (PCE)

The permeation data for PCE are shown in Table III. In this table and those showing the trichloroethylene and dibromoethane results (Tables IV and V), only breakthrough time, defined as that time at which a rate of 5 mg/min/m² was detected, the steady-state permeation rate, and the approximate time that rate was reached are listed.

Two sets of tests were conducted with the Saranex-laminated Tyvek, one with the Saranex toward the challenge and the other with it toward the collection side of the cell. With the Saranex toward the challenge, breakthrough occurred within a few minutes and the rate then increased to a constant value within about an hour. When the Saranex was toward the collection side, Tyvek toward the challenge, the rate peaked within four minutes and then decreased to a steady-state value, slightly lower than in the previous two tests. The reason for these different results is unknown, but they do show that with composite materials at least, permeation behavior may depend on which side sees the challenge or collection medium.

An early peak in the rate, followed by a decrease to steady-state, was also noted with one of each of the PVA and Teflon samples with PCE and one Teflon sample with DBE (Table V). These data are similar to those described by Nelson, *et al.*⁽⁸⁾ as type D permeation behavior. They ascribed this type to membranes which exhibited moderate to heavy swelling when exposed to the challenge. In the present cases, how-

ever, swelling was negligible, as shown by the volume swelling tests (Figures 6 and 8) that are discussed below.

Of the materials tested, Viton type materials performed the best. That is, Viton, Viton SF, and Vitriole showed no breakthrough in 24 hrs. In fact, Viton and Viton SF showed no breakthrough after a reuse test. Of the other materials, nitrile showed a moderately high steady-state permeation rate, 450 mg/min/m², but breakthrough was not detected for 5 hrs. With Teflon, inconsistent results were obtained, with one sample showing breakthrough in 26 min, while the other showed no breakthrough in 24 hrs. Similar inconsistent results were also obtained with Teflon and DBE (Table V). We believe the reason breakthrough occurred was due to physical defects in the material rather than any chemical property. This damage was produced by thoroughly flexing the samples before they were placed in the permeation cell. The fact that damage does occur under these conditions can be seen in electron photomicrographs of flexed areas (Figure 2). As flexing or bending would undoubtedly occur whenever a glove is worn, all Teflon samples were similarly treated.

As PCE is often used at elevated temperatures in degreasing operations, Viton was also tested at 45°C (Figure 3). In this case, breakthrough occurred at approximately 3 hrs, and then increased to a steady-state rate of 42 mg/min/m² at about 12 hrs. At the end of 9 hrs, the maximum total length of time after first contact to be expected for a full work day, the rate was 38 mg/min/m².

From the data such as that in Figure 3, a use time could be estimated, given a permissible integrated dose. However, it needs to be emphasized that these data were obtained with material from one batch from one manufacturer. Permea-

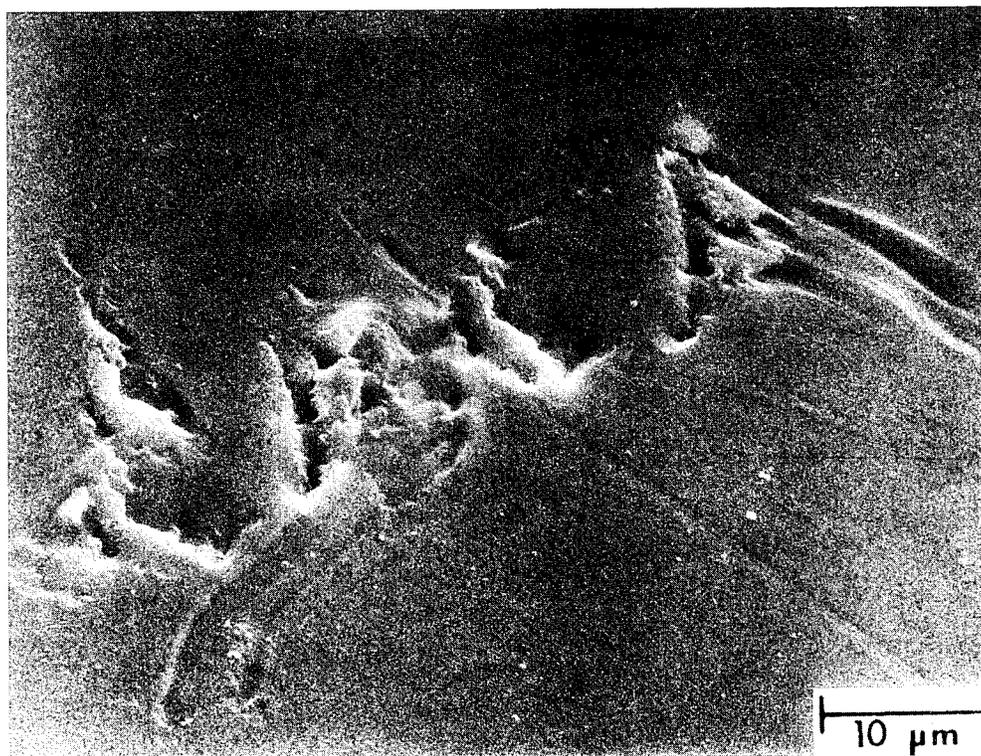


Figure 2 — Electron photomicrograph of damage to Teflon due to flexing.

9 mils thick

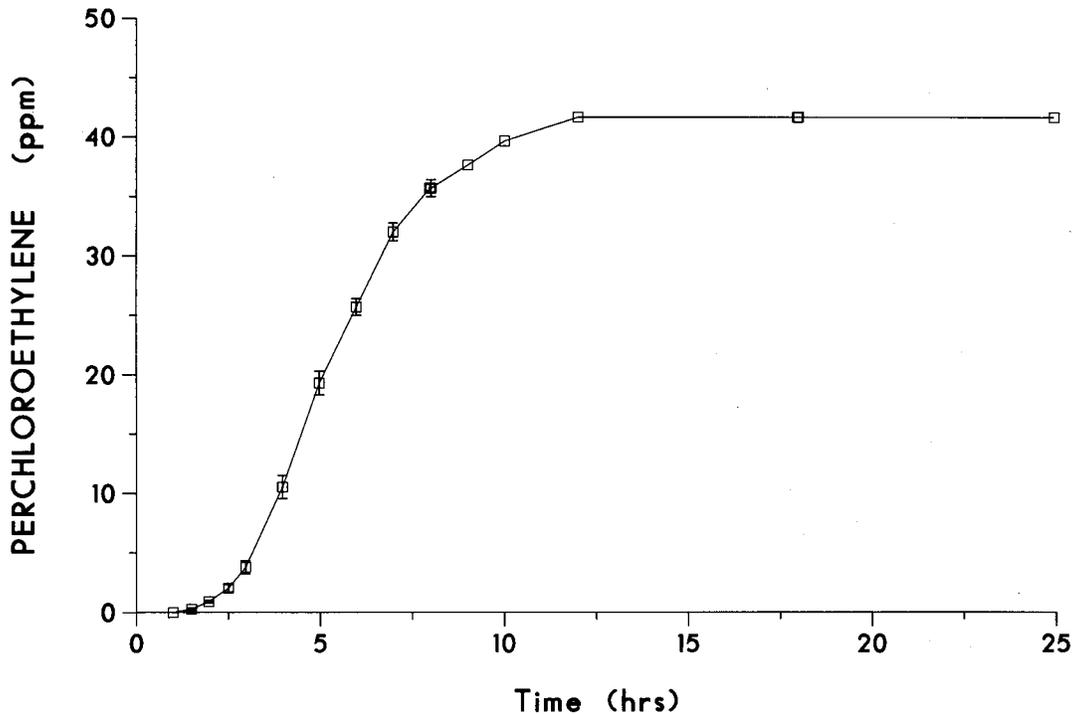


Figure 3 — Permeation of perchloroethylene through Viton at 45°C.

tion characteristics of materials from different manufacturers,⁽⁹⁾ and even from different batches from the same manufacturer, may differ. Therefore, these data for Viton, as well as all the data in this report, can only be considered indications of the permeation behavior of any specific garment material.

Trichloroethylene (TCE)

The data for TCE are shown in Table IV. The only materials which did not exhibit breakthrough at 23°C were PVA and Teflon. In fact, PVA did not show breakthrough either in a reuse test or for 24 hrs at 45°C. Unfortunately, there is an interaction between PVA and water. Electron photomicrographs of PVA samples which had been soaked in water (Figure 4) show what appear to be small holes. Because perspiration is often present when "impervious", protective gloves are worn, PVA gloves may not offer the protection suggested by these data. If perspiration were kept from contacting the PVA by using a water impermeable liner, possibly a surgical rubber glove, this material could perform very well.

Of the remaining materials, Viton had the longest breakthrough time, 10 hrs, and the lowest average steady-state permeation rate at 24 hrs, 16.5 mg/min/m². On a reuse test, after air drying for 24 hrs, the breakthrough time was lowered to 5 hrs and a steady-state rate of 10 mg/min/m² was reached by 17 hrs. Viton was also tested at 10°C, at which temperature no breakthrough occurred, and 45°C, at which breakthrough occurred at 48 min. A steady-state rate of 220 mg/min/m² was reached by 160 min in this latter test. Vitrite and Viton SF, the next best materials, had break-

through times and steady-state rates of 8 and 4 hrs, and 130 and 33 mg/min/m², respectively.

In the permeation tests with Saranex-laminated Tyvek, it was necessary to increase the airflow through the cells to maintain the detector signal on scale. The data indicated an apparent increase in the steady state permeation rate as the flow increased. These results could be explained by either the detector response not being linear with concentration, or the permeation or vaporization rate of TCE increasing with increasing airflow. To investigate this further and to eliminate any effect of the Tyvek, two more permeation tests were conducted with the Saranex only, the Tyvek having been removed. The results of these two tests showed good reproducibility and were similar to the two tests with the laminated material.

The data from these tests indicated that detector nonlinearity was undoubtedly not the cause. As the flow through the cell was increased, the pressure in the collection side of the cell also increased. This should, if anything, decrease, rather than increase, the permeation rate. Because of its relatively high vapor pressure, 60 torr at 20°C,⁽¹⁰⁾ it also appears unlikely that all the TCE would not vaporize at the lower flows. However, it is not possible to calculate vaporization rate, a kinetic property, from the vapor pressure, a thermodynamic property. It is possible that attraction of the TCE to the Saranex is such that the first TCE which permeates is held tightly to the downstream side of the membrane. That is, its free energy, and thus vapor pressure, is much lower than for pure TCE. This could hinder the permeation of more challenge. As the airflow increased, the concentration of TCE in the air would tend to drop, increas-

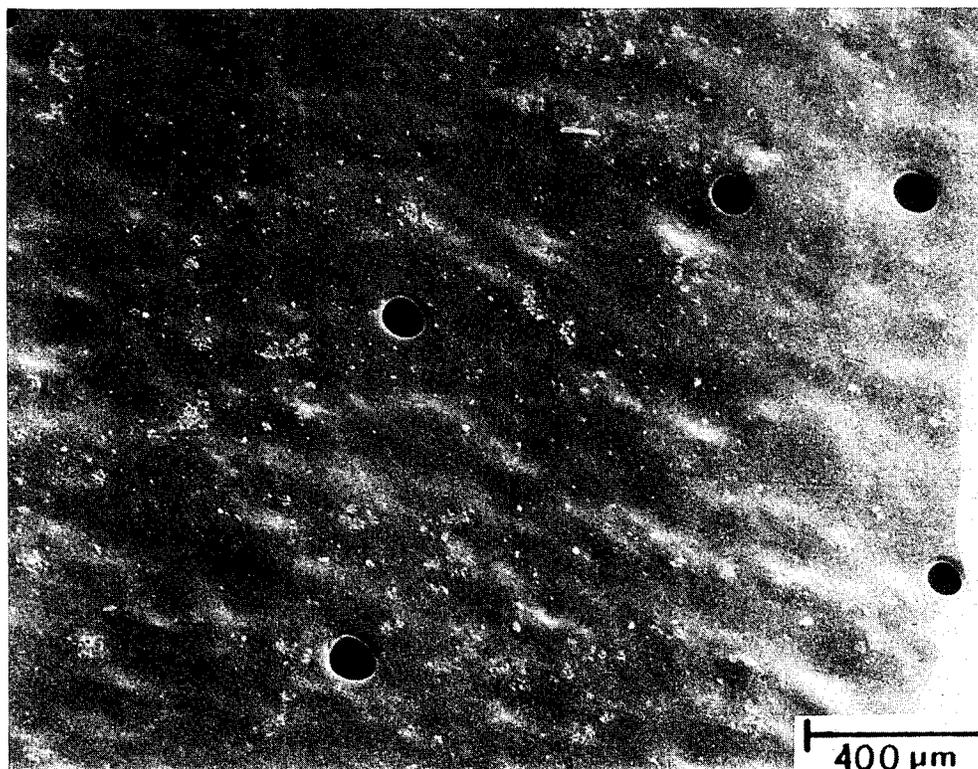


Figure 4 — Electron photomicrograph of PVA samples soaked in water.

ing the driving force for vaporization. It is suggested that with all permeation testing using a flowing gas stream collection medium, the effect of flow rate should be determined.

1,2-Dibromoethane (DBE)

Because of the carcinogenic potential of DBE, all operations involving the bulk liquid were carried out in a glove box or a hood with personnel wearing full-face respirators. Viton gloves were used for skin protection.

The permeation results obtained with this compound are shown in Table V. Only PVA and the Viton type gloves had breakthrough times longer than 2 hrs. Although two Teflon samples exhibited no breakthrough for 24 hrs, the third

showed it after about 1 hr. This latter sample behaved similarly to one Teflon sample with PCE. That is, the rate rose rapidly after breakthrough and then started to fall. In this case, the sample was replaced before steady-state was reached. Both Viton and PVA were tested for reuse. Neither showed breakthrough in 24 hrs.

Weight and Volume Changes

All materials, except Saranex-laminated Tyvek, were soaked in the challenge liquids and the weight and volume changes which had occurred at the end of 24 hrs determined (Table VI). Saranex-laminated Tyvek was not tested because the Tyvek, which affords little permeation resistance, soaks up

TABLE VI
24-Hr Weight and Volume Changes

Material	Epichlorohydrin		Perchloroethylene		Trichloroethylene		1,2-Dibromoethane	
	Weight Percent	Volume Percent	Weight Percent	Volume Percent	Weight Percent	Volume Percent	Weight Percent	Volume Percent
Surgical Rubber	30	30	770	530	700	580	480	240
Butyl Rubber	3	0	510	280	440	320	65	30
Polyethylene	0	15	15	85	20	70	20	35
Polyvinyl Alcohol	-7	-7	-6	-12	-2	-10	4	0
Neoprene	100	120	360	320	400	410	500	^A
Nitrile	340	240	95	60	310	220	580	230
Viton	20	35	4	0	8	20	3	0
Viton SF	25	35	4	0	12	15	3	0
Vitrile	480	350	65	45	290	200	690	290
Teflon	0	0	0	0	0	0	2	0

^ASample disintegrated.

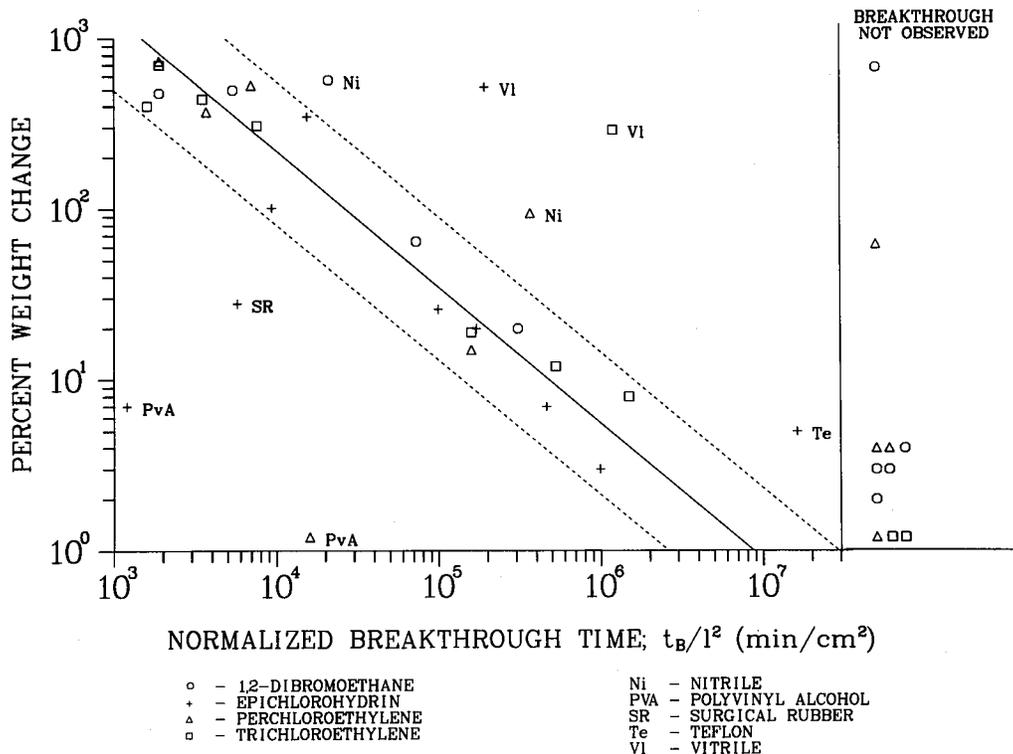


Figure 5 — Percent weight gain versus normalized breakthrough time.

the liquid, making the weight change measurements meaningless while, at the same time, the laminates separate, making the volume measurements worthless.

These data, as percent change in the physical property, are shown in Figures 5 and 6 plotted against the breakthrough time (t_B) divided by the square of the membrane thickness

(l^2). The dashed diagonal lines, also shown in Figures 7 and 8 and explained below, bracket the majority of the data. The garment materials are specified for only those experimental points which fall outside the area enclosed by the diagonal lines. Weight and volume changes less than 1 percent or negative are plotted as 1.2 percent change. This was done

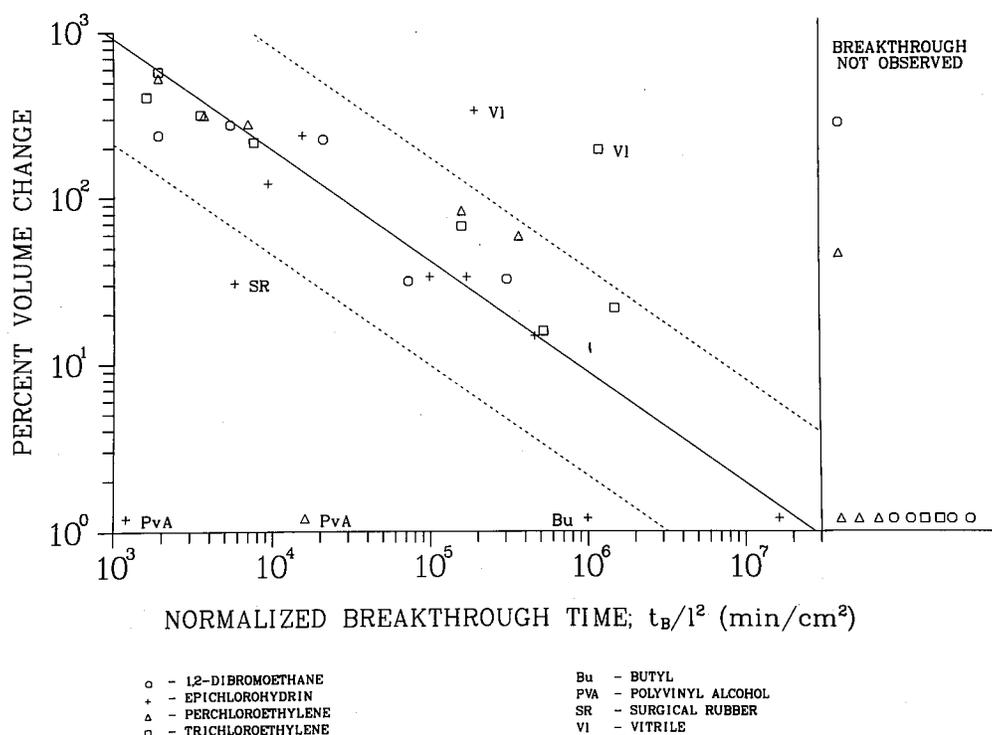


Figure 6 — Percent volume change versus normalized breakthrough time.

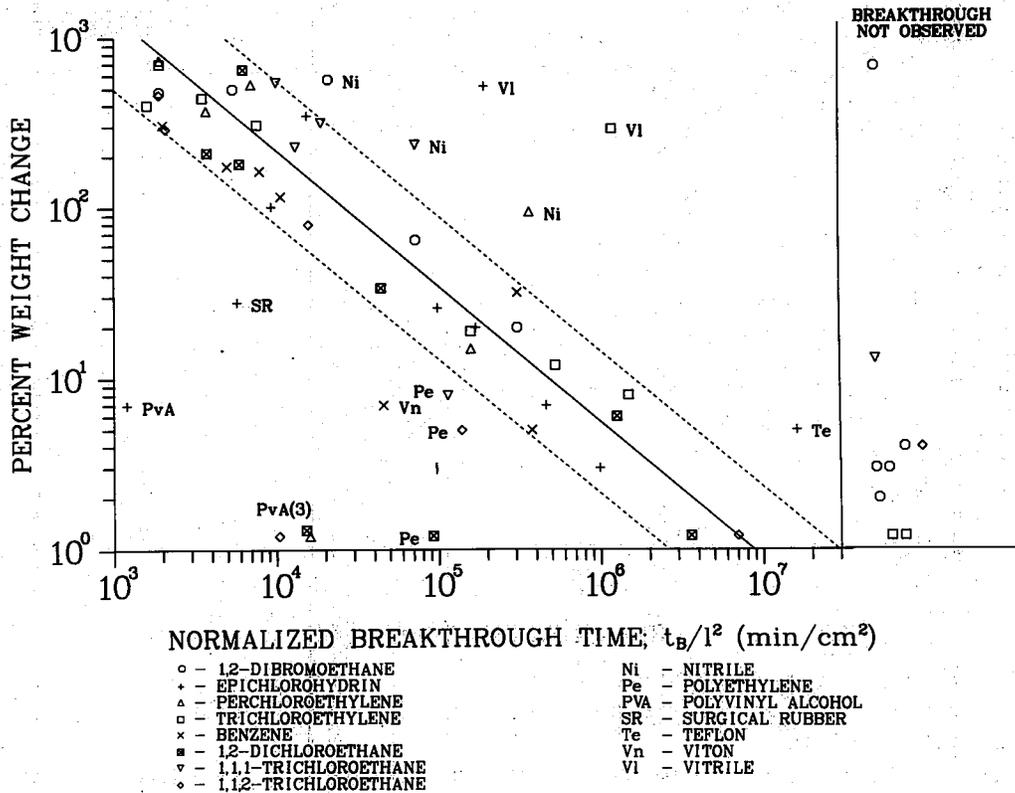


Figure 7 — Percent weight gain versus normalized breakthrough time.

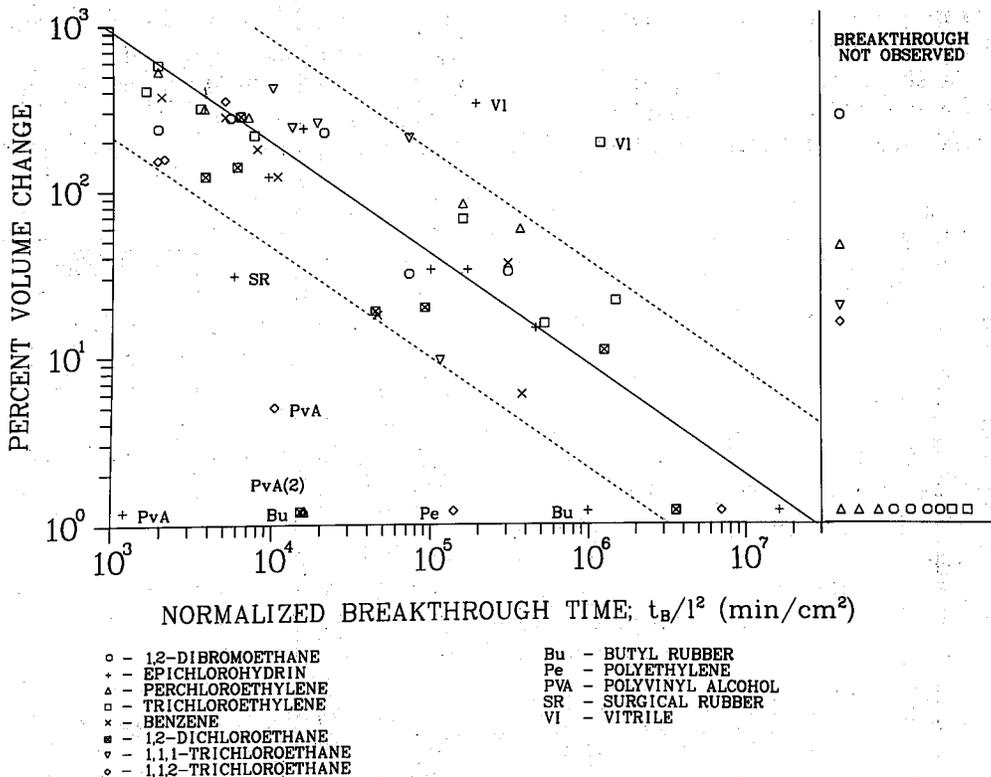


Figure 8 — Percent volume change versus normalized breakthrough time.

because (1) negative changes cannot be plotted on the graph; (2) we believe a 1 percent change is within the error of the measurements; and (3) the points were plotted at 1.2 rather than 1 percent to make them more visible.

The reason for the approximate correlation shown in these figures is not obvious. While theoretically⁽¹¹⁾ the permeation rate, breakthrough time, and solubility of the challenge in the material are all mathematically related, and the

weight and volume changes are measures of the solubility, the values which are calculated refer to a given challenge/material combination. One other factor involved is the diffusion coefficient, the value of which is also a function of the challenge and the material. Thus, it is not readily apparent why the correlation shown, which can be described by:

$$\log Y = s \log \frac{t_B}{l^2} + c \quad (4)$$

Where: Y = percent weight or volume change,
s and c = constants,

should hold. However, we believe these empirical relationships may be useful in predicting breakthrough time.

In Figures 7 and 8, the same data shown in Figures 5 and 6 have been combined with previous results obtained at this laboratory.^(12,13) In all, the data for eight different challenge liquids have been plotted for the garment materials used in the present program. While all the present materials were not used in the former work, the data for a total of 69 challenge/material combinations are shown. The earlier data were all collected using a water collection medium. Of the challenge liquids, six are halogenated hydrocarbons, one is an aromatic hydrocarbon, and one an epoxy compound. Five of the halogenated hydrocarbons contain chlorine, three are saturated, and two unsaturated. The other is a saturated hydrocarbon containing bromine.

In these figures, the further to the right a point falls, the longer the breakthrough time for a given material thickness and the greater the protection afforded. The lower diagonal line, which was positioned visually, separates the majority of the data points from the few that lie in the lower left portion of the figure. The equation for this line in Figure 7, which gives a conservative estimate for the great majority of the experimentally-determined breakthrough times is:

$$\log t_B = \frac{\log W - 5.07}{-0.79} + \log l^2 \quad (5)$$

Where: W = percent weight change.

For these data, the breakthrough times calculated using Equation 5 would predict a minimum, or safe, breakthrough time for 87 percent of all the permeation tests, or 91 percent if the data from three PVA tests which used a water collection medium are discarded.

The upper, dashed, diagonal line, which was also visually placed, separates the outliers in the upper right portion of the figure and was drawn parallel to the lower line but offset approximately one order of magnitude in t_B/l^2 . All of the points in the upper right-hand portion are for either nitrile or Vitriole. Vitriole is a composite material containing both nitrile and Viton. The weight gains associated with this material are due primarily to the nitrile, while the permeation resistance is determined primarily by the Viton. Thus, it would not be expected that the breakthrough time would follow the same correlation as with the noncomposite materials. Neglecting all the Vitriole data and that from the PVA experiments with water collection, and including the data for the three material/

challenge combinations which showed no breakthrough or weight gain, 71 percent of the points fall between the dashed lines. The equation for the heavy diagonal line, which was drawn midway between the two dashed lines is:

$$\log t_B = \frac{\log W - 5.49}{-0.79} + \log l^2 \quad (6)$$

This equation predicts the breakthrough time within a factor of 3.4, 71 percent of the time.

Figure 8 is a similar plot showing volume rather than weight changes. With the same assumptions as detailed above, the solid line predicts 89 percent of the breakthrough times within a factor of 8.3:

$$\log t_B = \frac{\log V - 4.93}{-0.66} + \log l^2 \quad (7)$$

Where: V = percent volume change.

For all data except those for PVA with water collection, only 8 percent fall to the left of the lower dashed line. The equation analogous to Equation 5 for the weight change data and which, again, supplies a conservative estimate of the breakthrough time is:

$$\log t_B = \frac{\log V - 4.32}{-0.66} + \log l^2 \quad (8)$$

While predictions accurate to only factors of 3 or 8 are not good, they do provide starting points for screening garment materials on the basis of weight and volume changes. It is also true that Equations 6 and 7 were derived only from data for specific challenge liquids and materials and may well not hold for other combinations. Even if found to be generally applicable or, possibly, applicable to classes of challenge compounds, further testing should be performed before a given material is used with any specific hazardous challenge. With mixtures, the weight change caused by one component may overshadow that of another, more important, component. Thus, any correlation probably will not hold as well for mixtures as single component challenge liquids. Finally, as illustrated above with the Vitriole, predictive capability for composite materials will probably be poor. However, the calculated breakthrough time will probably be shorter than the actual time.

Summary

Of the four challenge liquids tested, only EPI showed breakthrough with all 11 materials. However, this was delayed for more than 8 hrs with butyl rubber. Teflon showed a relatively long breakthrough time (7 hrs). However, damage can be done to this material when it is flexed, as would probably happen when a glove is worn. To test for reuse, the butyl samples were air dried for 24 hrs and then another permeation test conducted. In these tests, breakthrough occurred in 5 min, but the subsequent steady-state rate was low, 1.3 mg/min/m².

With PCE, neither Viton or Viton SF (with either fresh or reused samples) nor Vitriole showed breakthrough at 23°C. Nitrile breakthrough occurred in 5 hrs.

All materials but PVA and Teflon were permeated by TCE. No breakthrough was noted with PVA in a reuse test or a test at 45°C. Because PVA reacts with water, such as that in the perspiration which could be present inside a glove, this material may not offer the protection indicated by the data. However, by using a water-impermeable liner it could provide excellent protection. At 23°C, Viton showed breakthrough in 10 hrs with fresh material and 5.5 hrs in a reuse test. At 45°C, breakthrough occurred in 48 min. Viton SF and Vitriole exhibited breakthrough in 4 and 8 hrs, respectively, at 23°C.

When challenged with DBE, PVA, Viton, Viton SF, and Vitriole exhibited no breakthrough in 24 hrs nor was any detected in reuse tests with PVA and Viton.

With the Saranex-laminated Tyvek the apparent steady state permeation rate of TCE increased as the flow through the cell increased. There is a need to determine whether this flow dependence is a common phenomenon and, if so, what flow will provide permeation results which most closely resemble those which would actually be encountered in the field.

It needs to be emphasized that the data in this report were obtained with specific garment materials. Permeation characteristics of materials from different manufacturers, and even from different batches from the same manufacturer, may differ. Therefore, the results can only be considered as indications of the permeation behavior of specific garment materials.

There appears to be a moderately good correlation between the weight and volume changes, which occurred when the garment materials were soaked in the challenge liquids, and the normalized breakthrough time, here defined as the breakthrough time divided by the square of the material thickness, t_B/l^2 . While weight and volume changes have been used in the past as indicators of permeation resistances, we have tried to put these tests on a more quantitative, generally applicable, basis. Certainly these correlations are semi-quantitative at best, there is no apparent theoretical justification for them, and they probably do not apply to all materials or challenge liquids. However, there may be sim-

ilar correlations which hold for compound classes or those with specific physical properties. We suggest that those with access to the appropriate data determine whether these or similar correlations apply.

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