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Permeation Through Five Commercially Available Glove Materials by Two Pentachlorophenol Formulations

J.B. SILKOWSKI[A], S.W. HORSTMAN[B] and M.S. MORGAN[B]
[A]U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010;
[B]Department of Environmental Health, University of Washington, Seattle, WA 98195

Five glove materials were tested for permeation by two commonly used formulations of pentachlorophenol (PCP). Permeation was conducted using the method used in two prior studies by NIOSH. The lower limit of PCP quantitation in the receiving side of the permeation cell was 70 parts per billion (ppb). When challenged with a 4.3% PCP in diesel oil solution, both the Dayton Flexible Products Triflex (PVC) and the Best 64 NFW (natural rubber) gloves exhibited breakthrough times thirty seconds after exposure. The Playtex #835 (latex/neoprene) glove exhibited breakthrough after sixty minutes, but showed a five fold greater rate of permeation than the Dayton and the Best glove. Neither the Edmont Sol-Vex (nitrile rubber) nor the Granet Glo-Gluv (PVC) gloves had been permeated after testing for 8 and 16 hours respectively. Following challenge with a 4.2% sodium pentachlorophenate solution, only the Best (natural rubber) glove allowed breakthrough; this only thirty seconds after exposure. Neither the Dayton (5 hours), Playtex (7.5 hours), Edmont (15.5 hours), nor Granet (15.5 hours) gloves had been permeated following completion of testing after the listed duration. This study has shown that different gloves offer differing resistance to permeation by PCP based upon the composition of the glove and the PCP formulation tested.

Introduction

In many industries, employees often come in contact with substances of varying physical and chemical properties. In most cases these workers are required by their employers to wear personal protective equipment of some sort. Gloves are the first line of protection in cases where manual contact with chemicals is necessary or where incidence of chemical splash is common. The gloves selected for use must first be proven to withstand the rigors of the job performed. In this case, strength, rigidity, and dexterity are the determining factors. Factors such as temperature, the gloves' composition, and the chemical used are all capable of influencing the degree of chemical resistance provided by the glove. The breakthrough time, or the length of time following initial contact of a chemical with a glove until that chemical is detected on the interior surface of the glove, is one measure in assessing the degree of chemical protection. The rate of permeation and the coefficient of diffusion are two other parameters which characterize the adequacy of chemical resistance of a glove material. The coefficient of diffusion, as a characteristic of permeability, has advantages over permeation rate. Diffusion coefficient, D, values allow judgements to be made about the permeability of a glove material regardless of the challenge concentration, thickness of glove material, or

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TABLE I
Permeation Data - 4.3% Pentachlorophenol in Diesel Oil

Material	Breakthrough[A] time (min)	Normalized Breakthrough time (min/mm^2)	m, Slope of Permeation Curve (μg/mL-min)	J, Permeation rate (μg/min-cm^2)	Diffusion Coefficient, D (cm^2/min)
Vinyl Exam glove unsupported 0.19 mm	0.5	13.850	0.0132 (r = 0.974)	0.259	1.162×10^{-7}
Natural rubber supported 1.64 mm	0.5	0.186	0.0011 (r = 0.631)	0.022	0.838×10^{-7}
Latex/neoprene flock lined 0.41 mm	60	356.930	0.0686 (r = 0.952)	1.345	12.699×10^{-7}
Nitrile rubber (NBR) unsupported 0.64 mm	>480	>1171.875	---	---	---
Polyvinyl chloride (PVC) supported 1.08 mm	>960	>823.045	---	---	---

[A]Breakthrough time - time at which receiving cell concentration was greater than 70 ng/mL.

area exposed. D, then, is dependent only upon the glove material and the solute used. The permeation rate, conversely, is dependent upon concentration, thickness, and D.

The coefficient of diffusion alone, however, is not a universal predictor of chemical resistance, for D is determined only after a steady-state permeation rate is reached. Exposure to permeated chemicals before steady-state has been achieved necessitates the measurement of another parameter, *i.e.* breakthrough time. The use of breakthrough, or first detectable amount permeated, has important applications where carcinogenic risk or rapid skin absorption are associated with the permeant. Where some contact with the permeant is permissible, the diffusion coefficient of the material can provide the best means of assessing the protection afforded.

Because of the widespread use of pentachlorophenol (PCP) as a wood preservative and in light of the fact that PCP and its metabolites have been found in the urine of wood treatment workers, this study was undertaken to assess the efficacy of protection provided by commonly used industrial gloves when exposed to two PCP solutions: sodium pentachlorophenate and pentachlorophenol in diesel oil.

Materials and Methods

A solution of 4.2% sodium pentachlorophenate in aqueous NaOH was prepared from a concentrated commercial mixture (Koppers Co.). Normal concentrations of sodium pentachlorophenate used in the wood preserving industry to prevent sapstain range from 0.1% to 0.5% in aqueous base.[1] The 4.2% vol. % pentachlorophenate solution was used to simulate a rare case of contact with high concentrations and to assure that analytical sensitivity could be reached in the permeation cell in a reasonable period of time.

Technical grade pentachlorophenol (86%) was diluted to 4.3% by volume PCP with diesel oil. This concentration is recommended for long term preservation of wood.[2] This concentration also mirrors that of the sodium pentachlorophenate used and as such provides a good means of comparison.

Glove materials selected for the study were: 1) natural rubber (Best Manufacturing Co., 64 NFW), 2) neoprene with latex (International Playtex, Inc., #835), 3) nitrile rubber (Edmont Division, Becton, Dickinson and Co., Sol-Vex 37-165, and 4) polyvinyl chloride (Inco Safety Products Co., Glo-Gluv #1012). Selection of these gloves was based on use and acceptance by employees in the local wood preserving industry. A vinyl (PVC) examination glove (Dayton Flexible Products, Triflex) was chosen because of its flexibility and its wide use in many laboratories.

A device for permeation testing similar to that previously reported was employed using distilled water as a collection medium.[3] Discrete samples (2 mL) were taken from the receiving cell at predetermined time intervals and extracted in 2 mL of toluene within 24 hours after being taken. Analysis was obtained using a Varian 3700 gas chromatograph with a fused silica (SE-54) capillary column and electron capture detector. Hydrogen was used as the carrier gas with a column flow of 40 mL/minute. Column temperature was programmed at 90 °C for one minute, ramp 8 °C/minute up to 300 °C for 5 minutes. Linear calibration and numerical integration was performed using a Spectra Physics 4100 integrator. Calibration standards were run at appropriate intervals. Lower limit of quantitation for PCP in the receiving cell was 70 ng/mL.

The concentrations of pentachlorophenol found in the aliquots taken from the receiving solution were corrected to account for the dilution effects of fresh distilled water which was added throughout the test to maintain the proper volume. The method for concentration has been previously reported.[4] Breakthrough was defined as the time at which the receiving cell concentration was greater than 70 ng/mL. Breakthrough times were normalized to account for thickness differences based on the breakthrough time per thickness squared (T_B/x^2) as previously illustrated.[5,6] Permeation rates were determined over the period of steady state flux by the equation:

$$J = \frac{mV}{A}$$

TABLE II
Permeation Data - 4.2% Sodium Pentachlorophenate in Aqueous Base (pH ≅ 11)

Material	Breakthrough[A] time (min)	Normalized Breakthrough time (min/mm^2)	m, Slope of Permeation Curve (μg/mL-min)	J, Permeation rate (μg/min-cm^2)	Diffusion Coefficient, D (cm^2/min)
Vinyl exam glove unsupported PVC 0.19 mm	>300	>8310.249	---	---	---
Natural rubber supported 1.64 mm	0.5	0.186	0.0011 (r = 0.873)	0.022	0.859×10^{-7}
Latex/neoprene flock lined 0.41 mm	>450	>2676.978	---	---	---
Nitrile rubber (NBR) unsupported 0.64 mm	>930	>2270.508	---	---	---
Polyvinyl chloride (PVC) supported 1.08 mm	>930	>797.325	---	---	---

[A]Breakthrough time - time at which receiving cell concentration was greater than 70 ng/mL.

where J = permeation rate, $\mu g/min\text{-}cm^2$
m = slope of concentration vs. time curve at steady state, $\mu g/mL\text{-}min$
V = volume of collection medium (distilled water), 100 mL
A = area of test material, 5.1 cm^2

In addition to permeation rate, the steady state coefficient of diffusion was also determined.[7] This parameter, like the normalized breakthrough time, provides information which eliminates the thickness variable and is concerned with the analytes' permeation rate as a unique property of the glove material.[3] The steady state diffusion coefficient was determined using:

$$D = \frac{Jx}{C}$$

where D = coefficient of diffusion, cm^2/min
J = steady state permeation rate, $\mu g/min\text{-}cm^2$
x = glove thickness, cm
C = permeant concentration in the challenge cell, $\mu g/mL$

Permeation tests for pentachlorophenol in diesel oil were run in triplicate to assess reproducibility. Sodium pentachlorophenate tests were run in duplicate due to time restraints.

Results and Discussion

Tables I and II show thickness, breakthrough times, normalized breakthrough times, slopes of permeation curves, permeation rates, and diffusion coefficients of the five gloves tested for permeation by pentachlorophenol in diesel oil and sodium pentachlorophenate respectively. Of the five gloves tested for permeation by 4.3% pentachlorophenol in diesel oil, only the vinyl (PVC) examination, natural rubber, and latex/neoprene gloves showed permeation before 8 hours had elapsed. (See Figures 1 through 3). The nitrile rubber (NBR) glove exhibited no permeation after 8 hours had elapsed nor did the Granet PVC glove, which was exposed for 16 hours without detection of PCP on the receiving side. Both the vinyl examination and the natural rubber gloves showed breakthrough at the time of the initial aliquot. The apparent breakthrough after only 30 seconds was a cause for

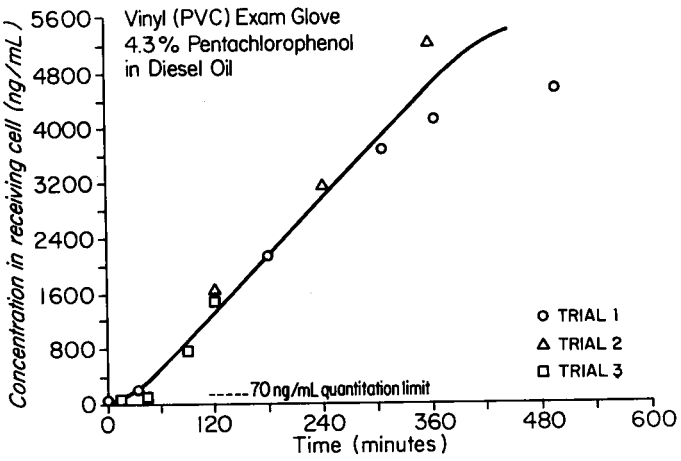

Figure 1 — Concentration of PCP in distilled water vs time (Pentachlorophenol/vinyl (PVC) examination glove).

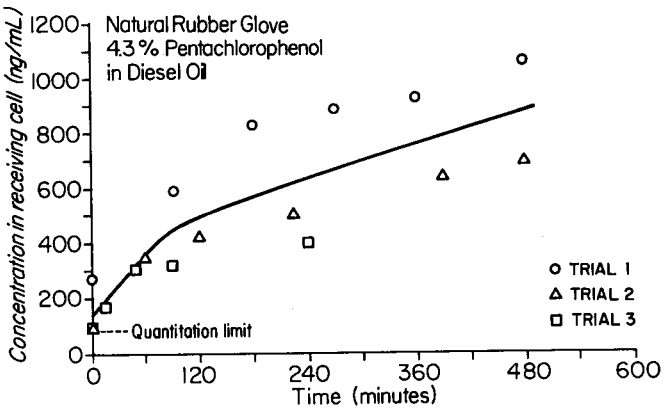

Figure 2 — Concentration of PCP in distilled water vs time (Pentachlorophenol/natural rubber glove).

skepticism; however, a review of the literature showed similarly rapid breakthroughs for other permeants while using much less sensitive analytical techniques.[3,4] The latex/neoprene glove did not exhibit permeation until 60 minutes following initial exposure to the challenge PCP.

It is interesting to note that while the breakthrough of the latex/neoprene glove occurred almost 1 hour after the vinyl and natural rubber gloves, the coefficient of diffusion of this glove was in excess of ten times greater than the diffusion coefficients of the other two. This exemplifies the importance of reporting both an initial breakthrough time and some rate parameter when conducting studies of this type.

When these same five glove materials were challenged with a 4.2% sodium pentachlorophenate solution, only the natural rubber glove exhibited any breakthrough or permeation. (See Figure 4). (It must be noted that the vinyl examination glove experiments were stopped after five hours due to time constraints. No breakthrough was observed up to that point.) That any glove would exhibit permeation with this solution was surprising considering the lipophilic nature of the glove and the hydrophilic characteristics of the phenate. It is hypothesized that some of the other components of the commercial phenate solution, *i.e.*, isopropanol, acetone, and ethylene glycol may facilitate pentachlorophenate diffusion across the membrane. Adding to this oddity is the fact that the calculated diffusion coefficients through the natural

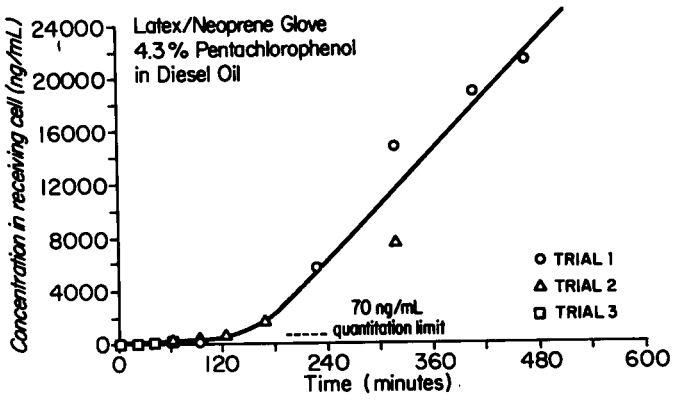

Figure 3 — Concentration of PCP in distilled water vs time (Pentachlorophenol/latex/neoprene glove).

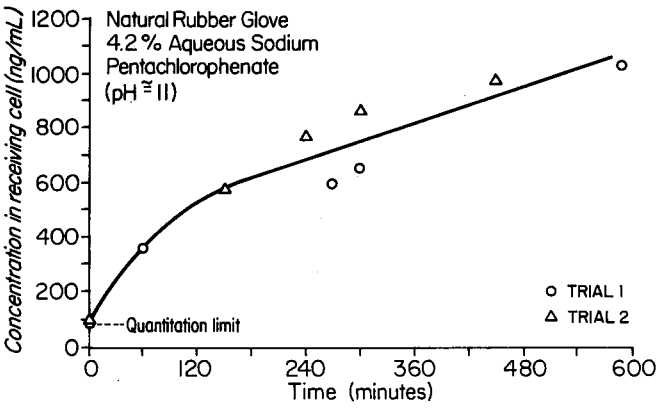

Figure 4 — Concentration of PCP in distilled water vs time (Sodium pentachlorophenate/natural rubber glove).

rubber were nearly identical for both the pentachlorophenol and the sodium pentachlorophenate. Since the solvents are so dissimilar and the data points showed considerable scatter, more experimentation is needed before this apparent similarity can be confirmed or explained.

The variability of the collected data throughout the experiment was rather wide, as evidenced by the r-values for the steady-state slopes, and contamination of the receiving cell was common. Mean analytical error for individual points on permeation curves (Figures 1 through 4) was 7% (range 2% to 15%). During the course of the experimentation, laboratory techniques were reevaluated constantly. Both the experimental setup and the ubiquitous nature of PCP in the water supply contributed to the overall variability.

The analytical techniques employed in this study are considerably more sensitive than in prior glove permeation tests. The use of the electron capture detector on the gas chromatograph permitted evaluation of the breakthrough and permeability two orders of magnitude below several previous studies which examined a variety of chemicals.[3,4,6,8,9] None of those studies tested PCP. This has allowed use of a fairly dilute PCP solution to determine permeability and still retain a reasonable sampling duration (approximately 8 hours). The use of dilute solutions is important because in very few instances do lumber handlers come in contact with the concentrated form of PCP. Rather these workers are exposed to the 5% and lower concentrations.

One might assume that the degree of protection afforded by the tested gloves to PCP could be extrapolated to other chlorophenols. Several studies, however, have shown that some chemically similar compounds can have widely different permeation characteristics.[3,8,9] Making assumptions about permeability based on chemically congeneric relationships is therefore advised against; however, in the absence of data for a particular chemical, it would be practical to assume that an homologous relationship exists.

Summary and Conclusions

This study has examined the relative protection provided by five commercially available gloves to two different commonly used formulations of pentachlorophenol. It was found that the nitrile rubber and PVC (Granet) gloves provide the best protection against either PCP formulation. The vinyl (PVC) examination glove, although tested for only five hours, showed good protection characteristics against the phenate solution. Adequate protection was also provided by the latex/neoprene glove when challenged with pentachlorophenate.

The sensitivity of the GC/EC analysis performed in this study has permitted observation of permeation characteristics at levels far below those previously reported. The use of sensitive analyses can permit investigation of permeabilities using fairly dilute formulations of permeants which approximate exposures commonly found in industry. Detection of permeants at extremely low levels also has application when the permeant is a carcinogen, in which the adequacy of a gloves' protection is assessed by breakthrough time. The use of GC/EC for this purpose is limited only by the permeants' EC detectability.

The study of glove permeation characteristics is still in its infancy. Methods of reporting data and of determining breakthrough times and permeabilities vary from study to study. This investigation has reported data as breakthrough time, normalized breakthrough time, steady-state permeation rate, and the diffusion coefficient. In the future, standard methods of reporting, such as those found in American Society for Testing and Materials Method F739-81,[10] should be followed so that meaningful comparisons can be made. The occupational health and safety specialist can then prescribe appropriate protective materials for use in specific chemical environments.

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