

# Transport of a Solvent Mixture Across Two Glove Materials When Applied in a Paint Matrix

Jackelin Q. Tran · Diana M. Ceballos ·  
Russell L. Dills · Michael G. Yost · Michael S. Morgan

Received: 1 September 2011 / Accepted: 27 February 2012 / Published online: 21 March 2012  
© Springer Science+Business Media, LLC 2012

**Abstract** The transport of mixed paint solvents through natural rubber latex (4 mil) and nitrile rubber (5 mil) gloves was evaluated after spray application of the paint formulation directly on the glove surface. Glove materials and thicknesses were those selected by the majority of spray painters in the local automobile repair industry. A flat panel containing glove specimens mounted in multiple permeation cells permitted evaporation of solvents from the applied paint and incorporated a solid sorbent receiving medium for measuring glove membrane transport. The panel was sprayed in a paint booth to simulate use conditions. Charcoal cloth under the glove adsorbed transported solvents, which were quantified by gas chromatography. For each solvent component, results were expressed as mass transported through the glove relative to the mass applied, per unit area, during 30 min after spray application. The paint formulation contained ketones, acetates, and aromatics. Natural rubber latex allowed 6–10 times the transport of solvents relative to nitrile rubber for all eight solvent components: methyl ethyl ketone, toluene, styrene,

ethyl benzene, xylene isomers, and 2-heptanone. *m*-Xylene showed the largest difference in transport between the two glove materials. This solvent also had the highest transport for each material. The results indicate that nitrile rubber gloves offer somewhat greater chemical resistance to all eight solvents studied compared with natural rubber latex gloves, regardless of the chemical properties of the individual solvent components. However, it must be emphasized that neither of the glove materials, in the thicknesses used in this study, provide adequate protection when exposed by direct spray painting. Simulation of realistic spray conditions may offer a source of useful information on the performance of chemical protective gloves because it accounts for solvent evaporation and the effect of paint polymerization after application on glove transport.

Gloves are a primary form of personal protective equipment used in automobile-body painting to help control exposure to hazardous materials, including organic solvents. Solvents used in automobile paints may induce major health concerns because exposure can lead to effects on the central nervous system and may cause respiratory diseases and dermal irritation (Wang and Chen 1993; Berardinelli 1988). The tasks of concern for exposure to solvents are paint mixing and spraying because they present an opportunity for dermal exposure. Furthermore, many paint solvents have been identified as likely to permeate unprotected skin (National Institute for Occupational Safety and Health 2005). Although the majority of painters wear respiratory protection while spray-painting, they do not necessarily wear appropriate gloves to protect their skin. Whittaker and Whitaker (2009), of the Washington State Department of Labor and Industries, reported that although painters in 85 % of shops ( $n = 42$ ) wore gloves

---

J. Q. Tran · D. M. Ceballos · R. L. Dills ·  
M. G. Yost · M. S. Morgan  
Department of Environmental and Occupational Health  
Sciences, University of Washington, Seattle, WA 98195-7234,  
USA

*Present Address:*  
D. M. Ceballos  
Division of Surveillance, Hazard Evaluation and Field Studies,  
National Institute for Occupational Safety and Health,  
Cincinnati, OH 45213, USA

M. S. Morgan (✉)  
F-225B Health Sciences, P.O. Box 357234, Seattle,  
WA 98195-7234, USA  
e-mail: mmorgan@uw.edu

while spraying two-part clear coats, of these 51 % used natural rubber latex gloves and approximately 40 % used nitrile rubber gloves.

Glove manufacturing companies offer chemical compatibility charts using published laboratory data for pure chemical components (Ammex Corporation 2011; Microflex Corporation 2011; Kimberly Clark Professional 2011). However, solvents that are widely used in automobile painting are multicomponent. Several researchers have demonstrated that contact with binary mixtures of solvents led to enhanced permeation of one or both components relative to pure solvent (Mickelsen et al. 1986; Chao et al. 2008; Forsberg and Faniadis 1986). Chao et al. (2008) found, for example, that the more slowly permeating component of a mixture broke through nitrile rubber gloves earlier than its pure form. These investigators recommended that protective clothing permeation studies be performed using mixtures that reflect actual application conditions. In addition, glove chemical compatibility charts are based on breakthrough time and degradation of the glove material, which may not be reliable indicators of glove performance because they do not consider mixed solvent effects and assume that gloves provide absolute protection up to breakthrough (Mickelsen et al. 1986; Cherrie et al. 2004; Klingner and Boeniger 2002; Gunderson et al. 1989).

When selecting appropriate chemical protective gloves for a specific task, there are many factors to consider, such as cost, efficacy, productivity, dexterity, user comfort, durability, physicochemical properties of the agents involved, and toxicity (Klingner and Boeniger 2002). The most important factor to consider in the selection process, however, is the chemical barrier property of the glove material. The scope of this study encompasses the use of multiple solvents and a system to evaluate glove performance under conditions that simulate automobile painting.

A clear-coat paint formulation was selected for study because it contains the highest percentage of isocyanates compared with other paint formulations, such as basecoats and primer coats. The formulation chosen contained both hexamethylene diisocyanate and isophorone diisocyanate to further our knowledge about how well these gloves can resist permeation by the complex solvent mixture in the presence of isocyanates. Permeation of the isocyanate components of this formulation has been reported by Ceballos et al. (2011a), and results for the solvent components are described here. The cumulative mass collected on the inner surface of the glove material per unit area during 30 min was used as the measure of transport.

Solvent functional groups are known to affect glove integrity differentially; those most detrimental are the most important to study. Therefore, a clear-coat formulation with solvents containing ketone and aromatic groups,

which are known to affect the integrity of certain glove materials (Chao et al. 2008), was selected for this study.

Most previous studies have used American Society for Testing and Materials (ASTM) standard method F739 (American Society for Testing and Materials 1999) for testing permeation. This method uses a test cell together with a collection medium that is either flowing water or inert gas. Because some components of the mixture studied here were of limited water-solubility and of relatively low volatility, and because the goal of this study was to examine permeation under realistic painting conditions, a modified system was used to measure component transport. A solid sorbent collection medium was placed in contact with the inner surface of the glove, as described by Ehntholt et al. (1990) and De Kee et al. (2005), in a test cell that permitted direct exposure to sprayed paint. The test cells were incorporated in a permeation test panel designed and characterized by Ceballos et al. (2011a). The permeation panel consists of eight surface-mounted permeation cells that allow paint to be sprayed directly on the glove material. This approach simulates actual spray-painting conditions, including the ongoing effect of solvent evaporation during paint application and the effects of polymerization and cross-linking of the paint resin on solvent migration. Gloves sprayed directly also represent the most intense exposure.

Activated charcoal cloth was chosen as an adsorbent material to detect transport through glove material based on previous work by Perkins and Vescial (1997), who showed its potential for field monitoring of the efficacy of chemical protective clothing. Those investigators demonstrated the effectiveness of charcoal cloth material as a field monitor for heptane after permeation through polyvinylchloride gloves.

## Materials and Methods

### Chemicals and Glove Samples

Chemicals were obtained from Aldrich (Milwaukee, WI). A common automobile body paint commercial product—a clear-coat composed of high-solids polyurethane film former, catalyst hardener, and reducer—was used in this study. The solvents in each paint system component (Table 1) were analyzed by gas chromatography (Model 6890; Agilent, Wilmington, DE) with flame ionization detection. Bulk samples of the paint system components were diluted in carbon disulfide (low-benzene grade; Aldrich) before analysis. All solvents were separated on a 60-m DB-wax column (Agilent). The principal solvent components (Table 1) were methyl ethyl ketone (MEK); toluene; ethyl benzene; *o*-, *m*-, *p*-xylene; and 2-heptanone,

and trace amounts of styrene. Paint components were mixed in a ratio of four parts by mass high-solids polyurethane, one part hardener, and one part reducer before spraying panels during the experiments. These ratios were recommended by the manufacturer.

Powder-free natural rubber gloves (Gloveworks Industrial Latex) and nitrile rubber gloves (Xtreme Nitrile Industrial) were obtained from a local distributor (Ammex, Tukwila, WA). The samples were cut from the palm section of each glove. The thickness of glove samples was determined using a dial micrometer (Baker; American Printing Equipment and Supply, Elmont, NY). The average thickness of the glove samples was  $0.108 \pm 0.001$  (SD) mm for latex gloves and  $0.128 \pm 0.001$  mm for nitrile gloves. These materials were selected based on the findings of Ceballos et al. (2011b), who surveyed collision repair operations in Washington state and reported that 81 % of painters used one of these two materials. Thin gloves (0.05- to 0.13-mm thickness) were selected by the majority of users. Although neither thin natural rubber nor thin nitrile rubber are recommended in glove selection guides for this application (NIOSH 1998), their prevalence in the

automobile repair industry led to their use in this study. Glove samples showed no visible sign of pinholes or other defects, but they were not evaluated for penetration by hydrostatic testing.

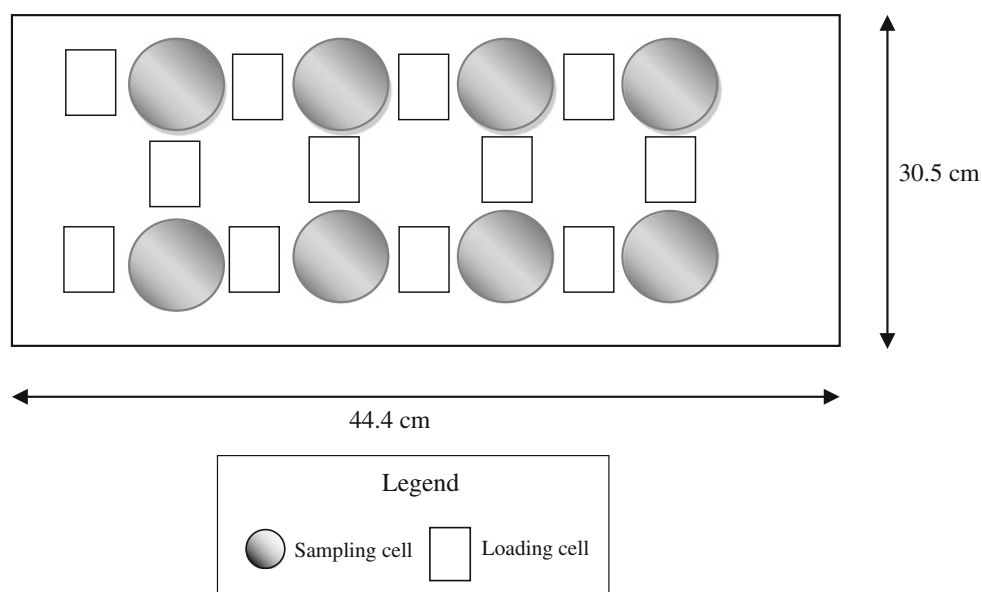
### Transport Experiments

Experiments were conducted at a painting-training facility to assess the solvent permeability of disposable gloves using a previously described version of a permeation cell ganged to form a permeation panel, which is shown schematically in Fig. 1. Briefly, permeation cells were assembled with glove material underlain by charcoal cloth disks held in place by the glass base window of the permeation cell (Fig. 2). O-ring seals insured that the base and body were leak-free. The charcoal cloth disks were in direct contact with the inner surface of the glove. In addition to the eight permeation cells, the surface of the panel contained eight preweighed polytetrafluoroethylene (PTFE) filters (Zefluor [47-mm diameter, 0.45- $\mu$ m pore size]; Pall, Port Washington, NY). Rectangular aluminum foil filter masks ( $7.62 \times 5.08$  cm) with a center hole (2.54-cm diameter)

**Table 1** Solvent composition of products (% by mass)

Component (mass ratio in mixture)	Methyl ethyl ketone	Toluene	Styrene	Ethyl benzene	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	2-Heptanone	Total solvent in component
Clear resin (4/6)	0.03	0.10	0.20	5.95	5.75	13.5	6.05	13.5	45.1
Reducer (1/6)	31.5	21	<0.01	0.01	0.02	0.04	0.02	<0.01	52.6
Hardener (1/6)	<0.01	<0.01	<0.01	<0.01	<0.01	6.77	<0.01	17	23.8
Mixture	5.27	3.57	0.10	3.97	3.84	9.01	4.04	11.8	41.6

**Fig. 1** Experimental layout of permeation panel



secured the PTFE filters to the surface of the panel with the exposed filter area matching that of the charcoal cloth disks. The change in weight of these filters after painting allowed determination of the loading of sprayed material per unit area and homogeneity of loading.

Permeation panel tests were conducted during 3 days in a temperature-controlled ( $21 \pm 1^\circ\text{C}$ ) painting booth. Each panel of eight glove samples (four each of latex and nitrile) was sprayed with the mixed formulation of clear coat. The panel was sprayed twice, with an approximately 7-min pause between spraying. The panel was oriented horizontally and sprayed with horizontal movements of the spray gun (parallel to the panel long axis), two spray passes for

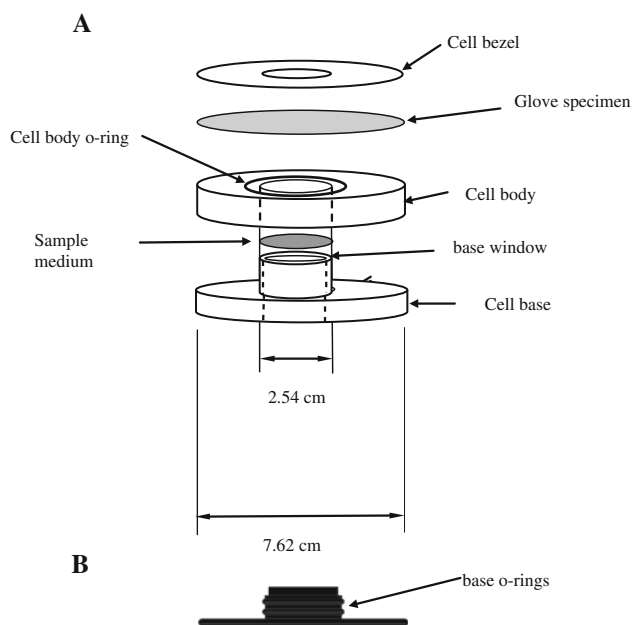
each row (three rows per panel) for a total of six passes per panel.

Applied paint-thickness measurements were made using a metal wafer attached to the panel in the space between a test cell and loading cell with half of the wafer surface masked. The thickness of the clear-coat layer was then measured (by difference) with a micrometer at several locations on the wafer without and with clear-coat after it dried.

Thirty minutes after the completion of spray application, the exposed charcoal cloth disks and PTFE filters were removed and stored individually in sealed glass vials at  $-25^\circ\text{C}$  until they were analyzed using the NIOSH 1501 method. Each disk was placed in an 8-mL glass vial; 2 mL of carbon disulfide containing internal standard (*n*-propylbenzene) were added; and the vial was closed with a Teflon-lined cap. After gentle agitation for 30 min, the liquid was transferred to an autosampler vial and analyzed by gas chromatography using flame ionization detection. Quality control included analysis of a blank cloth disk for each day of sampling and three spiked cloth disks with each batch of samples submitted. The estimated lower limit of detection for each solvent by the NIOSH method was  $1.0\ \mu\text{g}$ .

#### Preparation of Charcoal Cloth Disks

Charcoal cloth (Calgon; Pittsburgh, PA) was cut using a 2.54-cm diameter die. Disks were heated in a stainless steel tube at  $260^\circ\text{C}$  for 120 min under continuous flow of nitrogen. After this cleaning process, which rid the cloth of volatile organic compounds, the charcoal cloth disks were sealed in a glass vial with septum cap. This process decreased blank contamination to  $<1\ \mu\text{g}/\text{sample}$  for each compound (Table 2 [matrix blank<sup>b</sup>]). A less effective method was used for the first permeation panel exposure. Charcoal cloth disks were baked in a vacuum oven at



**Fig. 2** Permeation cell configuration. **a** Exploded view. **b** Edge view of cell base, showing o-rings

**Table 2** Data on solvents found in product components

Solvent	Solubility in water (g/L at $20^\circ\text{C}$ to $25^\circ\text{C}$ )	Vapor pressure (mmHg at $20^\circ\text{C}$ )	Boiling point ( $^\circ\text{C}$ )	Matrix blank <sup>a</sup> ( $\mu\text{g}$ )	Matrix blank <sup>b</sup> ( $\mu\text{g}$ )	Desorption efficiency <sup>c</sup> (%)
MEK	136	91	79.6	$<4$	$<1.0$	$77 \pm 15$ (12)
Toluene	0.535	21	111	14 (10)	$<1.0$	$84 \pm 15$ (6)
Ethyl benzene	0.160	7	136	$<1$	$<1.0$	$103 \pm 8$ (10)
<i>p</i> -Xylene	0.162	9	138	$<2$	$<1.0$	$103 \pm 14$ (10)
<i>m</i> -Xylene	0.162	9	139	$<2$	$<1.0$	$105 \pm 14$ (8)
<i>o</i> -Xylene	0.178	7	144	$<1$	$<1.0$	$101 \pm 8$ (10)
Styrene	0.30	5	145	$<4$	$<1.0$	$89 \pm 12$ (12)
2-Heptanone	4.30	3	151	$<2$	$<1.0$	$83 \pm 20$ (6)

<sup>a</sup> Vacuum bake ( $150^\circ\text{C}$ ) cleaning process; mean (SD);  $n = 9$

<sup>b</sup> Nitrogen purge ( $260^\circ\text{C}$ ) cleaning process;  $n = 5$

<sup>c</sup> Mean  $\pm$  SD ( $n$ ) from spiking with liquid mixtures

**Table 3** Paint loading thickness and uniformity of paint loading mass on PTFE filters

Day	Panel	Paint thickness (mm)	Net mass <sup>a</sup> (mg)	Top row <sup>b</sup> (mg)	Bottom row <sup>c</sup> (mg)
1	I	0.05	43.6 (7.8)	50.3 (4.4)	34.2 (2.7)
	II	0.03	46.1 (9.4)	53.5 (5.9)	35.3 (3.6)
2	I	0.05	44.9 (8.5)	51.8 (6.8)	35.4 (2.6)
	II	0.06	44.6 (7.0)	43.8 (1.5)	37.4 (4.0)
3	I	0.07	47.9 (9.7)	52.1 (5.2)	36.1 (2.0)
	II	0.07	39.0 (4.0)	40.4 (3.0)	34.4 (1.9)

<sup>a</sup> Mean (SD) of total filters ( $n = 12$ )<sup>b</sup> Mean (SD) for filters (top section) sprayed horizontally ( $n = 4$ )<sup>c</sup> Mean (SD) for filters (bottom section) sprayed horizontally ( $n = 4$ )

150 °C for 48 h. For this first panel exposure, the sample results were corrected for the background in the matrix blanks (Table 2 [matrix blank<sup>a</sup>]).

### Desorption Efficiency

Desorption efficiency was determined by spiking two disks with liquid containing 8 µg of each analyte and one disk with 20 µg of each analyte. Desorption efficiency, expressed as percent, was calculated by taking the mass recovered from spiked charcoal cloth divided by the mass spiked. The average desorption efficiency ranged from 77 to 105 % (Table 3); high cloth-disk blank values prevented desorption efficiency determination for many compounds at low spike levels when the lower-temperature vacuum oven-cleaning process was used. No differences were observed between desorption efficiency at high and low spiking levels. All sample results were corrected for desorption efficiency.

Comparison of transport values between the two glove materials, and among the paint-loading measurements for test of uniformity, were performed using Kruskal–Wallis rank sum test. This was used to avoid the assumption of normality in the underlying populations from which each sample was drawn.

### Results and Discussion

The appearance of the solvent components on the charcoal cloth could have occurred by way of a combination of (1) penetration, i.e., bulk flow through microscopic or macroscopic voids in the membrane, and (2) permeation, i.e., molecular diffusion through the membrane after solvent partitioning between the paint matrix and the membrane (Schwope et al. 1988). Because the experimental method

used in this study could not distinguish between these mechanisms, the results are described here as “transport” rather than permeation or penetration.

Transport was expressed as the mass found on the charcoal cloth per unit area over 30 min and as the percent of the mass of solvent applied to the exterior of the glove. The percent mass transport for each solvent was calculated as follows (Eqs. 1 through 3, respectively):

$$\begin{aligned} &\text{Amount of wet paint sprayed on the glove sample (X)} \\ &= \text{average dry weight on PTFE filter/average fraction} \\ &\quad \text{of solids in paint mixture} \end{aligned} \quad (1)$$

$$\begin{aligned} &\text{Amount of solvent loaded on the glove sample (Y)} \\ &= X \cdot \text{weight fraction of solvent in paint mixture} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Transport (\%)} &= 100 \\ &\quad \cdot (\text{mass of solvent on charcoal cloth/Y}) \end{aligned} \quad (3)$$

The average dry weight on PTFE filters was taken from the average of the filters laterally adjacent to the glove sample, consistent with the spray motion used by the painter.

Because the thickness of the gloves differed, results for nitrile rubber were adjusted to the thickness of the natural rubber gloves. Because steady-state diffusion through a polymer membrane is expected to depend inversely on membrane thickness (Schwope et al. 1988), the percent transport for nitrile rubber was multiplied by the ratio of nitrile rubber thickness to natural rubber thickness to make the transport values more comparable. This adjustment must be considered approximate because the experimental conditions did not permit evaluation of the approach to steady state, and transport by penetration could not be ruled out.

The painting instructor advised that a minimum paint thickness of 0.05 mm is desired in a clear-coat. The paint thickness in these experiments met that requirement (Table 3). Homogeneity of the spray application was assessed using the weight gain for the dry filters and measuring the thickness of the paint sprayed onto the filters. More paint was loaded onto the glove surface in the top half of the panel on the first day of sampling: There was  $6.7 \pm 4.4$  mg (mean  $\pm$  SD) more paint than the overall average ( $43.6 \pm 7.8$  mg) amount of paint loaded on eight filters. The inhomogeneity in loading seen in the first trial was less pronounced in the later ones. Taking the average of the filters laterally adjacent to each glove sample was more representative of how much paint was sprayed onto each glove sample because of the horizontal motion used to apply the paint. The filters in the middle row were not included in the average because they were sprayed more heavily. As listed in Table 3, the paint surface loading was homogeneous for the most part in the horizontal direction



of the spray motion. The within-row coefficient of variation ranged from 6 to 13 %, whereas the overall coefficient of variation varied from 10 to 20 %. There was more consistency in paint surface loading for the horizontal direction than the direction parallel to the panel short axis because the spray gun moved in the horizontal direction. On average, there was a 3 % difference between panels when comparing across 3 days of sampling with horizontal direction of spray and a 5 % difference with vertical direction of spray. Spatial variation in loading within each day could be a contributing factor to the observed variation in glove transport results.

As listed in Table 4, natural rubber latex gloves allowed substantially greater mean transport for all eight solvents compared with nitrile rubber gloves. *m*-Xylene showed the greatest transport difference between the two materials, i.e.,  $51 \pm 1.8$  % for natural rubber latex gloves versus  $6.7 \pm 1.0$  % for nitrile rubber gloves, and this solvent component had the highest percent transport through each material. This could not be explained by difference in volatility relative to the other components. The relative abundance of *m*-xylene and its low water solubility distinguish it from 2-heptanone, the component with the next highest transport. Losses of MEK, styrene, and toluene from the surface due to their higher volatility may have caused generally less material to be available for transport across the glove samples. Styrene and MEK had the lowest average percent transport for nitrile rubber gloves. However, these two compounds showed substantially greater transport through natural rubber latex:  $5.0 \pm 0.3$  % and  $1.5 \pm 0.6$  %, respectively. Despite their wide difference in

physical properties, *o*-xylene and 2-heptanone were nearly indistinguishable in transport through natural rubber latex (24 vs. 22.5 %) and through nitrile rubber (3.1 vs. 3.7 %) gloves (Table 4).

Whether present as a neat solvent or as a component in a solvent mixture, permeation involves absorption into the polymer membrane, followed by diffusion and desorption from the membrane to the receiving medium (De Kee et al. 2005). For a neat solvent, the qualitative permeation behavior through different glove materials has been explained successfully on the basis of certain properties of the polymer and the permeating solvent. These properties include polarity, solubility parameter, and octanol–water partition coefficient. However, this description does not appear to apply to a mixture of solvents (Chao et al. 2008). Solvents in a mixture will interact in a complex way with the glove polymer and with each other (Perron et al. 2002). Therefore, the suggestion made, e.g., by Forsberg and Faniadis (1986) and Forsberg (1986), that a solvent component with a lower octanol–water partition coefficient (more polar) will have a stronger attraction to and permeation through a polar glove material (nitrile), will not explain the present findings that xylene (less polar) and heptanone (more polar) had transport fractions that were similar to each other for both glove materials.

The ASTM method uses a permeation chamber submerged in a 25 °C water bath and requires that the challenge liquid be in continuous contact with the glove material. In the ASTM cell, the solvent mass applied to the test membrane is not a limiting factor to permeation. In contrast, the system used here limits the solvent to the mass

**Table 4** Cumulative 30-minute transport for 3 days of sampling (six panels)

Solvent	Natural rubber		Nitrile rubber <sup>d</sup>		
	Percent of initial loading <sup>a</sup>	Mass transported (μg/cm <sup>2</sup> )	Percent of initial loading <sup>a</sup>	Percent of initial loading (adjusted for thickness) <sup>c</sup>	Mass transported (μg/cm <sup>2</sup> )
	Mean (SD)	Range	Mean (SD)	Mean (SD)	Range
MEK <sup>b</sup>	1.48 (0.62)	7.4–40	0.15 (0.15)	0.18 (0.18)	0.8–3.1
Toluene	8.39 (0.52)	42–66	1.51 (0.52)	1.80 (0.63)	3.2–20
Ethyl benzene	21.7 (0.82)	140–180	2.53 (0.55)	2.99 (0.67)	11–34
<i>p</i> -Xylene	10.1 (0.37)	150–190	1.26 (0.39)	1.49 (0.48)	12–40
<i>m</i> -Xylene	50.9 (1.85)	330–410	5.75 (0.83)	6.77 (1.01)	25–78
<i>o</i> -Xylene	23.8 (0.73)	150–180	2.60 (0.55)	3.07 (0.67)	10–32
Styrene	5.04 (0.34)	0.65–0.94	<LOD <sup>e</sup>	<LOD <sup>e</sup>	<LOD <sup>e</sup>
2-Heptanone	22.5 (0.98)	440–550	3.13 (0.63)	3.69 (0.77)	42–130

Number of observations: latex gloves  $n = 20$ , nitrile gloves  $n = 20$

<sup>a</sup> Mean mass transported is expressed as a fraction of the initial mass loading for each solvent

<sup>b</sup> Solvents are listed in order of increasing boiling point (as in Table 2)

<sup>c</sup> Adjusted to the thickness of natural rubber. See text for details

<sup>d</sup> All differences between natural rubber and nitrile rubber are significant ( $p < 0.005$ )

<sup>e</sup> Results less than the limit of detection

applied during spraying, and it permits some applied solvent to evaporate to the atmosphere during the drying process. These two factors make the results of this study more likely to represent transport under actual use conditions. For this reason, the results of this study are also likely to differ from what would be found with the ASTM closed-cell system.

Other investigators have reported that components of a solvent mixture can induce swelling of the polymer membrane, thus enhancing permeation of some or all of the mixture components (Georgoulis et al. 2005; Chao et al. 2006; Zellers et al. 1992). Those observations were derived from studies using the ASTM standard method in which liquid solvent mixtures were held in contact with the outer surface of the polymer for periods of up to several hours. In the present study, no swelling was observed owing to the limited amount of solvent applied and to the allowance for evaporation of solvent during the 30-min application process. Therefore it seems likely that solvent-induced polymer swelling or degradation did not play a role in fostering transport of the solvent mixture components observed here.

The results of this study suggest that the glove materials and thickness favored by the majority of automobile body painters do not afford adequate protection from the solvent components in commercial isocyanate-based paints. Significant amounts of each solvent were found on the skin side of samples of natural rubber latex 30 min after a simulated paint application. For example, for 2-heptanone with a threshold limit value (TLV) of 230 mg/m<sup>3</sup>, the observed transport in mass/area-time through natural rubber yields an estimated mass transported to the skin for one hand (hand area of 425 cm<sup>2</sup> (Cross et al. 2008)) after 30 min that approaches 10 % of the inhaled dose during 8 hours at the TLV. Paint sprayed directly on a painter's gloves could therefore lead to important skin contact with solvents. For nitrile rubber gloves, the solvent transport was less, but it was still detectable at 30 min for all solvents except styrene. For both glove materials, the aromatic solvents with higher boiling points were transported across the membranes at higher fractions of applied mass than for MEK or toluene. 2-Heptanone also showed higher transport. All of these observations indicate that more protective glove materials and thicknesses should be chosen for this application.

#### Limitations of the Study

No attempt was made to characterize glove specimens regarding chemical composition of the polymer membrane or the “area density” as described by Phalen et al. (2007). Those investigators were able to show that in the case of the copolymeric nitrile rubber membranes, the mass fraction of acrylonitrile was correlated with observed permeation rate. They also found that area density (membrane

mass/exposed area) was influential in affecting permeation. The results in the present article also could have been affected by these unmeasured variables.

This study did not assess the effects of temperature (Zellers et al. 1992), exposure duration, or user practices, all of which can affect the performance of personal protective equipment under use conditions. This experiment presented a relatively severe exposure setting of direct contact with solvents in the clear-coat paint formulation, and the results from this study are only applicable to this particular clear-coat formulation. Solvents that are part of a mixture may exhibit greater or lesser transport behavior than would the same solvents in pure form (Forsberg and Faniadis 1986). Because only two glove types from one vendor were selected for this study, the results of this experiment cannot be generalized to all nitrile rubber or all natural rubber latex gloves, especially because glove thickness was not a major variable.

Solvent loss from the glove surface by evaporation was not measured, but its effect is reflected in the calculation of average solvent transport when expressed as percent of initial (wet) loading. Generally, solvents with the highest vapor pressure would have the greatest loss assuming there are no appreciable deviations from Raoult's law. The preferential loss of higher volatility solvents reflects the reality of workplace exposures.

The use of a solid collection medium in the modified ASTM method has been described by others, but this technique has not been fully validated by comparison with measurements using flowing gas or liquid (De Kee et al. 2005). Furthermore, the effects of processes, such as polymer swelling and solvent evaporation, if they occur after application, are likely to be difficult to predict from theory and will require careful investigation under well-controlled experimental conditions.

#### Conclusion

Our study employing a simple method for measurement of solvent transport during actual use situations is intended to bridge the gap between laboratory data and real-world performance as recommended by several investigators (Cherrie et al. 2004; Klingner and Boeniger 2002). The technique used here offers an appealing approach to some of the problems in interpreting results from the ASTM permeation procedure in the context of painting applications. In particular, solvent evaporation was permitted, and membrane swelling by solvent was less likely.

Overall, nitrile rubber gloves had greater resistance to solvent transport compared with natural rubber latex gloves. The latter material exhibited the greater percent transport for each of the eight solvents in this study. During 30 min, nitrile rubber gloves allowed 3.0–6.8 % transport for ethyl benzene,

*m*-xylene, *o*-xylene, and 2-heptanone and <2 % transport for the remaining compounds; corresponding transport rates for natural rubber latex were 5–10 times those values.

Although most painters choose natural rubber latex gloves over nitrile rubber gloves for their comfort and dexterity advantages, natural rubber gloves offer relatively little chemical resistance to solvents in the clear coat formulation. Nitrile rubber, although somewhat better, does not offer meaningful improvement in protection in the thin form used in this study.

The use of an experimental method that simulates solvent application to gloves within a paint matrix may offer useful information on transport in addition to that derived from the standard ASTM permeation test procedure. This conclusion is tentative, and should be verified by expanded investigation.

**Acknowledgments** The study was supported by the Department of Environmental and Occupational Health Sciences at the University of Washington and by Chevron Environmental, Inc. The latter did not participate in the design or execution of the study or in the preparation of this manuscript. The authors thank all personnel for their assistance in conducting the experiments (Emmett Connelly, Byron Jennings, Carolyn R. Whitaker, and Todd Schoonover from the Washington Department of Labor and Industries). We are grateful to the spray-painting facilities and the professional spray-painters in lending their valuable time and knowledge. Special thanks in particular to the University of Washington Environmental Health Laboratory (Maureen Cornell-Endres and Jianbo Yu) for chemical analysis and advice on experimental method procedures.

## References

- American Society for Testing and Materials (1999) Standard test method F739-99 for resistance of materials to permeation by liquids and gases under conditions of continuous contact. ASTM International, West Conshohocken, PA
- Ammex Corporation (2011) Chemical Resistance Chart. Available at: <http://www.ammex.com/ChemRes.php>. Accessed 16 May 2011
- Berardinelli SP (1988) Prevention of occupational skin disease through use of chemical protective gloves. *Dermatol Clin* 6:115–119
- Ceballos DM, Yost MG, Whittaker SG, Whitaker CR, Camp J, Dills R (2011a) Development of a permeation panel to test dermal protective clothing against sprayed coatings. *Ann Occup Hyg* 55:214–227
- Ceballos DM, Fent KW, Whittaker SG, Gaines LGT, Thomasen JM, Flack SL et al (2011b) Survey of dermal protection in Washington State collision repair industry. *J Occup Environ Hyg* 8:551–560
- Chao KP, Lai JS, Lin HC, Hsu YP (2006) Comparison of permeability determined by permeation cell and immersion methods for organic solvents through protective gloves. *Polym Test* 25:975–984
- Chao KP, Hsu YP, Chen SY (2008) Permeation of aromatic solvent mixtures through nitrile protective gloves. *J Hazard Mater* 153:1059–1066
- Cherrie JW, Semple S, Brouwer D (2004) Gloves and dermal exposure to chemicals: proposals for evaluating workplace effectiveness. *Ann Occup Hyg* 48:607–615
- Cross A, Collard M, Nelson A (2008) Body segment differences in surface area, skin temperature and 3D displacement and the estimation of heat balance during locomotion in hominins. *PLoS ONE* 3(6):e2464
- De Kee D, Liu Q, Hinestroza J (2005) Viscoelastic (non-Fickian) diffusion. *Can J Chem Eng* 83:913–929
- Ehntholt DJ, Cerandolo DL, Bodek I, Schwope AD, Royer MD, Nielsen AP (1990) A test method for the evaluation of protective glove materials used in agricultural pesticide operations. *AIHA J* 51:462–468
- Forsberg K (1986) Selection of chemical protective clothing using permeation and toxicity data. In: Barker RL, Coletta GC (eds) *The First International Symposium on the Performance of Protective Clothing*. American Society for Testing and Materials Committee F23, Philadelphia, PA
- Forsberg K, Faniadis S (1986) The permeation of multi-component liquids through new and pre-exposed glove materials. *AIHA J* 4:189–193
- Georgoulis LB, Morgan MS, Andrianopoulos N, Seferis JC (2005) Swelling of polymeric glove materials during permeation by solvent mixtures. *J Appl Polym Sci* 97:775–783
- Gunderson EC, Kingsley BA, Witham CL, Bromberg DC (1989) A practical study in laboratory and workplace permeation testing. *Appl Ind Hyg* 4:324–329
- Kimberly Clark Professional (2011) Chemical compatibility chart. Available at: <http://www.kcprofessional.com/us/Product-Catalog/Gloves/gloves.asp>. Accessed 16 May 2011
- Klingner TD, Boeniger MF (2002) A critique of assumptions about selecting chemical resistant gloves: a case for workplace evaluation of glove efficacy. *Appl Occup Environ Hyg* 17:360–367
- Mickelsen RL, Roder MM, Berardinelli SP (1986) Permeation of chemical protective clothing by three binary solvent mixtures. *AIHA J* 47:236–240
- Microflex Corporation (2011) Product literature. Chemical resistance guide. Available at: <http://www.microflex.com/Products/~media/Files/Literature/Microflex%20Chemical%20Resistance%20Guide.ashx>. Accessed 16 May 2011
- National Institute for Occupational Safety and Health (1998) Recommendations for chemical protective clothing: a companion to the NIOSH pocket guide to chemical hazards. Available at: <http://www.cdc.gov/niosh/ncpc/ncpc1.html>. Accessed 18 Apr 2011
- National Institute for Occupational Safety and Health (2005) NIOSH pocket guide to chemical hazards. Publication no. 2005-149. NIOSH, Cincinnati, OH. Available at: <http://www.cdc.gov/niosh/npg/>. Accessed 3 May 2011
- Perkins JL, Vescial K (1997) An evaluation of charcoal cloth as a potential field monitor for the efficacy of chemical protective clothing. *Appl Occup Environ Hyg* 12:362–366
- Perron G, Desnoyers JE, Lara J (2002) Permeation of mixtures of organic liquids through polymeric membranes: role of liquid-liquid interactions. *J Appl Polym Sci* 86:195–215
- Phalen RN, Que Hee SS, Xu W, Wong WK (2007) Acrylonitrile content as a predictor of the captan permeation resistance for disposable nitrile rubber gloves. *J Appl Polym Sci* 103:2057–2063
- Schwope AD, Goydan R, Reid RC, Krishnamurthy S (1988) State-of-the-art review of permeation testing and the interpretation of its results. *AIHA J* 49(11):557–565
- Wang JD, Chen JD (1993) Acute and chronic neurological symptoms among paint workers exposed to mixtures of organic solvents. *Environ Res* 61:107–116
- Whittaker SG, Whitaker CR (2009) Characterizing the health and safety needs of the collision repair industry. *J Occup Environ Hyg* 6:273–282
- Zellers ET, Ke HQ, Smigiel D, Sulewski R, Patrash SJ, Han MW et al (1992) Glove permeation by semiconductor processing mixtures containing glycol-ether derivatives. *AIHA J* 53:105–116