



Testing of Glove Efficacy against Sprayed Isocyanate Coatings Utilizing a Reciprocating Permeation Panel

Diana M. Ceballos^{1,4*}, Miyoko Sasakura¹, Carolyn Reeb-Whitaker², Kendra Broadwater¹, Mark Milbauer³, Robert Crampton¹, Russell Dills¹ and Michael G. Yost¹

1.Department of Environmental and Occupational Health Sciences, University of Washington, Box 357234, Seattle, WA 98195-7234, USA 2.Safety & Health Assessment & Research for Prevention (SHARP) Program, Washington State Department of Labor and Industries, PO Box 44330, Olympia, WA 98504-4330, USA;

3.Green River Community College, Autobody Technology Program, 12401 SE 320th Street, Auburn, WA 98092-3622, USA *Author to whom correspondence should be addressed. Tel: +1-513-841-4439; fax: +1-513-458-7147;

e-mail: dceballos@cdc.gov

4.Present address: 4676 Columbia Parkway R-11, Cincinnati, OH 45226, USA. Submitted 26 September 2012; revised version 28 August 2013; accepted 11 September 2013.

ABSTRACT

Objectives: Modify a permeation panel to evaluate dermal protective clothing for resistance to sprayed coatings with minimal variability in spray paint loading across the test panel. Determine isocyanate protection effectiveness of natural rubber latex (5 mil or 0.13 mm), nitrile rubber (5 mil or 0.13 mm), and butyl rubber (13 mil or 0.33 mm) glove materials against a commonly used automotive clear coat formulation. The latex and nitrile gloves were the type used by the local autobody spray painters.

Methods: Glove materials were tested by spraying paint onto an automated reciprocating permeation panel (permeation panel II). Temperature, relative humidity, and spray conditions were controlled to optimize paint loading homogeneity as evaluated by gravimetric analysis. Isocyanate permeation was measured using 1-(2-pyridyl)-piperazine-coated fiber-glass filters analyzed by a modified version of the OSHA 42/PV2034 methods.

Results: Latex exhibited a higher permeation rate compared with nitrile for isocyanates (1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate monomers) and both materials presented permeation at all of the time points suggesting a fast isocyanate breakthrough. Butyl material exhibited no permeation or breakthrough for isocyanates under the tested conditions. The spray application at $69 \pm 8^{\circ}$ F was optimally homogeneous at 45 ± 0.5 mg weight of dry clear coat per 5 cm².

Conclusions: The permeation panel II is a reliable method to assess dermal protective clothing performance against polymerizing coatings. Commonly used 5-mil (0.13-mm) latex and nitrile gloves were determined to be ineffective barriers against the isocyanates found in a commonly used clear-coat formulation while butyl gloves were protective.

KEYWORDS: automotive clear coats; butyl rubber; isocyanates; natural rubber latex; nitrile rubber; permeation; gloves

INTRODUCTION

Automotive polyurethane paint systems are complex mixtures of isocyanates (Sparer et al., 2004; Ceballos et al., 2011a). Isocyanates are strong irritants, sensitizers, and a leading cause of occupational asthma (Liu and Wisnewski, 2003; Redlich et al., 2007; Bakerly et al., 2008; Bello et al., 2008; Fisseler-Eckhoff et al., 2011). Animal studies suggest that skin contact with isocyanates may be a significant route of exposure, and may lead to systemic respiratory sensitization, resulting in work-related asthma (Erjefält and Persson, 1992; Rattray et al., 1994; Herrick et al., 2002; Bello et al., 2007). Isocyanates absorbed through the skin can rapidly achieve a dose equivalent to that received through inhalation exposure at established regulatory limits (Thomasen and Nylander-French, 2012). Thus, substantial dermal exposure to isocyanates (Liu et al., 2007; Fent et al., 2008) may occur during spray painting of polyurethane systems, yet information is lacking on the efficacy of the protective clothing used during spray painting (Bello et al., 2008; Ceballos et al., 2011a).

Automotive clear coats are the clear, non-pigmented topcoats that are applied over base-coat paints to improve the general appearance and durability of the vehicle coating system. Clear coats contain the highest isocyanate content of automotive paints (Sparer et al., 2004). Clear coats typically result from the combination of three constituents: the 'clear', mainly comprised of polyols, the 'hardener', which contains isocyanates, and the 'reducer' comprised of solvents (PPG Industries, 1997). It is not possible to predict the surface chemistry of an individual product with any certainty because the manufacturers consider the precise composition of clear-coat systems and the role of individual constituents to be proprietary. The most common isocyanates found in clear coats are monomeric and oligomeric 1,6-hexamethylene diisocyanate (HDI) and monomeric and polymeric isophorone diisocyanate (IPDI) (Sparer et al., 2004). Clear-coat formulations contain a wide variety of solvents including ketones, acetates, and aromatic hydrocarbons (U.S. Environmental Protection Agency, 1999; Ceballos et al., 2011a,b; Tran et al., 2012).

Nitrile gloves have been recommended when handling isocyanate automotive paints Environmental Protection Agency, 1999; Liu et al., 2000). The US Environmental Protection Agency cautions that nitrile gloves may not be protective against strong solvents in automotive paints, such as methyl ethyl ketone, and suggest that butyl may be more protective (U.S. Environmental Protection Agency, 1999). PPG Industries (1997) Berardinelli (1988) have also recommended butyl glove use against automotive paints. However, the recommendations do not address material thickness as a variable of protection partly because a systematic investigation of glove permeation using polyurethane systems has not been conducted. Most collision repair shops use disposable gloves rather than nondisposable chemical protective gloves (Whittaker and Reeb-Whitaker, 2009; Ceballos et al., 2011b) because the former are cheaper and graded as acceptable in some supplier-provided glove compatibility charts. Therefore, there is a need to develop effective best practices for the selection and use of dermal protection during spray of widely used polyurethane paints in the collision repair industry (Bello et al., 2008; Ceballos et al., 2011a,b).

Protective clothing compatibility charts have published some permeation results for pure isocyanates or hardeners, which may only adequately inform workers potentially exposed in a manufacturing plant. Consequently, for the end-user of polyurethane paint systems, it is critical to evaluate clothing permeation using commercial clear-coat formulations (Ceballos et al. 2011a). However, the permeation of polyurethane paint systems is difficult to evaluate using conventional permeation testing (e.g. ASTMF739) because isocyanates have low volatility and low water solubility (Anna, 2003). A complex mixture can complicate conventional permeation testing (Anna, 2003; Chao et al., 2008, Ceballos et al., 2011a). Additionally, the use of conventional immersion permeation testing is not practical for polyurethane paint system that cure (harden), rendering the non-disposable conventional test cell unusable (Ceballos et al., 2011a). Thus, evaluating glove effectiveness for protection against polyurethane paint systems needs to be done using alternative methods such as that suggested by Ceballos et al. (2011a). A novel device, called a permeation panel, was developed to test protective clothing under conditions that simulate spray paint exposure (Ceballos, 2009; Ceballos et al., 2011a). The panel determined permeation of isocyanates (Ceballos et al., 2011a) in a commonly used clear-coat formulation and found that commonly used 5-mil (0.13-mm) latex and nitrile gloves in the collision repair industry by spray painters are not protective.

In this study, a modified permeation panel was tested using a reciprocator (referred to herein as permeation panel II). In order to use the permeation panel II, the panel itself had to be modified so that it could be mounted vertically, a requirement of the reciprocator. The objectives of this study were to (i) minimize paint loading variability in permeation panel experiments to obtain reproducible isocyanate permeation data and (ii) assess isocyanate protective effectiveness of 5-mil (0.13-mm) latex, 5-mil (0.13-mm) nitrile, and 13-mil (0.33-mm) butyl materials against a commonly used automotive clear coat. We provide in this publication preliminary recommendations on the use of protective gloves while using spray-painted clear-coat formulations. In a subsequent paper, the permeation panel II is used to obtain permeation data for solvents and a wider range of glove materials and material thicknesses used in the collision repair industry. The ultimate goal is to identify glove materials that effectively protect against automotive polyurethane paint formulations.

METHODS

Glove materials and clear-coat formulation

The glove materials tested are listed in Table 1. Latex and nitrile materials were selected based on their common use in Washington State's collision repair industry (Whittaker and Reeb-Whitaker, 2009, Ceballos *et al.*, 2011b). Although there is no evidence that butyl gloves are used during spray painting in the collision repair industry, it served as a negative control because butyl material is known to have high chemical resistance and have been recommended for spray painting (Berardinelli, 1988; PPG Industries, 1997; U.S. Environmental Protection Agency, 1999).

Glove material was prepared as described by Ceballos et al. (2011a). Briefly, material was cut from the palm of the glove and thickness was measured (Mitutoyo dial thickness gauge No. 7326S, Victor Machinery Exchange, Inc. Brooklyn, NY, USA). Any powder residue in the glove material was washed with hot water before testing.

The clear-coat formulation used the same hardener, clear 'A', and reducer '" described in Ceballos et al.

Table 1. Total isocyanate permeation rate (ng NCO cm⁻² min⁻¹) and breakthrough time (min) by glove material

Glove material	Description	Average measured	Linear regression		
		thickness, mil, %CV	Permeation rate, ng NCO ^a cm ⁻² min ⁻¹	Breakthrough time, min	R ²
5-mil (0.13-mm) latex	5-mil natural rubber latex powder-free, exam grade SAS Safety Value-Touch, Long Beach, CA, USA	3.9 (3.6)	2.27	<10	0.7
5-mil (0.13-mm) nitrile	5-mil nitrile rubber powder-free, industrial grade Ammex Xtreme, Tukwila, WA, USA	4.1 (6.3)	0.52	<26	9.0
13-mil (0.13-mm) butyl	13-mil butyl rubber industrial grade North", Honeywell, Cranston, RI, USA	13.4 (7.3)	ND^b	>185	Z

Total isocyanate was the sum of HDI and IPDI and monomeric IPDI (equivalent to 0.019–01 μg NCO-IPDI), and 0.2-mg total NCO oligomers. ND = not determined because all values were below the limits of quantitation

 \Box^{p}

63

78

 \mathbb{R}^2

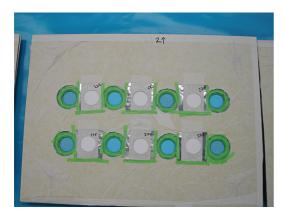
(2011a), mixed with a ratio of 4 parts clear:1 part hardener:1 part reducer and sprayed as recommended by the manufacturer. Isocyanate and solvent composition was reported by Ceballos *et al.* (2011a). The clear-coat formulation resulted in a composition of 0.04% w/w HDI monomer, 0.04% w/w IPDI monomer, 8.0% w/w HDI oligomer, 5.9% w/w IPDI oligomer, 11.8% w/w 2-heptanone, 0.05% w/w methyl isobutyl ketone, 4.0% w/w ethyl benzene, 3.6% w/w toluene, 4.0% w/w *o*-xylene, 9.0% w/w *m*-xylene, and 3.8% w/w *p*-xylene.

Permeation panel II design

Eight second-generation permeation panels were constructed using two aluminum plates $(42 \times 31 \times 0.18 \text{ cm}, \text{Fig. 1})$. Holes (9.5 cm diameter) machined into the top panel plate and holes (7 cm diameter) machined into the bottom panel plate positioned and secured eight permeation cells per panel. Permeation cell design and construction has been previously described (Ceballos, 2009; Ceballos *et al.*, 2011a).

Media used

Quantitative permeation media for isocyanates One-inch (2.54 cm) 1-(2-pyridyl)-piperazine (2-PP)-coated fiber-glass filter circles (SKC 225–9002, SKC Inc., Eighty Four, PA, USA) were prepared and analyzed as described by Ceballos *et al.* (2011a).



1 The front of second-generation permeation panel ready to be sprayed with clear coat. The top surface was covered with masking tape to protect against the clear coat. The panel held eight permeation cells loaded with glove material to measure isocyanate permeation. Six filters were interspaced between the permeation cells for gravimetric analysis to assess the mass of dry clear coat (paint loading) deposited across the panel.

Permeation media blanks

At least two laboratory and two field blanks were also analyzed with each batch sample submission. No blanks were contaminated and therefore no corrections for blanks were made.

Clear-coat loading media

Teflon® filters (Zefluor 47 mm 0.5 mm Supported PTFE P/N P5PQ047 Pall—Life Sciences, Ann Arbor, MI, USA) were prepared, mounted, and analyzed as described by Ceballos et al. (2011a). In brief, the mass gain on the filter accounted for the mass of dry clear coat deposited during the spray application. Six Teflon® filters were housed and mounted between the permeation cells using 50×50-mm²-thick aluminum foil with a 1-inch (2.54 cm) diameter opening (locations shown in Fig. 1). The center of the loading filters aligned with the center of the permeation cells in two rows. The spraying achieved a consistent horizontal stroke as the spray gun moved from right to left; therefore, areas of the panel equidistant from the center of the spray nozzle achieved a homogenous spray pattern. Loading average and percentage of coefficient of variation (%CV) of the Teflon® filters throughout the panel were used to estimate the homogeneity of the spray application. The mass of isocyanate or solvent detected on the permeation media was normalized by dividing by the average loading of dry clear coat on the panel.

Booth conditions and spray painting

The temperature-controlled (~70°F) semi-downdraft paint booth (Spraybake, Coastal Finishing Systems, Bellingham, WA, USA) was monitored using wireless HOBO External Data Loggers (Model H08-004-02; Onset Computer Corporation, Pocasset, MA, USA). Prior to spray application, panels were placed inside the booth for temperature (T) and relative humidity (RH) conditioning. Booth airflow was measured with a Spatial Anemometer ALNOR model RVA501 (TSI Incorporated, Huntington Beach, CA, USA).

A reciprocator or electric paint brush (Compuspray Test Panel Spray Equipment model 360120, Spraymation® Inc., Fort Lauderdale, FL, USA) with a 1.3-mm nozzle fixed gun (LPH400, ANEST IWATA USA, Inc., West Chester, OH, USA) was used to spray toward a reciprocating arm holding the modified permeation panel (Fig. 2).

One experienced painter mixed the paint and operated the spray gun for the first 2 days of experiments and a second experienced painter did this for the third day.

Several parameters were controlled to obtain reproducible and homogeneous spraying conditions. Air pressure at the gun was monitored with a pressure gauge (172 kPa or 25 psi); the distance from the body of the gun to the fan and the fluid control set knobs on the gun were measured with calipers; the gun was checked for secure seating on its holding pin; the gun and its nozzle were aligned with prescribed dots; and the gun's air cheater valve was fully opened. A laser was mounted on the gun to track the panel's centerline to ensure the vertical relationship between the gun and the panel and the proper seating of each panel in the holder was the same between experiments. Before the start of each experiment, a solvent spray pattern check was performed onto a cardboard target. For the permeation experiments, panels were sprayed for ~6 s (equivalent to three passes of clear coat or 1.5 reciprocator cycles) in two separate applications (equivalent to two coats), with ~7 min between applications (to mimic actual product usage when spray painting). In between coats, the gun nozzle was rotated 180 degrees to balance any vertical nozzle bias and provide a homogeneous spray pattern. The panels remained inside the temperature-controlled booth for the duration of the experiment.



2 Permeation panel II set-up. Modified panel is mounted in its reciprocating arm, in line with the spray gun that is fixed at the front of the unit. The painter triggers the spray gun to apply clear coat as the panel moves left to right.

Characterization of the reciprocating permeation panel set-up (permeation panel II)

Experiments to determine the permeation rate and breakthrough time of isocyanates through select glove materials were performed to characterize the reproducibility of the permeation panel II, see Table 2. Filter media were placed throughout the panel to measure isocyanates for the same glove material and clear-coat formulation (Table 2). Permeation times were recorded starting at the end of the second (final) spraying application and ranged from 10 to 184 min (Supplementary Table 1, available at Annals of Occupational Hygiene online). Permeation time was the time at which the solid media was collected from the permeation cell. Experiments to measure permeation at different time points were performed on three separate days for latex and nitrile materials and on one day for butyl material (Table 2).

For the purpose of this publication, we call permeation as the accumulated mass collected on the permeation media touching the inner surface of the glove material per mass of dry clear coat loaded at a specific time point. Permeation rate and breakthrough time for the linear regression of total isocyanates were calculated as described by Ceballos et al. (2011a). The permeation rate (ng cm⁻² min⁻¹) was equivalent to the slope (ng mg⁻¹ min⁻¹) multiplied by the average loading of the permeation cells for all panels (45 mg) and divided by the cross-sectional area of the glove material exposed (5 cm²). This permeation rate is equivalent to the steady state permeation rate described by traditional permeation cell experiments. The estimated breakthrough time was the time at which the predicted line regression intersected with the *x*-axis or y-axis. When no data points were available to confirm the estimated breakthrough time, the earliest time point with a permeation result above the limit of detection was used as the breakthrough time. Variability for the loading of dry clear coat was assessed by one-way analysis of variance for factors such as day, panel, and spray painter.

Collection of permeation and loading samples

Permeation media were randomly removed from the permeation cells at pre-specified times after spraying as shown in Fig. 3 and described in Ceballos *et al.* (2011a). 2-PP filter samples were stored, transported, and analyzed as described by Ceballos *et al.* (2011a).

Downloaded from http://annhyg.oxfordjournals.org/ at CDC Public Health Library & Information Center on February 20, 2014

Table 2. Permeation experiments using two types of permeation media" and one clear coat formulation

Day	Spray	Panel	Glove	Average	At panel		At spray gun		Average
	painter	name	material [®]	loading dried clear coat ^c , mg (%CV)	Average temperature ^{d} , ${}^{\circ}$ F (%CV)	Average relative humidity ^d , %RH (%CV)	Average temperature ^{d} , $^{\circ}$ F (%CV)	Average relative humidity ^d , %RH (%CV)	booth air flow d,e , ft 3 min $^{-1}$ (m 3 min $^{-1}$)
П	1	·II	5-mil latex	46.3 (1.9)	71.9 (0.4)	27.1 (3.9)	72.2 (1.0)	27.7 (7.7)	6445 (185)
		ii	5-mil nitrile	45.8 (2.2)					
2	1	·ī	13-mil butyl	44.9 (2.3)	68.7 (0.7)	35.1 (2.6)	71.4 (0.7)	31.5 (3.3)	5885 (166)
		>	5-mil latex	44.4 (3.8)					
		vi	5-mil nitrile	42.7 (3.1)					
3	2	·ī	5-mil latex	43.3 (6.7)	66.8 (4.1)	25.2 (2.9)	66.6 (4.5)	25.3 (3.0)	6954 (197)
		viii	5-mil nitrile	47.5 (3.4)					
				45.0 (4.9)	69.1 (3.7)	29.1 (17.9)	70.1 (4.3)	28.2 (11.0)	6428 (182)

"Media = a total of 4, 1-inch diameter, 1-(2-pyridyl)-piperazine-coated fiber-glass filters to capture isocyanates were used per panel.

**Latex material was S-mil (0.13-mm) powder-free exam grade; nitrile material was S-mil (0.13-mm) powder-free industrial grade; and butyl material was 13-mil (0.33-mm) industrial grade.

Loading of dried clear coat per permeation cell was calculated using gravimetric analysis of eight PTFE filters spaced between the permeation media. Temperature, relative humidity, and booth air flow measurements apply to all the panels used within the same day.

Twenty linear velocity measurements were performed in a grid 2-5 cm from the spray booth exhaust vents. Volumetric flow (ft³ min⁻¹ or m³ min⁻¹) was calculated by multiplying the average velocity in ft min⁻¹ (m min^{-1}) with the exhaust surface area in ft² (m^2). Collection, storage, and analysis of Teflon® filters, as well as permeation panel, clean up and transport followed that described by Ceballos *et al.* (2011a).

RESULTS

Seven permeation panel II experiments using the same clear-coat formulation resulted in an average loading of dry clear coat of 45.0 mg per 5.1 cm² with a CV of 4.9% with a range of 1.9-6.7% (Table 2). The panel with the highest loading variability (Day 3, Panel viii, with 6.7%CV) had one high loading value of dry paint mass of 48.9 mg per 5.1 cm² (Supplementary Table 2, available at Annals of Occupational Hygiene online), which if removed would result in a Panel viii average loading variability of 2.5%CV instead of 6.7%CV. Although high, this value was not higher than 2.5 SD from the panel mean, so it was preserved in the analysis. One-way analysis of variance of all the loading results determined that there were no significant differences in loading due to spray painter (P = 0.445). However, significant differences in loading were found due to panel (P = 0.0001) and day (P = 0.026).

Latex material (average measured thickness of 0.10 mm or 3.9 mil) exhibited a total isocyanate permeation rate greater than nitrile material (average measured thickness 0.10 mm or 4.1 mil, Table 1). Both materials presented permeation at all time points suggesting a fast isocyanate breakthrough (Fig. 4). Butyl material (average measured thickness of 0.34 mm or

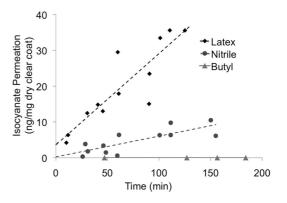


3 Opened permeation cell showing solid media. Isocyanate permeation was measured using 1-inch diameter 1-(2-pyridyl)-piperazine-coated fiber-glass filters analyzed by a modified version of the OSHA 42/PV2034 methods.

13.4 mil) exhibited no permeation or breakthrough for isocyanates under the tested conditions (Table 1). Detailed isocyanate permeation data with respect to post spray time is presented in Supplementary Table 1 (available at *Annals of Occupational Hygiene* online).

DISCUSSION

The first goal of this study was to minimize the variability of paint loading across the permeation panels. We developed a method to measure isocyanate permeation against sprayed coatings in a reproducible manner. The Ceballos et al. (2011a) permeation panel was modified and used with an automatic reciprocator rather than relying upon manual spray. Using permeation panel I, Ceballos et al. (2011a) reported an average loading variability of 11.9%CV in the range of 8.8-15.5%CV after running 10 permeation panel experiments. Thus, the permeation panel II reduced the variability by more than half, both in average (4.9%CV versus 11.9%CV) and range of variability (1.9-6.7%CV versus 8.8-15.5%CV) when studying a total of seven permeation panel experiments. The permeation panel II resulted in paint loading across the panel within the range of 2–5%CV, a range of variation that was expected and is typical of the reciprocator used (Diana Ceballos and Spraymation® Inc., personal communication, Spraymation® Inc.). The low loading variability was achieved regardless of whether the same or different spray painters operated the spray gun. The set-up described in Ceballos et al. (2011a)



4 Total isocyanate (NCO) permeation by glove material in time post spraying fitted to a linear regression. Permeation rate was in the following order: latex > nitrile > butyl. Values for butyl glove material were below the LOQ and were replaced by LOQ/sqrt(2).

reported no significant difference between panel-to-panel and day-to-day variability, whereas the permeation panel II showed significant differences due to panel (P=0.0001) and day (P=0.026). These differences are likely due to the smaller within-test variability, which enhances the ability to detect changes with the analysis of variance. To account for day-to-day and panel-to-panel variability, individual cell permeation data was normalized using the average mass loading data for each panel.

The second goal of this study was to assess the effective protectiveness of 5-mil (0.13-mm) latex, 5-mil (0.13-mm) nitrile, and 13-mil (0.33-mm) butyl materials against isocyanates found in a commonly used automotive clear coat. Latex material was found to be more readily permeated than nitrile material of similar thickness by isocyanates present in the tested clear-coat formulation (Table 1, Fig. 4). Permeation for latex and nitrile was measurable at all of the time points sampled (Supplementary Table 1, available at Annals of Occupational Hygiene online). Predicted linear models suggest immediate breakthrough as evidenced by the regression line intersecting the y-axis before the x-axis. In the experiments described here, initial permeation sampling first occurred at 10 min (latex) and 26 min (nitrile). Samples could be taken earlier than 10 min in future experiments to better identify at what time point on the regression line samples go from being below the limit of detection to being quantifiable. It is noted that the first data point for nitrile at 26 min is very close to the analytical limit of quantitation (Supplementary Table 1, available at Annals of Occupational Hygiene online), indicating that a breakthrough of nitrile material near 26 min is the earliest that could have been detected using the analytical methods described here.

The findings of nitrile performing better than latex confirm industry and agency glove recommendations for spray painting (PPG Industries, 1997; U.S. Environmental Protection Agency, 1999; Health and Safety Executive, 2007). However, the findings are of concern considering many spray painters continue to use 4-mil to 5-mil (0.10-mm to 0.13-mm) latex and nitrile gloves, with the nitrile being used with a sense of confidence in their level of protectiveness (Ceballos *et al.* 2011b). We also found that butyl material did not exhibit isocyanates permeation under the tested conditions, exhibiting more protectiveness than latex

and nitrile materials. This finding also confirms the chemical protective properties of butyl material and as such has been recommended for use by spray painters (Berardinelli, 1988; PPG Industries, 1997; U.S. Environmental Protection Agency, 1999).

The latex material permeation rate of 2.27 ng NCO cm⁻² min⁻¹ derived from a linear regression supports findings reported in Ceballos et al. (2011a) where the permeation rate was 2.90 ng NCO cm⁻² min⁻¹. Although the same clear coat and spray conditions (e.g. temperature) were used in both studies, the small difference in permeation rate may be attributed to the modifications in the permeation panel set-up. Spray paint loading was also different between the two experiments but the corrections performed to account for loading seem to have accounted for the difference. Average loading for Ceballos et al. (2011a) was 34 mg dry paint per 5.1 cm², whereas average loading for this study was 45 mg dry paint per 5.1 cm². As reported by Ceballos et al. (2011a), we did not find isocyanate oligomers permeating the glove materials tested and HDI monomer dominated the permeation compared with IPDI monomer (Supplementary Table 1, available at *Annals of Occupational Hygiene* online).

As stated by Tran et al. (2012), a limitation of the current permeation experiments is that mass measured in the solid media does not differentiate from permeation and penetration through the glove material. To minimize the potential for penetration in our experiments, each glove was inspected to avoid perforations or large pores in the samples tested. Another limitation of our study is that there are no commercially available butyl gloves of the similar thickness as the latex and nitrile materials tested; however, thickness is a variable that affects permeation through a material (Jencen and Hardy, 1989). Further, it was not possible to control for material grade (industrial or exam); we encourage grade to be considered a variable for future studies. Also, this study tested gloves from the same box; therefore, it did not take into consideration the variability of the different lots of the product. Lastly, more data points would help validate with better accuracy the estimated breakthrough times having in consideration detection limits of the chemical analysis.

The main advantage of the permeation panel II described here was the minimized variability of paint loading across the surface of the panel that allowed for

easier comparison of permeation test cells. Another advantage of the current set-up was that the permeation panel II was lighter, smaller, cheaper to construct, and more versatile than its predecessor, the permeation panel I. Additionally, the 2-PP filter media provided a practical method to measure isocyanate permeation rate and breakthrough time for different glove materials. This method may be used also for the testing of other protective clothing materials including coveralls (Broadwater *et al.*, 2011). As this method becomes standardized, it may be possible to use fewer samples to characterize permeation.

Thin, 5-mil (0.13-mm) latex and nitrile gloves were not protective against a sprayed automotive clear coat. Butyl gloves would be recommended based on their protection efficacy; however, commercially available 0.33-mm or 13-mil (0.33-mm) butyl gloves may not have the dexterity and fit desired by most spray painters (U.S. Environmental Protection Agency, 1999). The findings from this study should be considered for future interventions to improve the selection and use of protective gloves by spray painters.

CONCLUSIONS

The permeation panel II provided reliable and consistent paint loading of clear coat applied on the glove materials for permeation testing. Permeation rate and breakthrough time showed that 5-mil (0.13 mm) latex and nitrile may not provide adequate protection to spray painters with the tested clear-coat formulation. Lower permeation of nitrile material compared with latex material indicated that nitrile material is superior than latex at protecting against isocyanate found in the clear-coat formulations. A thicker nitrile glove material may be needed to provide acceptable protection. Butyl material of 13 mil (0.33 mm) provided adequate protection against the tested clear-coat formulation. However, potential interventions to promote the use of butyl gloves may face challenges. Butyl gloves are more expensive than latex and nitrile disposable gloves and may not provide the dexterity and fit sought by spray painters. Butyl gloves are a typically a multiple-use glove rather than a single-use disposable glove. Research with glove manufacturers to design and manufacture butyl gloves that would appeal to spray painters is warranted, as well as field studies assessing the use and reuse efficacy of any new generation butyl-based gloves.

SUPPLEMENTARY DATA

Supplementary data can be found at http://annhyg.oxfordjournals.org/.

FUNDING

National Institute for Occupational Safety and Health (NIOSH R01 OH009364-01).

ACKNOWLEDGEMENTS

Thanks to the University of Washington's Environmental Health Lab for chemical analysis, especially Jianbo Yu. Thanks to Michael Morgan for support and mentoring and Mark Davey, Maria Tchong-French, Cole Fitzpatrick, and Todd Schoonover for their assistance in the field. Thanks to Green River Community College Autobody Program for their support, especially Keith Line for his knowledge and spraying of the panel.

REFERENCES

- Anna DH. (2003) Chemical protective clothing. Fairfax, VA: AIHA Press. ISBN-10: 1931504466.
- Bakerly ND, Moore VC, Vellore AD *et al.* (2008) Fifteen-year trends in occupational asthma: data from the Shield surveillance scheme. Occup Med (Lond); 58: 169–74.
- Bello D, Herrick CA, Smith TJ et al. (2007) Skin exposure to isocyanates: reasons for concern. Environ Health Perspect; 115: 328–35.
- Bello D, Redlich CA, Stowe MH *et al.* (2008) Skin exposure to aliphatic polyisocyanates in the auto body repair and refinishing industry: II. A quantitative assessment. Ann Occup Hyg; 52: 117–24.
- Berardinelli SP. (1988) Prevention of occupational skin disease through use of chemical protective gloves. Dermatol Clin; 6: 115–9.
- Broadwater K, Sasakura M, Ceballos D, *et al.* (2011) Assessing isocyanate permeation of used coveralls in the auto body repair industry [Abstract]. In: American Industrial Hygiene Association Conference 2011, Portland, OR.
- Ceballos D. (2009) Evaluation of protective gloves used in the collision repair industry. PhD dissertation, ProQuest® publication number 3377073. Seattle, WA: Department of Environmental and Occupational Health Sciences, School of Public Health, University of Washington.
- Ceballos DM, Fent KW, Whittaker SG *et al.* (2011b) Survey of dermal protection in Washington State collision repair industry. J Occup Environ Hyg; 8: 551–60.
- Ceballos DM, Yost MG, Whittaker SG *et al.* (2011a) Development of a permeation panel to test dermal protective clothing against sprayed coatings. Ann Occup Hyg; 55: 214–27.

- Chao KP, Hsu YP, Chen SY. (2008) Permeation of aromatic solvent mixtures through nitrile protective gloves. J Hazard Mater; 153: 1059–66.
- Erjefält I, Persson CG. (1992) Increased sensitivity to toluene diisocyanate (TDI) in airways previously exposed to low doses of TDI. Clin Exp Allergy; 22: 854–62.
- Fent KW, Jayaraj K, Ball LM *et al.* (2008) Quantitative monitoring of dermal and inhalation exposure to 1,6-hexamethylene diisocyanate monomer and oligomers. J Environ Monit; 10: 500–7.
- Fisseler-Eckhoff A, Bartsch H, Zinsky R *et al.* (2011) Environmental isocyanate-induced asthma: morphologic and pathogenetic aspects of an increasing occupational disease. Int J Environ Res Public Health; 8: 3672–87.
- Health and Safety Executive. (2007) COSHH and vehicle spray painters—key messages. Available at http://www. hse.gov.uk/coshh/industry/mvr.htm. Accessed April 2013.
- Herrick CA, Xu L, Wisnewski AV et al. (2002) A novel mouse model of diisocyanate-induced asthma showing allergictype inflammation in the lung after inhaled antigen challenge. J Allergy Clin Immunol; 109: 873–8.
- Jencen DA, Hardy JK. (1989) Effect of glove material thickness on permeation characteristics. AIHA J; 50: 623–6.
- Liu Q, Wisnewski AV. (2003) Recent developments in diisocyanate asthma. Ann Allergy Asthma Immunol; 90(Suppl. 2): 35–41.
- Liu Y, Bello D, Sparer JA et al. (2007) Skin exposure to aliphatic polyisocyanates in the auto body repair and refinishing industry: a qualitative assessment. Ann Occup Hyg; 51: 429–39.

- Liu Y, Sparer J, Woskie SR *et al.* (2000) Qualitative assessment of isocyanate skin exposure in auto body shops: a pilot study. Am J Ind Med; 37: 265–74.
- PPG Industries. (1997) PPG two-component polyurethane coating systems guidelines for safe use. PAM 9379 8/97.
- Rattray NJ, Botham PA, Hext PM et al. (1994) Induction of respiratory hypersensitivity to diphenylmethane-4,4'-diisocyanate (MDI) in guinea pigs. Influence of route of exposure. Toxicology; 88: 15–30.
- Redlich CA, Bello D, Wisnewski AV. (2007) Isocyanate exposures and health effects. In: Rom WN, editor. Environmental and occupational medicine. Philadelphia, PA: Lippincott-Raven. pp. 502–16.
- Sparer J, Stowe MH, Bello D et al. (2004) Isocyanate exposures in autobody shop work: the SPRAY study. J Occup Environ Hyg; 1: 570–81.
- Thomasen JM, Nylander-French LA. (2012) Penetration patterns of monomeric and polymeric 1,6-hexamethylene diisocyanate monomer in human skin. J Environ Monit; 14: 951–60.
- Tran JQ, Ceballos DM, Dills RL *et al.* (2012). Transport of a solvent mixture across two glove materials when applied in a paint matrix. J of Hazard Mat; 63: 169–76.
- U.S. Environmental Protection Agency. (1999) Choosing the right gloves for painting cars. Publication EPA/744-F-00-005. Available at http://www.epa.gov/dfe/ pubs/auto/gloves/gloves.pdf. Accessed April 2013.
- Whittaker SG, Reeb-Whitaker C. (2009) Characterizing the health and safety needs of the collision repair industry. J Occup Environ Hyg; 6: 273–82.