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Development of a Permeation Panel to Test Dermal Protective Clothing Against Sprayed Coatings

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Objectives: Design, construct, and characterize an apparatus to evaluate dermal protective clothing for resistance to polymerizing materials. Specifically, we evaluated the permeation of the most common glove material used in automotive collision repair (0.10–0.13 mm or 4–5 mil latex) with representative isocyanate-containing clear coats. Our ultimate goal is to make informed recommendations on dermal protective materials to prevent isocyanate exposures and reduce the likelihood of occupational illness in automotive collision repair and other industries.

Methods: A novel permeation panel was developed to assess dermal protective clothing. With this apparatus, up to eight test materials may be evaluated under typical-spray application conditions. Solid collection media comprised of 1-(2-pyridyl)-piperazine (2-PP)-coated fiberglass filters or colorimetric SWYPE™ pads were placed behind test materials to capture permeants. The 2-PP-coated filters were subsequently analyzed using a modified OSHA42/PV2034 method. Color change in the SWYPEs provided an immediate field estimate of breakthrough time. In addition, Teflon filters were mounted proximal to the permeation cells to measure the mass of clear coat applied to the panel and to evaluate loading homogeneity. This study evaluated the permeation of isocyanates through 0.10–0.13 mm latex glove material at a fixed time (30 min post-spraying) and over a time course (6–91 min post-spraying).

Results: Monomers 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) permeated through (0.10–0.13 mm) latex glove material under typical glove use conditions (30 min). The latex glove material exhibited immediate breakthrough, with a permeation rate of 2.9 ng min^{-1} cm^{-2}. The oligomeric forms of HDI and IPDI did not permeate the latex glove material. The spray application at 71 ± 5°F was fairly homogeneous (33.7 ± 8 mg weight of dry clear coat per 5 cm^2).

Conclusions: The permeation panel is a viable method to assess dermal protective clothing performance against polymerizing materials. Thin (0.10–0.13 mm) latex gloves were determined to be ineffective barriers to the isocyanates commonly found in clear coats. Because this type of glove is used frequently in auto body shops, the potential for isocyanate exposure is of concern. Permeation tests with other dermal protective clothing materials and other clear coat formulations are needed to make recommendations about alternative materials.

Keywords: automotive clear coats; automotive repair; coatings; gloves; isocyanates; latex; permeation; permeation panel; protective clothing

INTRODUCTION

Dermal protective clothing remains a primary means of preventing skin exposures in many workplaces

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(Bello *et al.*, 2007). Although substitution for less hazardous materials and robotic processes are preferred ways to minimize chemical exposure during spray applications, these approaches are frequently not feasible (Boman *et al.*, 2004). Selecting appropriate protective clothing is an essential step toward an effective worker protection program along with ventilation and employee training (Boman *et al.*, 2004). Also important is the adherence to good work practices including the adequate use and removal of protective clothing [Health and Safety Executive (HSE), 2009]. In order to make informed decisions about worker protection, it is essential to determine permeation and breakthrough of protective clothing for chemicals of interest.

The efficacy of chemical protective clothing may be evaluated by assessing degradation, penetration, and permeation (Anna, 2003). In this present study, we focused on measuring permeation, which is the process of chemical diffusion through pores or molecular gaps (Anna, 2003). Material permeation resistance generally is characterized by breakthrough time and permeation rate (Anna, 2003). Breakthrough time provides information on the minimum time for the permeant to first be measured at the inner surface. Permeation rate provides information on the mass flux that permeates the material per unit time per unit area. The steady-state permeation is a state that is reached when the permeation rate becomes virtually constant (Boman *et al.*, 2004).

Gloves usually are selected based on laboratory permeation testing following US ASTM Method F739-07 'standard method for resistance of protective clothing materials to permeation by liquids or gases under conditions of continuous contact' or European EN 374-3 'Protective gloves against chemicals and microorganisms—determination of resistance to permeation by chemicals'. Gloves with lower permeation rates and longer breakthrough times offer more protection against a chemical than those that exhibit greater permeation rates and shorter breakthrough times (Boman *et al.*, 2004). The breakthrough time indicates the potential useable time. If the glove is removed before the breakthrough time, there is less likelihood for exposure. If the glove is worn beyond the breakthrough time, the steady-state permeation rate may provide an upper bound estimate of dermal exposure (Berardinelli, 1988).

No study to date has systematically quantified permeation of a complex chemical mixture like polymerizing coatings. Most permeation studies are performed with pure compounds or a binary mixture (Mickelsen *et al.*, 1986; Evans *et al.*, 2001). Mickelsen *et al.* (1986) determined that binary mixtures of solvents permeate differently than the pure components. These authors recommended that protective clothing permeation studies should be performed using mixtures that reflect actual working conditions. However, the ASTM standard method (ASTM F739) cannot be used to test polymerizing materials because the materials harden inside the apparatus.

The lack of glove material recommendations for many chemicals reflects the absence of a standard method for testing breakthrough and permeation of chemicals with low vapor pressures and low water solubility (Ehntholt *et al.*, 1990; Klingner and Boeniger, 2002; Anna, 2003). Chemicals with these properties generally include higher molecular weight chemicals, such as polynuclear aromatics, polychlorinated biphenyls, some pesticides (Anna, 2003), and isocyanates. Another challenge of the ASTM Method F 739 is that the studied chemical must be soluble in a fluid and that fluid must not permeate the tested material (Klingner and Boeniger, 2002). However, isocyanates are soluble in solvents like toluene and methyl ethyl ketone, which have been demonstrated to permeate through latex and nitrile (Georgoulis *et al.*, 2005).

Solid collection media have been used to evaluate permeation of chemicals with low vapor pressures and low water solubility (Ehntholt *et al.*, 1990). This technique involves placing a solid highly absorbent film directly against the test material. Ehntholt *et al.* (1990) designed a test cell that employed a silicone rubber material to collect pesticides. An alternative approach is the use of a liquid splash collection (Anna, 2003), where a solvent medium is briefly placed in contact with the protective clothing material and the extract analyzed for the chemical of interest (Raheel, 1996). This alternate approach, however, presents the same challenges than the standard method; the solvents used as collection may compromise the integrity of the test material.

Isocyanates are a leading cause of work-related asthma in Washington State (Whittaker and Reeb-Whitaker, 2009) and elsewhere (Liu and Wisnewski, 2003; HSE, 2005a,b; Bakerly *et al.*, 2008). Isocyanates are also known irritants and sensitizers (Redlich *et al.*, 2007). Of particular concern are the findings in animal studies that respiratory sensitization may be initiated by dermal exposure (Erjefalt and Persson, 1992; Rattray *et al.*, 1994; Bello *et al.*, 2007). Isocyanates are present in high concentrations in clear coats (Sparer *et al.*, 2004), which are non-pigmented top-coats designed to

improve appearance and durability. They are also present in some primers and sealers (Sparer *et al.*, 2004). Isocyanates in auto body shops are based on aliphatic isocyanates of 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), at times as blends of the two, with the monomers always present in small quantities in these formulations (Sparer *et al.*, 2004).

We developed a novel approach to test the efficacy of dermal protective clothing against polymerizing materials using a permeation panel. While standard permeation methods measure permeation continuously, the permeation panel measures permeation at specific time points. Each panel is comprised of eight permeation cells that quantify permeation through the protective materials. The permeation cells use a solid media behind the test material to collect permeants, similar to that published by Ehntholt *et al.* (1990). Quantitative filters and colorimetric pads were used as solid media, both coated with derivatization reagent [1-(2-pyridyl)-piperazine (2-PP)-coated fiberglass filters and surface SWYPE™] to stabilize the reactive isocyanates and prevent further chemical transformation. In addition, the mass of clear coat deposition across the panel is referred to as 'loading' and is measured on pre-weighed Teflon filters mounted in aluminum foil with 1-inch diameter openings; these filters are taped to the outside of the panel, interspersed between the permeation cells.

The goals of this study were to (i) design, construct, and characterize a permeation panel to evaluate dermal protective clothing material for resistance to polymerizing coatings, (ii) characterize the permeation panel by measuring permeation of aliphatic isocyanates through 0.10–0.13 mm latex glove material using representative automotive clear coat formulations under typical spray conditions, and (iii) measure aliphatic isocyanate permeation through 0.10–0.13 mm latex glove material in a time course to determine breakthrough time and permeation rate.

METHODS

Selection of clear coat formulations

In the auto body shop, painters typically combine three constituents to yield the final clear-coat spray mixture. The first constituent is the 'clear', which contributes the polyols (plus other solids and organic solvents). The second constituent is the 'hardener', which contains the isocyanates. The final constituent is the 'reducer' or 'thinner', which is a solvent mixture that lowers the viscosity of the mixture for spray application.

The clear coat formulations used in this study were chosen based on their frequency of use in the industry (confidential information provided by the manufacturer). Three clear coat formulations were evaluated that used two different clear products (referred to as 'A' and 'B' for confidentiality purposes) and two different reducers (referred to as 'i' and 'ii') as follows:

- Clear A/Reducer i,
- Clear B/Reducer i, and
- Clear B/Reducer ii.

The three formulations were prepared using the same aliphatic isocyanate-containing hardener product and were mixed using the ratios suggested by the manufacturer technical sheets (4 parts clear: 1 part hardener: and 1 part reducer). The formulations differed in the solvent content (Table 1). The formulations' technical data sheets reported an approximate composition of 47% solids and air-drying time of 16 h at 70°F.

The manufacturer reported that the batch of hardener used in this study contained 0.24% (w/w) HDI monomer, 0.24% (w/w) IPDI monomer, 47.9% (w/w) HDI oligomer, and 35.5% (w/w) IPDI oligomer. The formulations resulted in 13.9% total isocyanates in the mixture. The manufacturer also reported the isocyanate content in terms of the isocyanate functional group (NCO), 16.0–17.2% NCO.

The manufacturer material safety data sheets reported Clears A and B as acrylic based. Solvent composition for all unmixed clear coat components was determined by chemical analysis of the bulk products using US National Institute of Occupational Safety and Health (NIOSH) Method 1500 (NIOSH 2003) (Table 1). Solvent composition for clear coat formulations (Table 1) was calculated using mixing ratios provided by the manufacturer.

Construction of the permeation panel

Permeation cells construction. Permeation cell design and construction was described in detail elsewhere (Ceballos, 2009). A brief description follows here. The components of the cell are shown in Fig. 1A. The permeation cell used a 2.54-cm (1 in) diameter window (#NT46-098 high; Edmund Optics, Barrington, NJ, USA) as an inert base for the solid media and O-rings (McMaster, Elmhurst, IL, USA) to assure a tight seal.

Permeation panel construction. Two permeation panel frames were constructed from Pelican 1700 cases, 91.33 cm × 34.87 cm × 13.33 cm (Pelican Products, Inc., Torrance, CA, USA). Flanged holes

Table 1. Solvent composition for clear coat components and formulations (bulk analysis by NIOSH method 1500)

Clear coat component	*n*-Heptane	Methyl ethyl ketone	Methyl isobutyl ketone	Toluene	Ethylbenzene	*p*-Xylene	*m*-Xylene	*o*-Xylene	Styrene	2-Heptanone	Propylene glycol methyl ether acetate	Ethyl-3-ethoxy propionate	Methylcyclohexane	Petroleum distillates
	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w
Clear A[a]	0.02	0.03	0.06	0.10	5.95	5.75	13.5	6.05	0.20	13.5	0.04	0.90	<0.01	1.25
Clear B[a]	<0.03	0.05	9.2	0.1	4.95	5.15	12.5	5.35	0.15	10.5	<0.04	<0.04	<0.04	1.2
Reducer i[a]	2	31.5	0.06	21	0.01	0.02	0.04	0.02	<0.01	<0.01	23.5	<0.01	0.4	24
Reducer ii	27	17	<0.01	9.4	1.1	1.4	3.2	0.48		6	22	11		
Hardener	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	17	<0.01	<0.01	<0.01	0.45
Clear A/hardener/ reducer i[b]	0.3	5.3	0.0	3.6	4.0	3.8	9.0	4.0	0.1	11.8	3.9	0.6	0.1	4.9
Clear B/hardener/ reducer i[b]	0.33	5.28	6.14	3.57	3.30	3.44	8.34	3.57	0.10	9.83	3.92	Non detect	0.07	4.88
Clear B/hardener/ reducer ii[b]	4.50	2.87	6.13	1.63	3.48	3.67	8.87	3.65	0.10	10.83	3.67	1.83	Non detect	0.88

[a]Average of duplicate bulk analysis.
[b]Approximate composition based on mixing ratios provided by manufacturer technical sheets.

were machined in the top surface (Brandon Company Inc, Everett, WA, USA) to allow flush mounting the permeation cells. A photograph of a permeation panel is presented in Fig. 2.

Permeation measurement methods

Quantitative solid media. Isocyanates were collected on 2-PP-coated fiberglass filters (SKC 225-9002; SKC Inc., Eighty Four, PA, USA). A modified version of a current air sampling isocyanate technique (OSHA 42/PV2034 methods) was used for analysis. In brief, Occupational Safety and Health Association method 42 was modified so that the 2-PP derivatives of HDI, IPDI, and total oligomers were chromatographically resolved. Derivatives were eluted with a linear gradient of acetonitrile 5–100% >50 min with the balance being 0.02 M ammonium acetate (pH 6). The column was re-equilibrated with the initial mobile phase composition for 12 min between runs. A Hewlett Packard 1050 Series liquid chromatograph with a 1046A Programmable Fluorescence Detector (FLD) with a reverse-phase column (adsorbosphere UHS C18, 150 mm × 3.2 mm, 5 μ; Grace, Deerfield, IL, USA) was used at 30°C with a 240-nm FLD excitation and 370-nm emission wavelengths. Oligomers were calibrated based on the response of the HDI monomer derivative in a manner analogous to NIOSH method 5525. The monomer derivatives were obtained commercially (HDI; Restek Corporation, Bellefonte, PA, USA; IPDI; Aldrich, St Louis, MO, USA). Accuracy of the overall assay

Fig. 1. (A) Permeation cell components. (B) Inset showing assembled permeation cell (without test material or solid media). Prior to assembly, solid medium is placed on top of the base window and test material is held in place between the body and bezel using four screws. The base is then connected to the body/bezel, providing close contact between the solid media and test material and a leak-proof seal. The test material is exposed to clear coat through a 2.54-cm (1 inch) diameter opening in the cell.

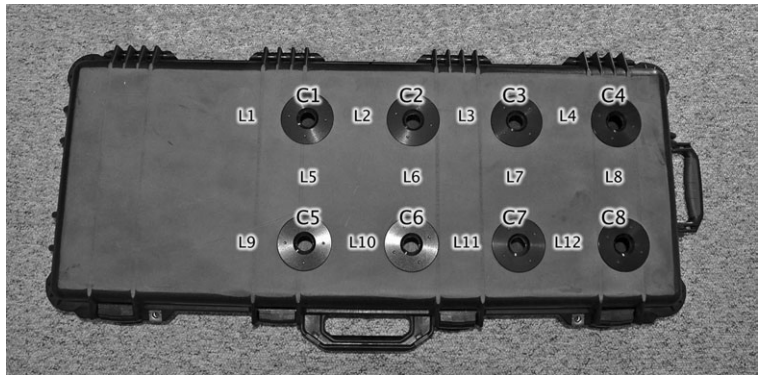

Fig. 2. Permeation panel (note top flat surface, eight permeation cells C1–C8, and 12 loading filter locations L1–L12).

was based on recovery from duplicate filter spiking of hardener bulk material at two levels (89% for HDI monomer and 88% for IPDI monomer). Instrument precision values were computed from duplicate blinded filter spiking of hardener bulk material at two levels [4.5% relative percent difference (RPD) for HDI monomer, 2.3% RPD for IPDI monomer, and 3.9–10.3% RPD for oligomers]. The limit of quantitation (LOQ) was set to the lowest standard that had a response: 0.05 μg monomeric HDI, 0.05–0.1 μg monomeric IPDI, and 0.5–1.0 μg total oligomers.

Colorimetric solid media. Colorimetric pads for aliphatic isocyanates (Surface SWYPE™ part No. 1023; Colorimetric Laboratories Inc., Des Plaines, IL, USA) also were used as solid media to provide an immediate field estimate of breakthrough time (detection limit of 3-5 μg per sample according to the manufacturer). SWYPE™ pads change color in a loading-dependent fashion (from yellow to orange/red) in the presence of the NCO (Ceballos *et al.*, 2009). The SWYPEs were used without developing solution (mineral oil) because we determined that this solution degraded latex.

One colorimetric pad was scanned as a field blank during every day of sampling. Also, one quantitative filter was opened to ambient air for a few seconds during the collection of samples and used as a field blank. Quantitative filter field blanks were stored and sent to the laboratory as any other sample. During analysis of the quantitative filters, at least two laboratory blanks were analyzed. All field and laboratory blanks were used for quality assurance and no corrections were made.

Loading measurements

Teflon filters (P5PQ047 Zefluor PTFE 47 mm 0.5 mm Pall Life Sciences, Ann Arbor, MI, USA) were temperature conditioned (67 ± 2°F) for pre- and post-weighing (AT261 DeltaRange analytical balance; Metler Toledo, Columbus, OH, USA). Mass gain on the filter accounted for the mass of dry clear coat deposited during the spray application. At least 12 Teflon filters were mounted between the permeation cells. Pre-weighed Teflon filters were mounted in 50 × 50-mm^2-thick aluminum foil with 1-inch diameter openings. Loading average and percent coefficient of variation (%CV) of the Teflon filters throughout the panel were used to estimate the homogeneity of the spray application. To facilitate normalization, the area exposed to the clear coat was the same for both the glove test material and the Teflon filter. The mass of isocyanate detected on the quantitative solid media was normalized by dividing by the average loading of dry clear coat in the panel.

Assembly of the permeation panel

Permeation cell assembly. The assembled cell is shown in Fig. 1B. Test material was cut from the palm of the glove and thickness was measured (thickness gauge E142/1B; Baker Gauges, Pune, India). Four holes were made in the perimeter of the test materials to be aligned with the screw holes of the cell. The test material was placed between the bezel and the body, ensuring that the outer surface of the glove material faced outwards.

Once the bezel and body were connected using screws, the top-body O-ring ensured a leakproof seal. Both glass-fiber filters and SWYPE™ were cut into 2.54-cm diameter circles, placed on the base window, and connected to the body to be in intimate contact with the test material. Position of the fiberglass filters was verified so the 2-PP coating was in contact with the protective clothing material being tested. Also, the SWYPE™s were placed making sure the plastic backing was resting on the base window. Solid media was handled and loaded inside a clean ventilation hood to avoid contamination. The base O-rings ensured that there was a seal between the base and the body, ensuring that any isocyanate contacting the solid media resulted only from permeation.

Permeation panel assembly. Labeled permeation cells were inserted into the permeation panel cases. Areas between the permeation cell openings were masked with tape to prevent contamination with overspray. The loading filters were then taped to the outside of the panel—interspersed between the permeation cells (locations shown in Fig. 2). Finally, the sides and underside of the panels were masked with tape and masking paper to avoid overspray contamination.

Spray painting the permeation panel and booth conditions

The downdraft paint booth (DeVilbiss by Global Finishing Solutions, Osseo, WI, USA) was maintained at a temperature typical for spray-application conditions of the clear coats (∼70°F). Prior to spray application, panels were placed inside the booth for temperature (*T*) and relative humidity (RH) conditioning. The *T* and RH were monitored using wireless HOBO External Data Loggers (Model H08-004-02; Onset Computer Corporation, Pocasset, MA, USA) mounted inside the permeation panel.

Booth airflow was measured in the temperature-conditioned booth with a Spatial Anemometer ALNOR model RVA501 (TSHI Company, Huntington Beach, CA, USA). Linear velocity was measured

2–5 cm from the floor vents. Several velocity measurements were made throughout the floor vents. Volumetric flow (cubic meters per minute) was calculated by multiplying the average velocity in meters per minute and floor vent area (square meters).

The clear coat formulations were applied to the panels by the same painter using the same spray gun (1.3 mm nozzle LPH400 operated at 20 psi; ANEST IWATA USA, Inc., West Chester, OH, USA). Panels were sprayed for ∼18 s in two separate applications, with ∼8 min between applications (to mimic actual product usage when spray painting). The panel remained inside the temperature-controlled booth for the duration of the experiment.

Collection of permeation and loading samples

Filters were removed at specific times after spraying while avoiding cross contamination. Permeation times ranged from 6 to 91 min and are listed in Tables 2 and 3. Permeation times were recorded starting at the end of the second (final) spraying application. Quantitative solid media were placed in their original storage cassettes, sealed with parafilm®, and placed in a cooler with blue ice for transportation to the laboratory, where they were stored at −20°C until analysis. SWYPEs were removed and immediately assigned a color change of positive (color change from yellow to orange/red) or negative (no color change).

The pre-weighed Teflon loading media also were removed from the exterior surface of the panel and placed inside their labeled filter holders. Loading media were post-weighed after 1 week and using an anti-static device to ensure a stable weight reading.

Permeation panel clean up

When sample collection was completed, all the remaining masking tape and paper were removed from the panel. Cells were disassembled and wiped with acetone or alcohol to remove any clear coat residue. Back at the laboratory, the cells were cleaned thoroughly (with acetone, *N*-methylpyrrolidone or NMP, and water/mild detergent sonication bath) before reuse. The cell cleaning procedure was evaluated by loading at least one permeation cell with 2-PP-coated filters for 1-h prior to the permeation experiments to serve as cell cleaning blanks.

Characterization of the permeation panel

Experiments to characterize the permeation panel (fixed time experiments) and to determine the breakthrough time and permeation rate of isocyanates through the glove material (time course experiments)

Table 2. Fixed time results for latex glove material (0.10–0.13 mm)

Day	Panel	Permeation time or time post-spraying (min)	SWYPE™ color change (±)[a]	2-PP-coated filters analyzed by modified OSHA42/PV2034[b]		
				HDI monomer (μg/sample)	IPDI monomer (μg/sample)	HDI and IPDI oligomers (μg/sample)
1	I	33	[c]	0.41	0.08	<0.5
	I		+	0.34	0.06	<0.5
	I		+	0.68	0.14	<0.5
	I		+	0.45	0.08	<0.5
	II	27	+	0.23	<0.05	<0.5
	II		+	0.35	0.08	<0.5
	II		+	0.18	<0.05	<0.5
	II		+	0.26	<0.05	<0.5
2	I	27	+	0.23	<0.05	<0.5
	I		+	0.12	<0.05	<0.5
	I		+	0.59	0.07	<0.5
	I		+	0.33	<0.05	<0.5
	II	27	+	0.11	<0.05	<0.5
	II		+	0.20	<0.05	<0.5
	II		+	0.22	<0.05	<0.5
	II		+	0.16	<0.05	<0.5

[a]Positive (+) indicates that the surface SWYPE™ changed color within 2 min (limit of detection = 3–5 μg).
[b]HDI LOQ was 0.05 μg, IPDI LOQ was 0.05–0.1 μg, and HDI and IPDI oligomers LOQ was 0.5–1.0 μg.
[c]Sample discarded because the glove sample was damaged during the experiment.

Table 3. Time course results for latex glove material (0.10–0.13 mm)

Day	Panel	Permeation time or time post-spraying (min)	2-PP-coated filters analyzed by modified OSHA42/PV2034[a]		
			HDI monomer (μg/sample)	IPDI monomer (μg/sample)	HDI and IPDI oligomers (μg/sample)
3	I	8	0.1	0.1	<0.5
	I	10	[b]	[b]	[b]
	I	29	0.2	<0.05	<0.5
	I	30	[b]	[b]	[b]
	II	9	<0.05	0.1	<0.5
	II	20	0.1	<0.05	<0.5
	II	31	0.3	0.2	<0.5
	II	31	0.1	<0.05	<0.5
4	I	7	0.2	0.1	<0.5
	I	20	0.3	0.1	<0.5
	I	20	0.3	0.1	<0.5
	I	30	0.4	0.2	<0.5
	II	6	0.2	0.1	<0.5
	II	13	0.2	0.1	<0.5
	II	30	0.4	0.2	<0.5
	II	30	0.6	0.2	<0.5
5	I	43	0.7	<0.1	<1
	I	50	0.7	<0.1	<1
	I	61	1.3	0.2	<1
	I	91	1	<0.1	<1
	II	38	0.8	0.1	<1
	II	49	1.1	<0.1	<1
	II	60	1.1	0.2	<1
	II	89	1.8	0.2	<1

[a]HDI LOQ was 0.05 μg, IPDI LOQ was 0.05–0.1 μg, and HDI and IPDI oligomers LOQ was 0.5–1.0 μg.
[b]Samples discarded because they were inadvertently contaminated with clear coat.

were performed, see Table 4. Latex glove material (powder-free Gloveworks Industrial Latex 5 mil, TLF46100; Ammex, Tukwila, WA, USA) was tested during all experiments. Disposable latex gloves were chosen because they are the most commonly used gloves in Washington State's collision repair industry (Whittaker and Reeb-Whitaker, 2009).

Fixed time experiments. Latex glove material was tested to evaluate performance, reproducibility, and handling of the panels. Two panel experiments were performed each day for 2 days to characterize the between- and within-day variability of permeation. Two clear coat formulations (Ai and Bi) were tested randomly throughout the fixed-time experiments. A permeation time of 30 min was chosen because this is a realistic length of a spray-painting task, and disposable gloves are typically replaced in between tasks. As a reference, Sparer *et al.* (2004) documented tasks duration from 1 to 49 min with a median of 11 min.

Permeation was measured using both quantitative and colorimetric solid media. 2-PP-coated fiberglass filters were used to quantitatively evaluate permeation and surface SWYPE™ pads were used to qualitatively estimate breakthrough time. Permeation in nanograms per milligram (30 min post-spraying) was reported as the total amount of all isocyanate species detected in the quantitative solid media normalized by the average clear coat loading per panel. Permeation cells using SWYPEs were marked as positive (+) if color changed from yellow to light orange within the first 2 min post-spraying. Color change was first assessed by observing the pad through the glove material and verified after the cell was disassembled.

Variability for the permeation measured with quantitative solid media was assessed by one-way analysis of variance for factors such as day, clear coat (A and B), and panel (SPSS 15.0 for Windows; SPSS Inc., Chicago, IL, USA).

Table 4. Permeation panel tests of latex glove material (0.10–0.13 mm)

Experiment description	Day	Panel[a]	Isocyanate media	Clear	Reducer	Average loading dry clear coat[b], mg (%CV)	Average temperature, °F (%CV)	Average relative humidity, %RH (%CV)	Booth airflow, m[c] min^{-1} (%CV)
Fixed time (30 min post-spraying)	1	I	4 Filters[d], 3 Pads[c]	A	i	33.7 (12.0)	72.2 (0.8)	47.9 (1.0)	230
		II	4 Filter[d], 4 Pads[c]	A	i	35.8 (8.8)	[e]	[e]	
	2	I	4 Filters[d], 4 Pads[c]	A	i	31.5 (9.0)	71.5 (0.6)	51.5 (0.9)	278
		II	4 Filters[d], 4 Pads[c]	B	i	34.8 (12.9)	70.3 (0.7)	53.8 (1.0)	
			Fixed time average			33.9 (5.5)	71.3 (0.7)	51.1 (1.0)	254 (13.4)
Time course (5–90 min post-spraying)	3	I	4 Filters[d]	A	i	28.2 (12.4)	68.2 (0.8)	52.8 (7.6)	276
		II	4 Filters[d]	B	ii	26.8 (11.8)	69.2 (1.2)	49.7 (9.6)	
	4	I	4 Filters[d]	A	i	34.1 (13.4)	71.3 (2.2)	38.1 (4.6)	287
		II	4 Filters[d]	B	ii	34.5 (9.3)	[e]	[e]	
	5	I	4 Filters[d]	A	i	38.1 (12.9)	70.6 (1.4)	46.2 (7.7)	270
		II	4 Filters[d]	A	i	39.8 (14.9)	71.3 (1.5)	44.7 (6.7)	
			Time course average			33.6 (15.5)	70.1 (1.4)	40.3 (7.4)	278 (3.1)
				Total average		33.7 (11.9)	70.6 (1.1)	48.1 (4.8)	268 (8.3)

[a]During the same day, the Panel II was always sprayed after the Panel I.
[b]Filter = quantitative solid media, 2-PP coated fiber-glass filter.
[c]Pad = qualitative solid media, colorimetric surface SWYPE™ pad.
[d]Dry clear coat loading measured by gravimetric analysis using Teflon filters.
[e]Data missing.

Time course experiments. Two-panel experiments using latex glove material to measure permeation at different time points were performed on three separate occasions (Table 4). Two different clear coat formulations (Ai and Bii) were randomly tested using quantitative solid media that was removed at different time intervals. Days 3 and 4 data provided permeation information between 5 and 30 min post-spraying, while the results from Day 5 extended the timeline to 90 min post-spraying (Table 3). The slope of the permeation data in time describes the permeation rate (nanograms per square centimeter per minute), which is equivalent to the slope (nanograms per milligram per minute) multiplied by the average loading (milligram) and divided by the permeation area (square centimeters).

RESULTS

Fixed time experiments

Latex glove material (measured thickness of 0.10 mm, 1.6% CV) was tested under controlled conditions of clear coat formulation, clear coat loading, *T*, and RH (Table 4). Isocyanate permeation was detected on both quantitative and colorimetric solid media (Table 2). Permeation cells using quantitative solid media showed permeation of HDI monomer and IPDI monomer, although no oligomer species were detected (Table 2). Overall, the average permeation was 10.2 ng mg^{-1} (Fig. 3) with a permeation rate of 2.3 ng cm^{-2} min^{-1}. Figure 3 shows the variability within panel and day. A significant difference in permeation was found only between panels (F = 6.55, P-value = 0.023). When correcting for small differences in permeation time, however, differences between panels were found to be non-significant (F = 2.75, P-value = 0.082). Isocyanate analysis of blanks (laboratory, field, and cell cleaning) yielded results below the limit of detection.

Colorimetric solid media were all positive (light orange) within 2 min from the start of the experiments, indicating immediate permeation of isocyanates through latex glove material. During inspection of the test materials while disassembling the cells, we observed that there was some color transfer from the SWYPE™ to the glove material being tested.

Time course experiments

Latex glove material exhibited isocyanate permeation at all measured time points; HDI monomer was detected at higher concentrations than the IPDI monomer (Table 3, Fig. 4). Figure 4 indicates that the measured breakthrough time (6 min) is the first time point at which permeation was detected, while estimated breakthrough time (immediate) was based on the positive Y-intercept from the permeation rate

equation ($y = 0.43 \times +2.61$, $R^2 = 0.77$). Note that in Fig. 4, the intercept of zero permeation at 0 min was included and the value zero was assigned to samples below the limit of detection. Further, the slope (0.43 ng mg^{-1} min^{-1}) in Fig. 4 describes a permeation rate of 2.9 ng cm^{-2} min^{-1}.

DISCUSSION

The first goal of this study was to build an apparatus to test protective clothing against complex polymerizing coatings. We constructed a permeation panel that measured aliphatic isocyanate permeation against commonly used automotive clear coat formulations. The panel can test up to eight materials under typical work conditions. This apparatus is easy to use, sample materials were easily loaded and unloaded, and interferences or contamination were not observed with its reuse. The permeation cells are durable, inexpensive, and easy to clean.

The second goal of the study was to characterize the use of the permeation panel under typical use

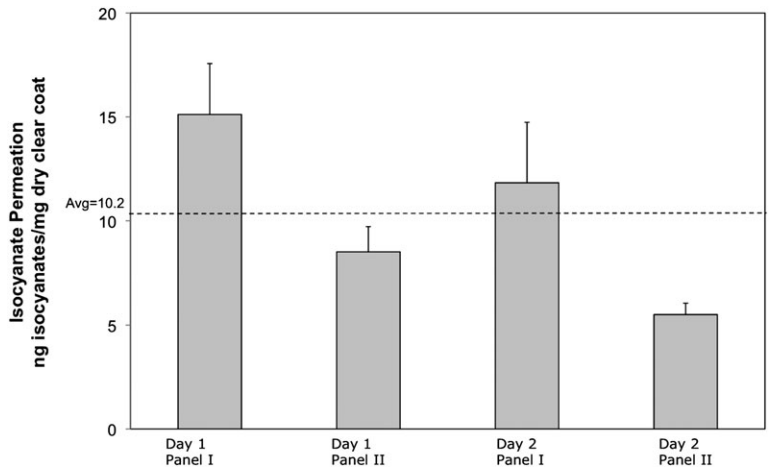

Fig. 3. Isocyanate permeation (sum of HDI and IPDI monomers) at a fixed time (30 min post-spraying) for Latex Glove (0.10–0.13 mm). 2-PP-coated filter permeation data were normalized by the mass of dry clear coat loaded and corrected for small differences in permeation time. Average permeation (10.2 ng mg^{-1}) indicates a permeation rate of 2.3 ng cm^{-2} min^{-1}.

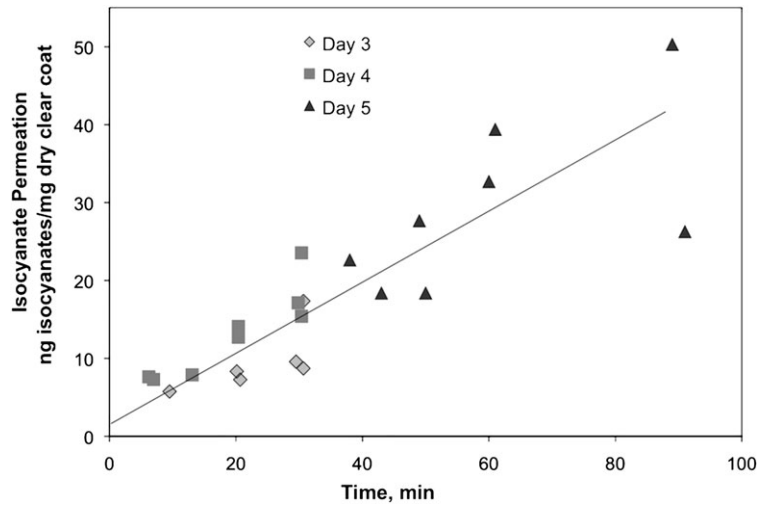

Fig. 4. Isocyanate permeation (sum of HDI and IPDI monomers) over Time (6–91 min post-spray) for Latex Glove Material (0.10–0.13 mm). 2-PP coated filter data were normalized by the mass of dry clear coat loaded. Permeation was evident 6 min after spraying of clear coat. Intercept (2.61 ng mg^{-1}) indicates immediate breakthrough of the isocyanates. Slope (0.43 ng mg^{-1} min^{-1}, $R^2 = 0.77$) suggests a permeation rate of 2.9 ng cm^{-2}-min.

conditions. After correcting for small differences in permeation time, we demonstrated that permeation variability was not significantly different within and between panels. These data indicate that thin latex gloves may not offer adequate protection as typically worn (average permeation of 10.2 ng mg^{-1} at a rate of 2.3 ng cm^{-2} min^{-1}, Fig. 3). Further, the immediate color change of the SWYPE™ indicates that thin latex gloves may not be appropriate for even >30-min spray applications (Table 2).

Paint loading onto the panel was highly consistent within and between panels because the same experienced painter applied the clear coat in all experiments. Overall variability of the mass loading from day to day was 11.9% (Table 4), regardless of the clear coat formulation or time of the day. Overall within panel variability was slightly higher than among panels (up to 14.9%, Table 4). This variability was lower than expected from manual spraying, which is typically 20% (David Kerzel Spraymation, Fort Lauderdale, FL, USA). Because the paint loading was consistent, we were able to normalize the isocyanate data against the average mass applied. Normalization could alternatively be presented by describing the total mass of isocyanates (or NCO mass) contained in the mass of dry clear coat.

The mass of dry clear coat was equivalent to 72.6 mg of wet coating (by using the information on percent of solids). Since the percentage of isocyanates in wet coating for both formulations was 13.9%, we determined that ~10 mg of isocyanates were loaded on each permeation cell. Using quantitative filter permeation results, the average thin latex permeation at 30 min was 336 ng of total isocyanates. This suggests that only a very small percentage of loaded isocyanate permeates through thin latex (0.003%). However, since isocyanates are known sensitizers, the dose–response for isocyanate-induced asthma may not be linear. Further, in the typical auto body shop, permeation through gloves is not the only source of skin chemical exposure; penetration, liquid splash, and overspray depositions are also common sources of dermal exposure.

We did not find any oligomers permeating the latex glove material tested. This means that the majority of the isocyanates may not have permeated the glove material (monomer was reported in this formulation as <0.5% of the isocyanate content). To know if there is oligomer breakthrough, more sensitive analysis (lower than 0.5 μg LOQ) may be needed.

When the same painter applies the coating, the most important contributing factors to variability are quality of the test material, clear coat formulation, clear coat application, clear coat loading homogeneity, curing rate, permeation time, and spray booth conditions. To reduce differences in test material quality, we used gloves from the same box. Spray booth conditions were fairly constant throughout all experiments (Table 4), with a temperature in the range of 68.2–72.2°F, a relative humidity in the range of 38.1–53.8%RH, and airflow in the range of 230–287 m^3 min^{-1} (8111–10 135 ft^3 min^{-1}).

The third goal of this study was to determine breakthrough time and permeation rate in 0.10–0.13 mm latex glove material. Time course experiments suggest that the breakthrough time for thin latex material is immediate (Fig. 4). In Fig. 4, data from three different days were plotted together, which suggest that the permeation rate of 2.9 ng cm^{-2} min^{-1} (R^2 = 0.77) was independent of the clear coat formulations studied. Solvent differences in the clear coat formulations (Table 1) did not seem to affect isocyanate permeation. When HDI monomer alone is plotted against time, the correlation improves to R^2 = 0.82, suggesting that HDI dominates the permeation.

A disadvantage of the current permeation panel experiments is that the results depend highly on the homogeneity of the coating application. Further standardization to decrease the variability of the spray application will not only include controlling the exact number of spray gun passes and the time interval between applications but also the stroke, speed, and distance of the spraying. To achieve this, the process would ultimately require automation of the spraying with a robotic applicator. This would allow numerous tests to be completed fairly rapidly. Further, some robotic applicators can reduce loading variability to as low as 1–2% (David Kerzel Spraymation). Tests could also be performed to ensure quality and homogeneity of test material. For example, test materials could be tested for holes (as described by Sohn *et al.*, 2000). There also is much to learn about the mass transfer mechanisms behind the polymerization process and the many variables that could be measured to model such a process. We encourage future studies in this area but note that it may be challenging because much of the information about product formulation remains proprietary.

We acknowledge that a possible disadvantage of using solid media to collect permeants, besides being time intensive, is that swelling of the test material may prevent uniform contact of the test material with the solid collection medium (Anna, 2003). However, we did not observe noticeable swelling of the test materials. Another potential limitation of the current permeation system is that it measures permeation at work temperature conditions rather than reflecting

potentially elevated temperatures proximal to a painter's gloved hand. One approach to address this limitation would be the use of a temperature-controlled case to maintain a higher temperature.

Considering that there was color transfer of the derivatization reagent used for the SWYPEs onto the test materials, it is reasonable to postulate that the same can happen with the 2-PP-coated filters. In the case of the SWYPE™, the color transfer was easy to observe, but more tests would be needed to verify the extent to which this may occur on 2-PP-coated filters. Excess 2-PP from the filter onto the test material could be identified by a wipe or spectroscopic surface method.

The principal advantage of the permeation panel compared to a conventional permeation cell is that the layer of sprayed polymerizing material is applied under typical workplace conditions. Standard methods generally employ immersion conditions, which is not appropriate for spray application. With the permeation panel, the test material is challenged with a layer of clear coat that mimics a gloved hand being sprayed or spilled upon. We have observed analogous situations during field visits to auto body shops.

Another advantage of the permeation panel is the ability to test a range of chemicals. For example, we have conducted parallel experiments in which solvent permeation was measured using the permeation panel. A charcoal cloth or colorimetric pad that changes color in the presence of solvent (such as permea tec by CLI laboratories) may be used as solid media.

We recommend that workers do not use thin (0.10–0.13 mm) latex gloves for mixing or spray painting with isocyanate-containing coatings because there is evidence of breakthrough within typical usage times. Recommending against the use of thin latex gloves also avoids the potential for development of latex allergy (Boman *et al.*, 2004). Our recommendation regarding the use of latex gloves agrees with that of Liu *et al.* (2000). Colorimetric wipe sampling revealed considerable contamination on skin and penetration through latex gloves after a single painting task (Liu *et al.*, 2000). Further, Bello *et al.* (2008) used skin colorimetric and quantitative wipe techniques and found HDI and HDI oligomers on the skin of auto body painters under protective gloves; the majority of workers (88%) in the study of Bello *et al.* (2008) used latex gloves. Regulatory agencies recommend discontinuing the use of latex gloves (EPA, 1999) for spray painters and recommend nitrile gloves when handling isocyanates (EPA, 1999; OSHA, 2002; HSE, 2007). Nitrile and butyl rubber gloves are recommended for the use of polyurethane coating systems by PPG Industries (1997).

Further permeation experiments with a wide selection of clear coat formulations, gloves, and coveralls are needed—similar to those published for aromatic isocyanates (API, 2001, 2002). It is also important to understand the effect that different solvents in the clear coat formulations have on isocyanate permeation. Selecting clear coats that permeate to a lesser extent could potentially help reduce dermal exposures. We demonstrated that changing the clear and reducer components was not sufficient to affect permeation. To observe a formulation effect, investigators may need to select clear coat formulations that are drastically different from each other, both in solvent and isocyanate content. Normalization or cofactor analysis with the amount of isocyanate may be necessary to evaluate the effect on permeation in these cases.

CONCLUSIONS

The permeation panel described here is a practical apparatus that can provide reliable assessment of dermal protective clothing efficacy against complex polymerizing coatings applied under typical work conditions. The panel can be used to screen test materials after a specific permeation time or test over a time course and to determine breakthrough time and permeation rate. The use of a robotic sprayer would allow faster sample collection and greater reproducibility. Extending the permeation panel testing to other sprayed coatings, liners, foams, and glues, is also desirable.

Results from the permeation panel can inform recommendations to workers to improve work practices and reduce illnesses linked to dermal exposures, such as dermatitis and work-related asthma. In this study, we found that commonly used thin latex gloves do not provide protection to painters from isocyanate-containing coatings paints. There is an urgent need for additional glove and coverall testing to provide recommendations to painters for the selection of appropriate dermal protective clothing when using isocyanate paints.

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