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Project Summary

A Method to Measure Protective Clothing Permeation Under Intermittent Chemical Contact Conditions

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A preliminary method was developed to measure chemical permeation of protective clothing under intermittent chemical contact conditions. The test presently used ASTM Method F739-85, measures permeation when the clothing material is in continuous contact with the chemical during the test, These ASTM results may overestimate the permeation resulting from intermittent chemical contacts typical in the manufacturing environment. The preliminary method summarized here was developed for the U.S. Environmental Protection Agency's Office of Toxic Substances (OTS). By using the method, OTS could assess the ability of protective clothing to reduce dermal exposure risks during the manufacture and use of new chemicals.

The proposed method involves repeated contact cycles of duration t_{cycle}: the chemical contacts the material for a short duration, denoted as t_{on}, the chemical is removed, and air sweeps the material surface for the remainder of the cycle. Tests were conducted using nitrile rubber/acetone, natural rubber/tetrachloroethylene, and various t_{on}/t_{cycle} ratios.

The results indicate that lower levels of chemical permeation would be measured using the proposed method than those using ASTM F739. The measured breakthrough times were comparable but the permeation rates were greatly reduced. Following detection of breakthrough, the permeation rates oscillate with a period equal to t_{cycle}. Although only a limited number of experiments were performed, the method appears to generate reproducible results that agree fairly well with mathematical model predictions derived from Fick's laws of diffusion. Further investigation of the applicability and limitations of the method is recommended.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Section 5 of the Toxic Substances Control Act (Public Law 94-469) requires prospective manufacturers to submit Premanufacture Notifications (PMNs). Approximately 2,500 PMNs are submitted annually. OTS must review these PMNs within 90 days of their submission before new chemicals are manufactured or imported. The primary objective of the review is to assess the potential risks to human health that could result from contacts during the manufacture, processing, and end use of the PMN substance. Many PMNs are not subjected to all aspects of the review process; those that are judged to pose health or environmental risks, however, require detailed assessments of the potential for releases and exposures. If sufficient concerns are raised to warrant regulation, engineering controls, work practice restrictions, or protective clothing and equipment are investigated as ways to reduce those risks.

Because the PMN submitter often recommends protective clothing as a way to minimize dermal exposures, OTS needs to be able to assess protective clothing performance; specifically its performance in limiting dermal exposures under realistic use conditions. One OTS option is to request that PMN submitters test the clothing materials and submit the resultant data. If testing is to be requested, however, OTS must then be able to specify relevant test methods and data reporting requirements.

At present, the recommended test method for measuring the permeation properties of protective clothing materials is ASTM Method F739-85. Because ASTM F739 specifies continuous chemical contact, however, exposure estimates based on these permeation data may overestimate actual exposures in the manufacturing environment. Often these contacts are infrequent and of short duration.

This study investigated the feasibility of developing a test method to measure permeation under chemical contact conditions thought to be more representative of actual workplace contacts. Several researchers have investigated methods to measure permeation under intermittent or "splash" conditions and each has defined the contact differently. Most of these studies focused only on the measurement of breakthrough times. In this study a preliminary method was evaluated for measuring breakthrough times, permeation rates, and cumulative permeation under conditions of intermittent chemical contact. The procedure involves repeated cycles of short-duration chemical contact. The approach was selected because it could be well controlled, would use the same apparatus as ASTM F739, should be broadly applicable and reproducible, and may be a realistic simulation of intermittent chemical contacts. Also, this controlled intermittent contact procedure can be modeled mathematically with the use of Fick's laws of diffusion.

Experimental Methods and Procedures

Materials

The experimental program was conducted using two combinations of chemicals and protective clothing materials. In the first combination, nitrile rubber was the clothing material and acetone the challenge chemical. This combination was selected because acetone readily permeates nitrile rubber under conditions of continuous chemical contact. In the second combination, natural rubber was the clothing material and tetrachloroethylene the chemical. This second combination was selected to explore the usefulness and reproducibility of the proposed method for a less volatile/more viscous chemical.

Analytical Methods

A Miran 80A Infrared Spectrophotometer (Foxboro Company, Foxboro, MA)* was employed to detect the concentration of the chemical in the collection medium. The spectrophotometer was calibrated prior to testing each day tests were run.

Permeation Test Procedures

Except for the modification to the chemical contact procedure, all permeation tests were conducted in accordance with ASTM Method F739-85. All tests were performed in the open-loop mode in which the collection medium, air, is continuously passed through the collection chamber of the test cell where it collects any permeant and carries it to the detector, from which it is exhausted. The collection air flow rate was set at 10 liters/min (Lpm) for the test duration.

The permeation tests were performed at 20°C and were continued until the permeation rates reached a steady state. Replicate tests were performed to investigate reproducibility. Permeation tests were conducted using the standard continuous contact procedure and several variations of the intermittent contact procedure for each chemical/material pair.

ASTM F739 Continuous Contact Tests – Permeation tests were performed using the ASTM F739 continuous contact procedure as the basis for comparison with the intermittent chemical contact results. The challenge chamber of the test cell was filled with the challenge chemical for the duration of the test.

Intermittent Chemical Contact Tests – The intermittent chemical contact procedure is defined as a cyclic process with each cycle having a duration equal to t_{cycle}. Each cycle began with an initial, full surface contact of the challenge chemical with the clothing material specimen for a short duration defined as t_{on}. At the end of t_{on}, the chemical was quickly drained (approximately 15 sec) from the challenge chamber of the test cell. The challenge chamber was then swept by a fresh air stream for a set period defined as t_{purge} to complete the contact cycle. The purge air flow was set at 2.5 Lpm.

t_{on} and t_{purge} define the contact cycle:

$$t_{cycle} = t_{on} + t_{purge} \qquad (1)$$

These cycles of short duration chemical contact/long duration air sweep were repeated for the duration of the permeation test. Three variations of chemical contact time and contact cycle time were studied:

- t_{on} = 1 min and t_{cycle} = 15 min,
- t_{on} = 5 min and t_{cycle} = 15 min, and
- t_{on} = 10 min and t_{cycle} = 60 min.

Results and Discussion

Experimental Results

The results for the series of continuous and intermittent contact tests are reported for nitrile rubber/acetone (Table 1) and for natural rubber/tetrachloroethylene (Table 2). The results are summarized in terms of breakthrough times, steady-state permeation rates, and the cumulative amounts permeated at 1 hr.

Under continuous chemical contact, permeation of the acetone through the

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1. *Continuous and Intermittent Contact Permeation Test Results for Acetone and Nitrile Rubber at 20°C*

Contact Condition	Ratio t_{on}/t_{cycle}	Thickness* (cm)	Breakthrough Time (min)	Steady-state Permeation Rate ($\mu g/cm^2$-min)	Cumulative Perm. at 1 hr ($\mu g/cm^2 \times 10^{-3}$)	Exp. No.
Continuous	1.0	0.056	18	1770	77.5	1
		0.054	16	1830	72.5	2
		0.053	16	1880	63.8	3
5 min/15 min	0.33	0.050	21	–†	23.0	6
		0.047	18	760	28.8	7
10 min/60 min	0.17	0.052	16	260	2.4	8
		0.052	18	250	2.5	9
1 min/15 min	0.07	0.046	43	280	1.5	4
		0.045	46	–†	1.2	5

*Nitrile rubber specimens were cut from commercially available gloves (Pioneer Stansolv A-14, 0.05 cm nominal thickness).
†Periodic oscillation in permeation rate did not reach a stable cycle.

Table 2. *Continuous and Intermittent Contact Permeation Test Results for Tetrachloroethylene and Natural Rubber at 20°C*

Contact Condition	Ratio t_{on}/t_{cycle}	Thickness* (cm)	Breakthrough Time (min)	Steady-state Permeation Rate ($\mu g/cm^2$-min)	Cumulative Perm. at 1 hr ($\mu g/cm^2 \times 10^{-3}$)	Exp. No.
Continuous	1.0	0.042	5.3	6170	370.7	10
		0.040	4.6	7400	304.9	11
5 min/15 min	0.33	0.043	4.9	–†	–†	14
		0.040	4.6	3750	175.0	15
1 min/15 min	0.07	0.042	9.0	1720	64.9	12
		0.040	6.0	1650	65.0	13

*Natural rubber specimens were cut from commercially available gloves (Edmont Fab-tek 26-668, 0.04 cm nominal thickness).
† Sample degraded after approximately 30 min.

nitrile rubber specimen was detected after an average of 17 min. An average steady-state permeation rate of 1,820 µg/cm²-min. In comparison, the intermittent contact tests demonstrate that the acetone permeation through the nitrile specimen is reduced relative to that for continuous contact. The reduction is mainly in permeation rates; breakthrough times generally remained unchanged. changed. Similarly for natural rubber/ tetrachloroethylene (Table 2), the permeation measured under intermittent contact conditions is reduced when compared with that measured under continuous contact conditions.

More specifically, the intermittent contact method produces a dramatic change in the permeation rate as a function of time. In all cases, a strong, periodic oscillation develops with a period equal to the cycle time, t_{cycle}. Eventually, a stable or steady cycling is reached (Figures 1 and 2). Note that this steady-state value, calculated as the integrated average value once the rates have reached a steady oscillation, appear to be reduced approximately by the ratio of (t_{on}/t_{cycle}) from that of the continuous contact case. This reduction was somewhat smaller for natural rubber/tetrachloroethylene and may be attributed to the lower vapor pressure of the tetrachloroethylene. Also note the good reproducibility between the replicate experiments.

Comparison with the Results of Other Investigators

The results generated in this study are consistent with the behavior measured by other researchers for related intermittent contact or splash tests. The other studies, however, focused on measurement of break-through times only.

Sansone and Jonas (1981) found that the breakthrough times measured for permeation of a chemical droplet were comparable to those measured for continuous liquid contact with the clothing material. Benzene and carbon tetrachloride permeation through several protective clothing elastomers were studied. In all cases, the droplet was free to evaporate as well as to permeate the clothing material. The authors reported that 70% to 90% of the deposited droplet evaporated and did not permeate the material.

Man *et al.* (1987) investigated a method involving cyclic contact: short duration liquid contacts followed by periods of continuous vapor contact. The procedure used the ASTM cell with a small volume of liquid chemical sealed in the challenge chamber; liquid splashes (achieved by tilting the cell so that the chemical/material contact occurred) were alternated with periods of vapor contact (during which the sealed cell was rotated so no liquid contacted the material surface). The authors studied the effect of varying the frequency of a 2-sec liquid splash on the breakthrough time and reported two modes of behavior for the chemicals tested. For chlorinated polyethylene, breakthrough times generally were longer as the frequency of the splashes was decreased. For a Viton/ nylon/chlorobutyl laminate, breakthrough times did not change with splash frequency and agreed with the results for the continuous contact method. They attributed these differ-ences to the wettability of material by the chemical.

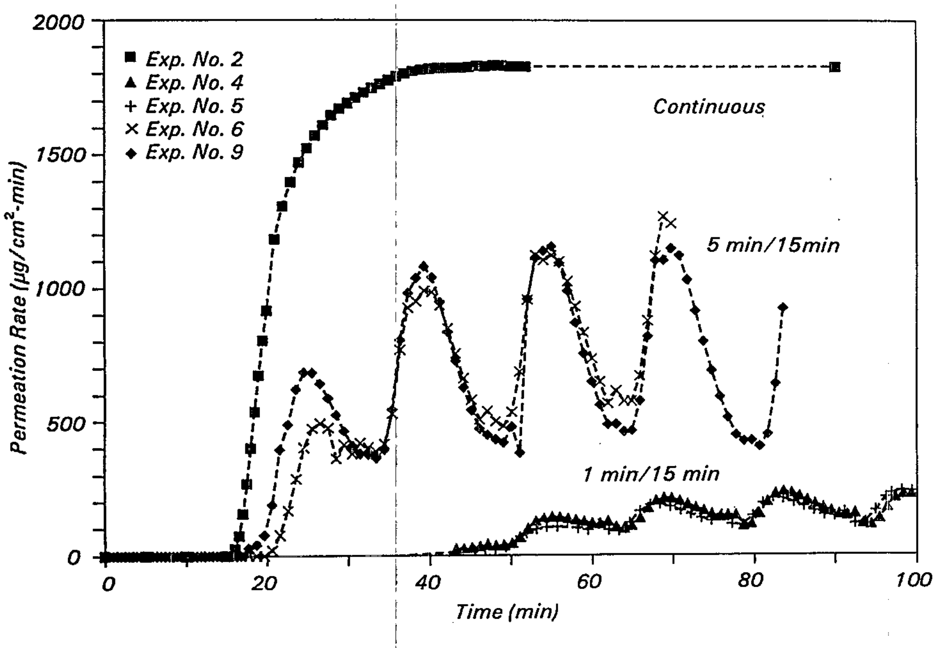

Figure 1. *Permeation of acetone through nitrile rubber at 20°C for continuous contact, 1 min/15 min intermittent contact cycle and 5 min/15 min intermittent contact cycle.*

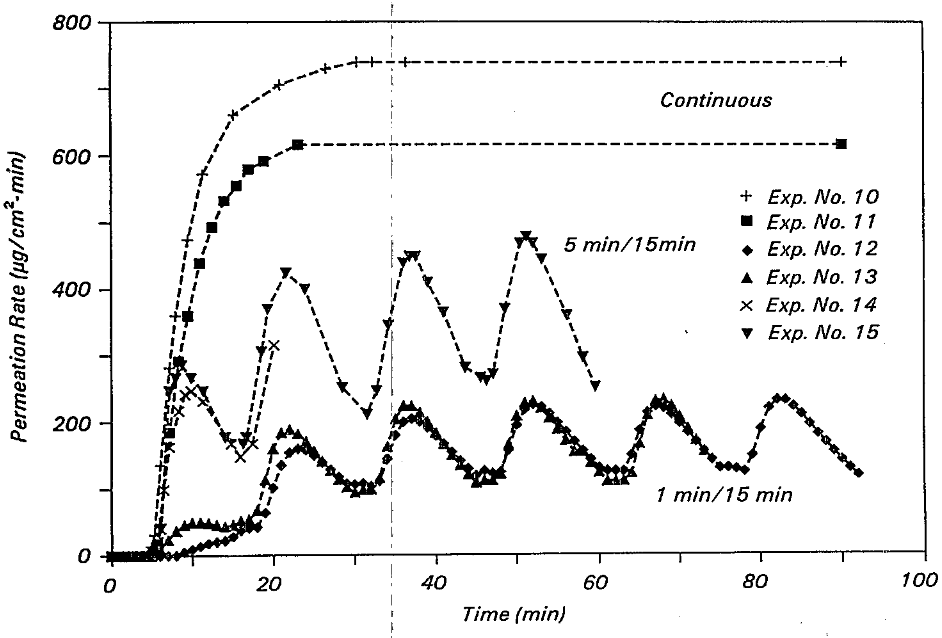

Figure 2. *Permeation of tetrachloroethylene through natural rubber at 20°C for continuous contact, 1 min/15 min intermittent contact cycle and 5 min/15 min intermittent contact cycle.*

For the nitrile/acetone and natural rubber/tetrachloroethylene systems studied here, the chemicals appeared to readily wet and be absorbed by the clothing materials; however, no direct measurements of wettability were made. Thus, the behavior observed by Man *et al.*, for the wetted chemical/material case, might also be expected in this study, i.e., essentially no variation in breakthrough time with contact frequency or duration.

Comparison with Mathematical Model Predictions

To aid interpreting and understanding the experimental results, a mathematical model of the intermittent contact scenario was developed. The model is based on Fick's law of diffusion–a mathematical relationship describing the diffusion of a species through a membrane for a specific set of boundary conditions. For this application, however, separate (but related) equations are required to describe the permeation behavior.

The intermittent contact permeation equations were derived from the general heat transfer solution of Carslaw and Jaeger (1973). The model assumes:

- A constant diffusion coefficient;
- No swelling of the membrane;
- No external mass transfer resistances; and
- That chemical contact begins instantaneously at the start of t_{on} and ends, also instantaneously at the end of t_{on} (defined also as the start of t_{purge}).

The Fick's law equations predict that:

- The permeation rates develop periodic oscillations with the period equal to t_{cycle}.
- Breakthrough times for the intermittent contact case will equal those measured for continuous chemical contact for the systems and t_{on}/t_{cycle} ratios studied here.

  (Note: Breakthrough time is defined as the time at which the permeation rate or cumulative permeation exceeds the lower detectable limit defined by the instrument sensitivity, collection medium flow rate, and surface area contacted. Differences in breakthrough time may be predicted for other systems, e.g., shorter t_{on} segments, less sensitive detection limits.)

- Eventually, the permeation rate-time curves will reach a steady or stable cycling with the same rates obtained at comparable fractions of a cycle. The number of cycles required to reach this stable oscillation period should be proportional to (L^2/Dt_{cycle}) where L is the material thickness and D, the diffusion coefficient.
- At this stable cycling state, the integrated average value of the permeation rate, P, during a contact cycle will vary as:

$$P = (t_{on}/t_{cycle})P_c$$

where P_c is the steady-state rate measured for continuous chemical contact.

In general, the test results are consistent with the model predictions given the simplifying assumptions that were used in developing the model. As reported in Tables 1 and 2, the breakthrough times are comparable with those for the continuous contact case. In one case, the 1 min/15 min intermittent contact for the nitrile/acetone, a significantly longer breakthrough time was measured. This result is not predicted by the model. One possible explanation is that some of the simplifying assumptions are not appropriate for very short duration intermittent contact scenarios.

The permeation rate results are also generally consistent with the model predictions. The periodic oscillations track fairly close with t_{cycle}, and the average permeation rates during the stable cycling period for the intermittent contact cases are reduced approximately by the ratio of t_{on}/t_{cycle}. The results for natural rubber/tetrachloroethylene are, however, reduced by a smaller ratio.

Conclusions and Recommendations

A test method was developed to measure protective clothing permeation under conditions of intermittent chemical contact that may simulate workplace contacts better than those of ASTM F739. The proposed method uses the ASTM F739 permeation cell and a straightforward modification to the ASTM F739 chemical contact procedure. The intermittent contact method could be incorporated as an optional procedure in that method. Breakthrough time, permeation rate, and cumulative permeation results from this feasibility study show good reproducibility; however, only two polymer/chemical combinations were tested, nitrile rubber/acetone and natural rubber/tetrachloroethylene.

Although the results of this preliminary study are promising, further evaluation is required to better define the reproducibility, applicability, and limitations of the proposed intermittent contact permeation test. We recommend additional testing be performed using chemical and polymer combinations that cover a range of physical properties (e.g., viscosity, volatility, and surface wetting) and permeation properties (e.g., short and long breakthrough times, high and low permeation rates). We recommend investigating a broader range of chemical contact times, t_{on}, and contact cycle times, t_{cycle}, to better understand the effect of these variables on the measured permeation data. This could be achieved by an inter-laboratory evaluation of the method coordinated through the ASTM.

In the long term, this procedure can be useful as a standard method for assessing protective clothing permeation under more realistic contact conditions. One goal should be to define a standard set of intermittent contact conditions as a baseline to compare results for various chemical and material combinations. This method is recommended as a possible way for OTS to improve their exposure assessment capabilities required for the thorough review of PMNs. The method could be specified by OTS in cases when permeation data are to be generated by the PMN submitter to demonstrate that the PMN substance can be safely handled using protective clothing. Specific intermittent contact conditions for testing could be recommended. The permeation rates or cumulative amount permeated should be reported as a function of time for the given t_{on} and t_{cycle} conditions. Also, OTS should require reporting of the breakthrough time, clothing material thickness and surface area, the analytical method sensitivity, the collection medium flow rate (open-loop systems) or volume (closed-loop systems), and temperature.

The mathematical model for the intermittent contact case could possibly be used by OTS to estimate the permeation that may occur during the handling of PMN substances. Although the model presently involves several simplifying assumptions, it is believed that the predicted results are representative and provide a satisfactory technique to estimate the effect of intermittent chemical contact as compared to continuous contacts.

The intermittent contact test method and mathematical model could also be applied to the study of protective clothing decontamination procedures. Modification of the method to include a surface washing/air drying step would enable one to study the effect of surface decontamination on residual chemical permeation during subsequent clothing use and chemical contact.

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***Esperanza P. Renard** is the EPA Project Officer (see below).*
The complete report, entitled, "A Method to Measure Protective Clothing Permeation Under Intermittent Chemical Contact Conditions," (Order No. PB 89-161 509/AS; Cost: $21.95, subject to change) will be available only from:
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