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Permeation of Chemical Protective Clothing by Three Binary Solvent Mixtures

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An evaluation of glove materials against three different binary chemical mixtures selected from common industrial solvents was conducted. Changes in breakthrough time and permeation rate of the mixture components were evaluated as a function of the mixture composition. An increase in employee risk resulting from early mixture breakthrough time and enhanced mixture permeation rate over that of the pure chemicals was demonstrated. The permeation of a binary mixture through chemical protective clothing could not be predicted by the permeation results of the pure components. It is recommended that chemical protective clothing be tested for its permeation characteristics with the use of the chemical mixtures and conditions that reflect the work site exposure.

Introduction

Chemical protective clothing (CPC) is used often as a first line of defense when engineering controls do not statisfactorily reduce the risk of dermal exposure to liquid chemicals. For many chemicals, occupational health guidelines state that exposed employees should be provided with and required to use impervious clothing.[1] This implies that impervious clothing exists and leads many people to a false sense of security when CPC is used.

CPC is not impervious to all chemicals. An increased awareness of the need to evaluate CPC prompted the formation of the American Society for Testing and Materials (ASTM) Committee F-23 on Protective Clothing. The ASTM committee has published a voluntary consensus standard test method, F739-81 for Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals.[2] Since publication, data obtained by using this method have appeared in technical journals[3] and in CPC manufacturers' product literature.[4,5] The major focus of this work has been to evaluate CPC against pure ACS reagent grade chemicals. In most industrial situations, however, workers wearing CPC are exposed to chemical mixtures.

A significant deviation in permeation of chemical mixtures over that of the pure chemicals has been noted in the literature. One study[6] suggests that the most rapidly permeating component of a mixture carries a more slowly permeating component through the CPC at a faster rate than if the slow component is tested in its pure form. The results of the same study also suggest that a mixture could have a collective mass permeation rate twice as fast as that of either of the unmixed components. In both cases, there is a greater risk for employee exposure to chemicals because of mixture permeation than if the components of the mixture are encountered in their pure form.

It is unclear from the literature whether the increase in risk resulting from enhanced permeation of mixtures over their pure components is a general rule, or if it is restricted to isolated cases. The objective of this study was to determine if the increased risk resulting from mixture permeation could be demonstrated by evaluating the performance of glove materials against three chemical mixtures.

Methods

Six solvents were selected based on their widespread industrial use and were paired to form three different binary combinations. The CPC material and chemical pair were chosen to simulate three scenarios: 1) A chemical with a long breakthrough time (>2 hr) and low permeation rate (<10 mg/m^2/sec) paired with a chemical of moderate breakthrough time (approximately 1 hr) and moderate permeation rate (approximately 100 mg/m^2/sec); 2) a chemical of long breakthrough time (>2 hr) and low permeation rate (<10 mg/m^2/sec) paired with a chemical of fast breakthrough time (<5 min) and high permeation rate (>1000 mg/m^2/sec); and 3) a chemical pair with similar and moder-

TABLE I
Detection Sensitivity for Breakthrough Time

Chemical	Minimum Detector Sensitivity (mg/m^3)	Minimum Permeation Needed For Detection (mg/m^2/sec)
n-Butyl acetate	17	0.28
n-Hexane	5	0.08
Methanol	17	0.28
Methyl ethyl ketone	10	0.16
Toluene	5	0.08
p-Xylene	7	0.12

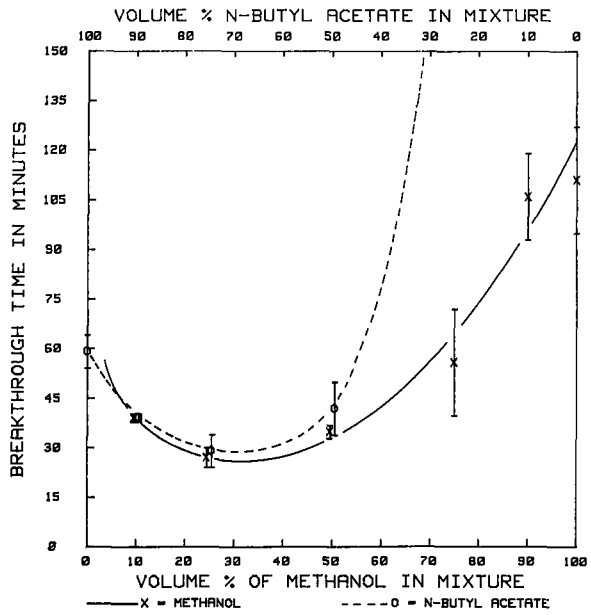

Figure 1 — For each component in the mixture, breakthrough time through 0.38 mm nitrile glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation with n=3. As the methanol concentration in the binary mixture increases along the abscissa, the n-butyl acetate concentration decreases. For mixtures of less than 50% n-butyl acetate, the n-butyl acetate component did not break through during the 6-hr test.

ate breakthrough time (approximately 1 hr) and permeation rate (approximately 100 mg/m^2/sec). For each chemical pair, a series of mixtures was generated to evaluate changes in breakthrough time and permeation rate through the CPC material as a result of changes in chemical composition. Each mixture was considered a treatment. Mixtures of methanol and n-butyl acetate and mixtures of toluene and p-xylene were used when evaluating specimens from nitrile-butyl rubber (nitrile) gloves, Scenarios 1 and 3, respectively. Viton® gloves were tested with mixtures of n-hexane and methyl ethyl ketone (MEK), Scenario 2.

The specimens were taken from the palm and back of finished gloves of the same lot for each material. The nitrile specimens were taken from Model 37-155, 0.38 mm (15 mil) nominal thickness, Edmont Becton Dickinson gloves; the Viton specimens were taken from Model F-091, 0.23 mm (9 mil) nominal thickness, Siebe Norton (North) gloves.

Each specimen was inspected visually for irregularities; thickness was measured (±0.01 mm) and assigned randomly to a treatment. Each specimen was mounted in an AMK[7] permeation cell. The AMK permeation cell has been demonstrated to be equivalent to the standard ASTM permeation cell.[8]

Materials, chemicals and equipment were room temperature, which varied only slightly (range from 20.0° to 24.5° C) over the duration of all the specimen test runs. Pure dry air, which was used as the collection medium, was preadjusted to a flow rate of 500 cc/min and hooked to the cell chamber to which the normal inside surface of the material specimen was exposed. The pure chemical components were measured by volume, mixed and then charged into the side of the cell, which exposed the outside surface of the material to a constant liquid chemical contact. At the instant the mixture was charged into the test cell, a timer was started. Carrier air, which passed through the collection half of the test cell, was diverted *via* a transfer pump through a gas sampling valve. The 0.5 mL sample loop of the gas sampling valve was purged continuously, and discrete samples were taken for analysis approximately every 3 min. Detector response values and elapsed time were recorded for each gas sample taken. The specimen test run was terminated after steady-state permeation was obtained or six hours had elapsed with no breakthrough, whichever came first.

Each sample was analyzed with the use of the Varian Vista 6000 gas chromatograph with flame ionization detector. The contaminants of the 0.5 mL air sample were separated on a 50 cm long, 0.32 cm outside diameter, 5% OV101 column before being analyzed. Standards were generated following each testing day. Static multilayered gas bags were used in producing the standards.[9] Bags were preconditioned and analyzed directly after they were generated. Standards were produced to encompass the test results. ACS reagent grade chemicals and pure dry air were used.

Triplicate tests were carried out in most instances. In two cases, only one test was conducted; *i.e.,* the 25% p-xylene, 75% toluene and the 75% p-xylene, 25% toluene mixtures.

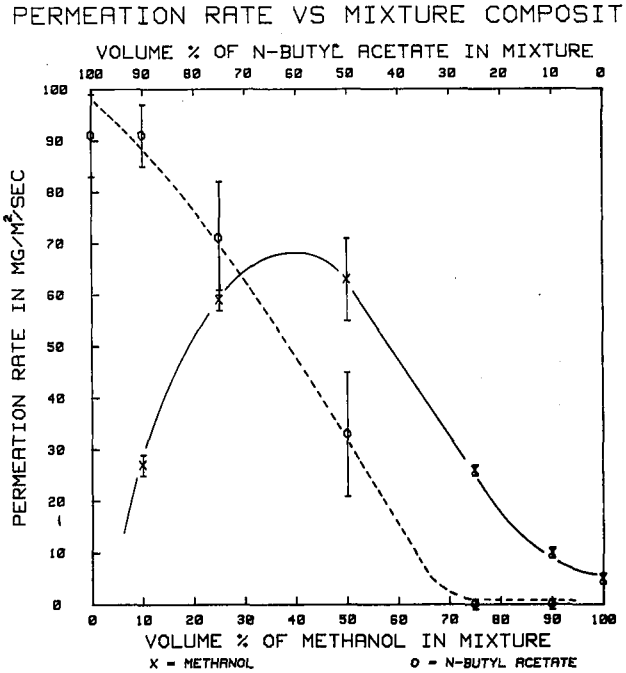

Figure 2 — For each component in the mixture, steady state permeation rate through 0.38 mm nitrile glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation with n=3. As the methanol concentration in the binary mixture increases along the abscissa, the n-butyl acetate concentration decreases. For mixtures of less than 50% n-butyl acetate, the n-butyl acetate permeation rate was below the detection limit.

Results and Discussion

For each glove material, the difference in specimen thickness between treatments was not significant (95% confidence, P=0.7). Mean thicknesses for the nitrile and Viton specimens were 0.36 and 0.26 mm, respectively.

The breakthrough time for each chemical component was recorded as the time of first detection of the component in the collection chamber. Table I lists the minimum detector sensitivity and the minimum permeation rate needed for determining breakthrough time for each chemical component.

The steady-state permeation rate, J, is calculated by[10]

$$J = C\,Q/A$$

where C is the concentration of the challenge chemical in the collection chamber, Q is the flow rate of collection air through the collection chamber, and A is the area of material available for permeation. For this study the flow rate, Q, was held constant at 8.33×10^{-6} m^3/sec (500 cc/min.) and the area, A, was 5.07×10^{-4} m^2.

Care must be exercised in interpreting these data. The data are limited by the duration of the test and the sensitivity of the detection system. A chemical which permeates a material at a low rate such that the lower detection limit is not reached in six hours will yield an experimental permeation rate that approaches zero and a breakthrough time that approaches infinity. The fact is that almost every chemical, given enough time, will permeate to some extent. In a practical sense, this 6-hr test gives a good indication of the protection that CPC will provide workers.

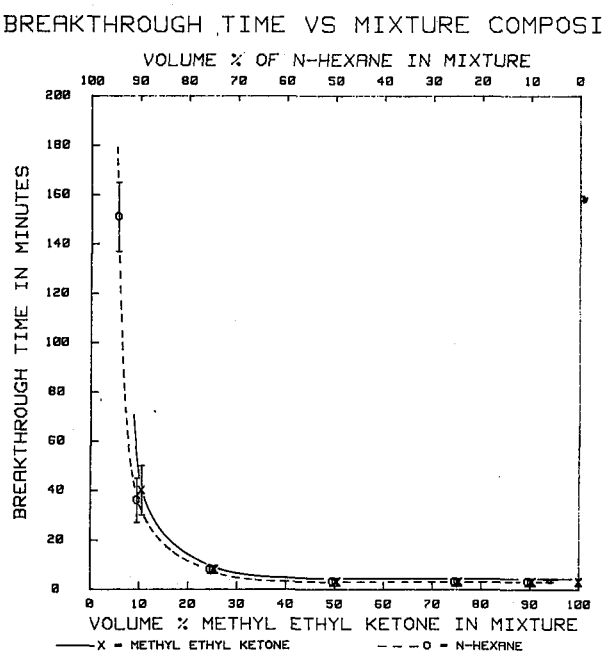

Figure 3 — For each component in the mixture, breakthrough time through 0.23 mm Viton glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation with n=3. As the MEK concentration in the binary mixture increases along the abscissa, the n-hexane concentration decreases. Pure n-hexane did not break through during the 6-hr test.

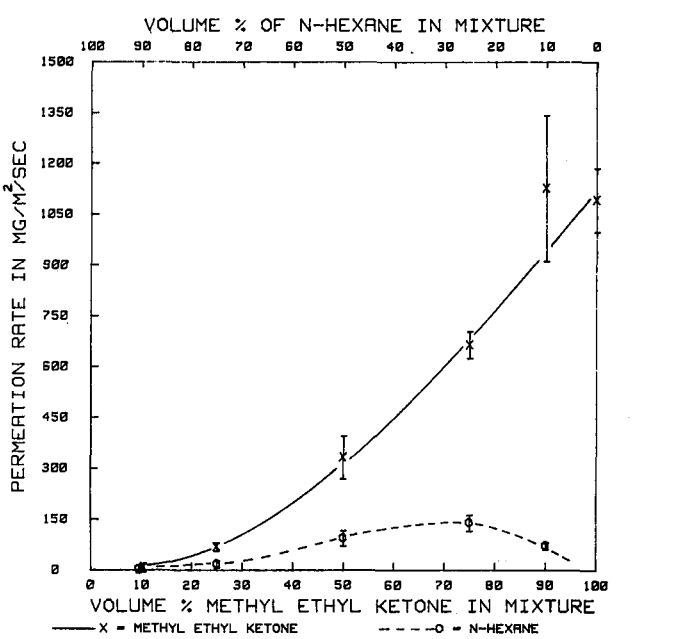

Figure 4 — For each component in the mixture, steady state permeation rate through 0.23 mm Viton glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation with n=3. As the MEK concentration in the binary mixture increases along the abscissa, the n-hexane concentration decreases.

Figures 1 and 2 are the plots of breakthrough time and permeation rate, respectively, through 0.38 mm nitrile glove material as a function of the volume percentage of methanol and n-butyl acetate in the mixture. Figures 3 and 4 are the plots of breakthrough time and permeation rate, respectively, through 0.23 mm Viton glove material as a function of the volume percentage of methyl ethyl ketone and n-hexane in the mixture. Figures 5 and 6 are the plots of breakthrough time and permeation rate, respectively, through 0.38 mm nitrile glove material as a function of the volume percentage of toluene and p-xylene in the mixture.

A smooth curve has been drawn through each set of data to help the reader visualize changes in the breakthrough time of each component of the mixture as a function of mixture composition. Time and analytical constraints did not permit the collection of data at the extremes. The mean response for each chemical composition tested is marked on the figures by a symbol with the bars representing one standard deviation.

As demonstrated in Figures 1 through 4, the permeation of CPC by mixtures may increase the potential chemical exposure of employees over that of the pure chemical components in three ways. First, it may decrease the breakthrough time for both components as seen in Figure 1. Pure n-butyl acetate had a mean breakthrough time of 59 min, and pure methanol broke through the nitrile specimens with a mean of 111 min. For mixtures of 75% n-butyl acetate and 25% methanol, however, the n-butyl acetate broke through in 29 min, significantly earlier than the breakthrough time for pure n-butyl acetate (95% confidence, t-test). The

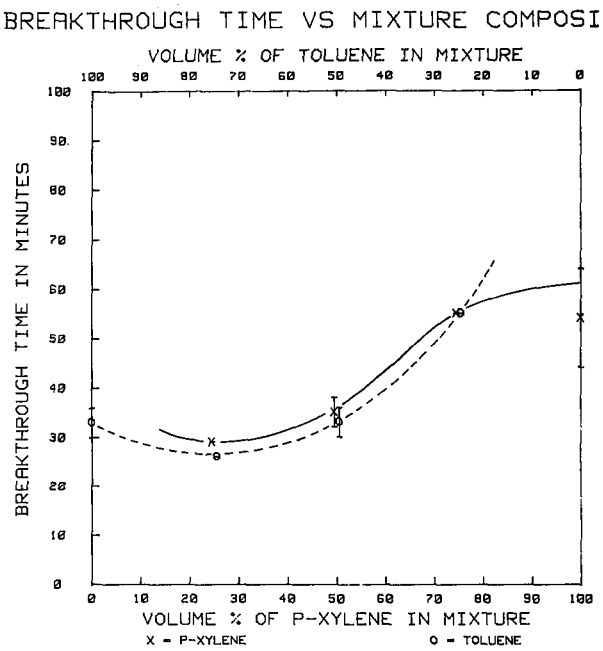

Figure 5 — For each component in the mixture, breakthrough time through 0.38 mm nitrile glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation. As the p-xylene concentration in the binary mixture increases along the abscissa, the toluene concentration decreases. No significant changes in the breakthrough time are noted as a function of mixture composition.

methanol broke through in 27 min, less than one-third of the time it took for the pure methanol to break through. This mixture of methanol and n-butyl acetate would increase significantly the potential to expose the employee as a result of faster breakthrough time. An early breakthrough time of the mixture would not be anticipated by looking at the pure component breakthrough times reported in the literature.

Second, the most rapidly penetrating component may function as a carrier for the more slowly penetrating substance. For each mixture of n-hexane and methyl ethyl ketone (MEK), the n-hexane permeated the Viton specimens along with the MEK, but pure n-hexane did not permeate during the 6-hr test (see Figures 3 and 4). An additional test was conducted exposing Viton to pure n-hexane over a 10-day period in which no chemical breakthrough was detected. The breakthrough time for n-hexane in the 90% n-hexane and 10% MEK mixture was at least 400 times faster than the pure n-hexane breakthrough time. Therefore, a chemical that does not permeate in its pure form but is transported through the CPC by another component in a mixture may pose a significant increase in risk of employee exposure to hazardous chemicals. This effect may be unexpected when looking at the pure component permeation responses.

Third, the collective permeation rate may be higher than either pure component permeation rate. Obtained by adding both permeation rate curves shown in Figure 2, the collective permeation rate for the 25% methanol and 75% n-butyl acetate mixture had a significant increase (95% confidence, t-test) of 1.4 times the rate of pure n-butyl acetate and over 20 times that of the pure methanol. These data show an increase in potential exposure due to higher collective permeation rates of this mixture composition and would not be anticipated by looking at the pure component permeation rates.

As demonstrated in Figures 5 through 6, the breakthrough times of toluene and p-xylene mixtures did not differ significantly from the pure component responses. The steady state permeation rates of the components in each mixture did not differ significantly from the expected values. Toluene and p-xylene are so similar chemically that these findings might have been anticipated.

Conclusions

An increase in employee risk as a result of early breakthrough time and enhanced mixture permeation rate over that of the pure chemical permeation was demonstrated by evaluating glove materials when chemical mixtures selected from common industrial solvents were used.

The permeation of CPC by binary mixtures may increase the potential chemical exposure of employees over that of the pure chemical components in three ways: 1) it may decrease the breakthrough time of the components; 2) a component that does not permeate in its pure form may be transported through the CPC by another component in the mixture; and 3) the collective permeation rate for the mixture may be higher than either pure component permeation rate.

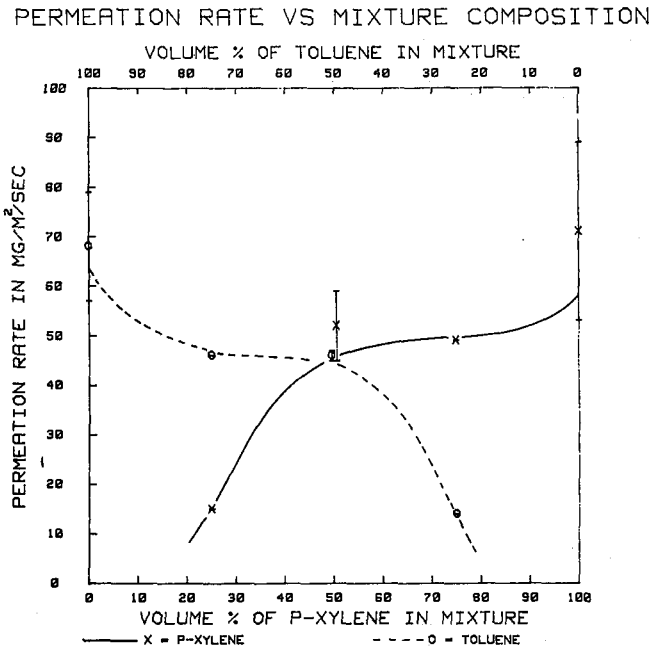

Figure 6 — For each component in the mixture, steady state permeation rate through 0.38 mm nitrile glove material is plotted against mixture composition. The bars on each symbol represent one standard deviation. As the p-xylene concentration in the binary mixture increases along the abscissa, the toluene concentration decreases. No significant changes in the permeation rate are noted as a function of mixture composition.

Since the permeation of binary mixtures through chemical protective clothing cannot be predicted by the permeation results of the pure components, it is recommended that chemical protective clothing be tested for its permeation characteristics with the use of the chemical mixture concentrations and conditions that reflect the work site exposure.

Future studies are needed to determine the mechanism of enhanced permeation of chemical protective clothing by chemical mixtures. Solubility parameter theory[11] is being considered as a way to predict permeation characteristics and will be used to analyze these data further.

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