Annals of Work Exposures and Health, 2019, Vol. 63, No. 5, 592–603
doi: 10.1093/annweh/wxz032
Advance Access publication 8 May 2019
Original Article

Original Article

Evaluation of Disposable Protective Garments against Isocyanate Permeation and Penetration from Polyurethane Anticorrosion Coatings

Michael P. Mellette[1,*], Dhimiter Bello[2], Yalong Xue[3], Michael Yost[4], Anila Bello[1] and Susan Woskie[1]

[1]Department of Public Health, University of Massachusetts Lowell, One University Avenue, Lowell, MA 01854, USA; [2]Department of Biomedical and Nutritional Sciences, University of Massachusetts Lowell, One University Avenue, Lowell, MA 01854, USA; [3]Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, MA 01854, USA; [4]Department of Environmental and Occupational Health Sciences, School of Public Health, University of Washington, 1959 NE Pacific Street, Seattle, WA 98195, USA

*Author to whom correspondence should be addressed. Tel: 1-(978) 339-9319; e-mail: michael.mellette@gmail.com.

Submitted 15 November 2018; revised 28 March 2019; editorial decision 2 April 2019; revised version accepted 17 April 2019.

Abstract

Background: Polyurethanes are a class of isocyanate-based organic coatings commonly used to control corrosion on high-value metallic structures. Despite their widespread use, dermal exposure to these isocyanate-containing coatings presents a significant occupational health risk to workers, including the development of allergic and irritant contact dermatitis and systemic sensitization. At present, little is known about the effectiveness of the protective garments commonly used to prevent dermal exposure to polyurethane coatings in construction trades.

Objectives: The primary objective of this study was to measure the permeation and penetration of isocyanates from polyurethane anticorrosion coatings though a selection of protective garments. In addition, a standardized spray procedure using a fixed-position spraying technique was evaluated as an option to minimize variability in coating application.

Methods: Five disposable garment materials were evaluated for resistance to isocyanates during this study: latex gloves (0.076 mm), nitrile gloves (0.078 mm), Tyvek coveralls (0.105 mm), polypropylene/polyethylene (PP/PE) coveralls (0.116 mm), and a cotton t-shirt (0.382 mm). A permeation test cell system was used to evaluate each garment material against two products: a polyurethane zinc-rich primer based on 4,4′-methylene diphenyl diisocyanate and an aliphatic finish coating based on prepolymers of 1,6-hexamethylene diisocyanate. Glass fiber filters pretreated with 1-(9-anthracenylmethyl)piperazine were used to collect penetrating isocyanates during the 120-min test period, which were analyzed by liquid chromatography–tandem mass spectrometry.

Polytetrafluoroethylene loading filters were sprayed in series with permeation test cells and analyzed gravimetrically to assess the homogeneity of coating application.

Results: The latex gloves demonstrated the highest rate of isocyanate permeation of all evaluated garments during testing with both coatings (primer: 27.38 ng cm^{-2} min^{-1}; finish coating: 7.39 ng cm^{-2} min^{-1}). Nitrile gloves were much more resistant than latex gloves (primer: 1.89 ng cm^{-2} min^{-1}; finish coating: 1.26 ng cm^{-2} min^{-1}) and were not permeated by the finish coating until after 15 min. The PP/PE coverall provided the most consistent resistance to both coatings (primer: 0.08 ng cm^{-2} min^{-1}; finish coating: 1.27 ng cm^{-2} min^{-1}), whereas the Tyvek coverall was readily permeated by the primer (primer: 3.47 ng cm^{-2} min^{-1}; finish coating: 0.87 ng cm^{-2} min^{-1}). The cotton t-shirt was rapidly permeated by the primer during the first 5 min of exposure (primer: 146.65 ng cm^{-2} min^{-1}; finish coating: 4.64 ng cm^{-2} min^{-1}). In addition, the fixed-position spraying technique used during this study demonstrated a significant reduction in loading variability within each batch of test cells when compared to manual spray application.

Conclusion: Nitrile gloves demonstrated superior resistance to both isocyanate-containing coatings in comparison to latex gloves. Although both coverall materials were resistant to permeating isocyanate within the established thresholds, the PP/PE coverall provided more consistent resistance to both coatings. Owing to the cotton t-shirt's high rate of penetration with both coatings, it is recommended only as a secondary barrier. Study results showed that the use of fixed-position spray techniques provided consistent and reproducible results within each batch of test cells. Additional test design modifications are necessary to further reduce variability between batches and ensure more consistent coating thickness.

Keywords: construction; coveralls; gloves; isocyanate; painter; permeation; polyurethane coating

Introduction

Polyurethanes coatings are formed during a polymerization reaction between isocyanates and active-hydrogen-containing compounds including water, alcohols, and amines (Bello *et al.*, 2004; Knudsen and Forsgren, 2017). Polyurethane coatings are commonly used for corrosion control on high-value metallic structures (e.g. bridges, storage tanks, wind turbines) for their excellent resistance to water, chemicals, and abrasion. These coatings are typically applied over large surface areas using high-volume low-pressure (HVLP) spray systems or with a roller or brush (Knudsen and Forsgren, 2017). Polyurethane coating demand continues to grow in response to our aging infrastructure. In the USA, >56 000 bridges are in need of repair or replacement (Federal Highway Administration, 2017; Kirk and Mallett, 2018). To support this demand, the general industrial coatings sector is expected to reach 8.9 million metric tons and $23 billion in global sales by 2020 (Pianoforte, 2018). In addition, industrial coating jobs are expected to increase by 6% in the next decade to >400 000 workers by 2026 (Bureau of Labor Statistics, 2018).

The application of polyurethane coatings creates a high potential for airborne and dermal exposure to these isocyanate-containing materials. Inhalation exposure has historically been the primary route of concern in the occupational setting and has been associated with severe respiratory diseases such as hypersensitive pneumonitis, reactive airway dysfunction syndrome, and isocyanate-induced asthma (Rom and Markowitz, 2007; Redlich and Herrick, 2008; Redlich, 2010). Significant health effects have also been associated with isocyanate skin exposures that range from mild or temporary localized irritation to allergic contact dermatitis (Larsen *et al.*, 2001; Daftarian *et al.*, 2002; Engfeldt *et al.*, 2012; Kieć-Świerczyńska *et al.*, 2014). Considerable evidence exists to suggest that dermal exposure to isocyanates leads to systemic sensitization and an increased risk for occupational asthma (Bello *et al.*, 2007; Redlich and Herrick, 2008; Cochrane *et al.*, 2015; Lockey *et al.*, 2015). This evidence highlights the importance of protective garment use with polyurethane coatings, however, there is limited information available to workers about barrier material effectiveness and proper garment selection.

The effectiveness of a protective garment is dependent upon its ability to prevent chemical transfer from the outside surface of the material onto the skin of the worker. Chemical transfer through highly impermeable barriers such as chemical-resistant gloves typically occurs through molecular diffusion (i.e. 'permeation') or physical degradation of the material. Breathable membranes and other porous materials are typically 'penetrated' by the chemical through voids or gaps in the garment material on a non-molecular level. The process of penetration is independent from molecular diffusion.

Although chemical resistance data are available from some protective garment manufacturers, this information is generally limited to a few monomeric isocyanate compounds such as toluene diisocyanate. Chemical resistance data do not commonly include many of the monomeric or polymeric forms of isocyanates that are found in polyurethane coatings. Garment manufacturers typically obtain this information using standard permeation test methods such as American Society for Testing and Materials (ASTM) method F739 (ASTM F739 2012) and International Organization for Standardization (ISO) Standard 6529 (ISO 6529 (2013). These test methods are not suitable for testing polymerizing materials as they will harden inside of the test apparatus and they do not take into account the product matrix effect (e.g. solvents, viscosity, solid additives) on garment stability and compound permeability.

A variety of permeation studies have been conducted to evaluate chemical protective clothing against polymerizing materials. Ceballos *et al.* (2011) developed a permeation test cell system to evaluate the effectiveness of latex gloves during contact with spray-applied automotive clear coats containing aliphatic isocyanates. Individual test cells containing solid test media were mounted on a fixed panel and manually sprayed with the clear coat. The test media was removed at times ranging from 6 to 91 min to establish a permeation profile. Although this test method was found to be reliable, the results were highly dependent upon the homogeneity of coating application (i.e. coating thickness). A robotic spray system was used during subsequent studies to significantly reduce average coating loading variability by more than half from 4.9 to 11.9%CV (Ceballos *et al.*, 2014b). These studies are important because they evaluate garment effectiveness against actual paint formulations using spray application to simulate realistic coating deposition.

Previous studies with spray-applied polyurethane coatings (Ceballos *et al.*, 2011, 2014b) have evaluated only the permeation of aliphatic [1,6-hexamethylene diisocyanate (HDI)- and isophorone diisocyanate-based] automotive clear coats, which vary significantly in isocyanate types (i.e. aromatic and aliphatic), solvent composition, and higher solids content when compared to the anticorrosion coatings used on high-value steel structures. Because these differences in formulation may significantly affect garment effectiveness, this study has specifically evaluated the resistance of five protective garments materials against permeation and penetration from two isocyanate-containing corrosion control coatings commonly used by industrial painters for outdoor steel structures. In addition, as an alternative to the robotic spray system used by Ceballos *et al.* (2014b), this study has evaluated a less expensive option to minimize spray variability during coating application and increase reproducibility using a fixed-position spray application technique.

Methods

Protective garment selection

Field observations and ancillary discussions with industrial painters have identified a wide range of protective garments used during industrial painting. Disposable nitrile and, to a lesser extent, latex protective gloves were commonly observed and therefore selected for testing. A focus was placed on thinner and lower-cost protective gloves readily available from 'brick and mortar' retailers to evaluate worst-case conditions for permeation. This focus was further supported by a protective garment survey identifying a preference for lower cost and thinner gloves due to their comfort and dexterity in a similar industry (Ceballos *et al.*, 2014a).

The types of protective clothing observed in the field varied significantly, ranging from hooded protective coveralls to typical 'street clothing'. On the basis of these observations, a disposable Tyvek and polypropylene and polyethylene (PP/PE) blend coverall were selected for testing. Both coveralls were readily available from brick and mortar retailers and recommended for painting applications. A 'heavy weight' [145 g m^{-2} (6.1 oz yd^{-2})] cotton t-shirt was also tested to evaluate the effectiveness of similar street clothing as a protective barrier.

A JEOL 7401F Field-Emission Scanning Electron Microscope (FE-SEM) was used to image the pore structure and fiber matrix of each 'breathable' clothing material. FE-SEM images from each clothing specimen have been included as Supplementary Figure 1 (available at *Annals of Work Exposures and Health* online). Descriptions for each of the five garment materials and their average measured thickness are summarized in Table 1.

Test chemical selection

A polyurethane zinc-rich primer and an aliphatic finish coating were tested based upon their observed use in the field and recommendations from their manufacturer for use on steel and marine structures. These coatings were also approved for use together as a multicomponent paint system for structural steel in high corrosion environments. Typically, a zinc-rich primer is applied on new or abrasive-blasted steel, followed by an intermediate coating (three coat system) and/or an aliphatic finish coat (two coat system).

The zinc-rich primer was composed of two separate parts mixed prior to application. Part 'A' was composed of the moisture-cured polyurethane binder containing 10–17% polymeric 4,4′-methylene diphenyl diisocyanate (MDI), 4% pure MDI, 1% generic MDI, and ≤3% *p*-toluenesulfonyl isocyanate, along with a blend of organic solvents and crystalline silica. The Part 'F' contained a zinc-dust additive that was mixed into the binder to provide cathodic corrosion protection. Analysis of the zinc dust by FE-SEM showed mostly spherical particles with polydispersed sizes ranging from 100 nm to 10 µm in diameter (see Supplementary Figure 2, available at *Annals of Work Exposures and Health* online). Small batches of primer were prepared by maintaining the binder to zinc-dust ratios provided in the product's technical data sheet (0.5-l binder: 0.9-kg zinc dust). The primer's dark green color provided adequate contrast to visualize garment penetration on the white collection media.

The aliphatic finish coating was a single part moisture-cured polyurethane coating containing 20–49% HDI polymer, ≤0.3% 1,6-HDI, and ≤3% *p*-toluenesulfonyl isocyanate, along with a blend of organic solvents, white pigmented titanium dioxide, and crystalline silica. The coating's white color did not provide adequate contrast to visualize garment penetration. A compatible red tint was added to each batch of coating to aid with visual indication. Additional information about the characteristics of each coating has been provided in Table 2. Each isocyanate bulk material was analyzed and characterized independently according to our earlier published protocols as described in the 'Sample analysis and quality control' (Bello *et al.*, 2002; Harari *et al.*, 2016).

Table 1. Tested garment materials and measured thicknesses.

Garment type	Manufacturer	Product no.	Thickness [mm (mils)][a,b]
Disposable gloves			
Latex	HDX	432202	0.076 (3.0)
Nitrile	HDX	953849	0.078 (3.1)
Clothing			
Tyvek coverall	Trimaco	14113	0.105 (4.1)
PE/PP[c] coverall	3M	4540+	0.116 (4.6)
Cotton shirt	Champion	T425	0.382 (15.0)

[a]Average thickness of all specimens measured with a dial caliper.
[b]1 mil = 0.001 in.
[c]PE/PP laminate film.

Test cell design

A complete description of the test cell system, to include its assembly and garment specimen preparation, is described in Mellette *et al.* (2018). Each test cell was mounted individually on a 15.24 × 15.24 cm single-walled corrugated cardboard panel to facilitate the efficient retrieval of solid collection media and simplify clean-up (see Fig. 1). The face of each test cell was masked with non-isocyanate containing painter's tape (ScotchBlue 2090; 3M Company, St Paul, MN, USA) to protect it from overspray.

Spray coating application process

A HVLP gravity-fed spray gun and two-stage 5.0 psi turbine (Fuji 2203G; Fuji Industrial Spray Equipment Ltd, Toronto, Ontario, Canada) with a 1.8-mm nozzle was used to apply each test coating. The spray gun was mounted 20 cm from the point of application in a ventilated fume hood and aligned with the center of each cardboard panel (see Fig. 1). The coating was consistently applied to each material by maintaining a constant spray interval of 8 s and fixing the spray gun adjustments (i.e. airflow, fluid volume, and spray pattern) throughout each batch of test cells. Prior to each test session, the spray system was visually calibrated using aluminum blanks to achieve the desired coverage. Variations in applied coating were found to occur at fixed settings after

Table 2. Characteristics of polyurethane test coatings.

Coating type	Isocyanates[a]		Solids[b]	Viscosity[c]	Surface cure
	(% weight)	(% volume)	(% volume)	(cm^2 s^{-1})	Time[b] (min)
Zinc-rich primer (MDI-based)	3.4–7.7	6.3–14.1	62	0.48	20
Aliphatic Finish (HDI-based)	20.0–52.3	23.9–62.2	52	4.63	60

[a]Derived from manufacturer-reported data and the mass of individual coating components.
[b]As reported by the manufacturer.
[c]Coating measured with #4 Ford viscosity cup. Zinc-rich coating was tested as mixed (i.e. with zinc dust).

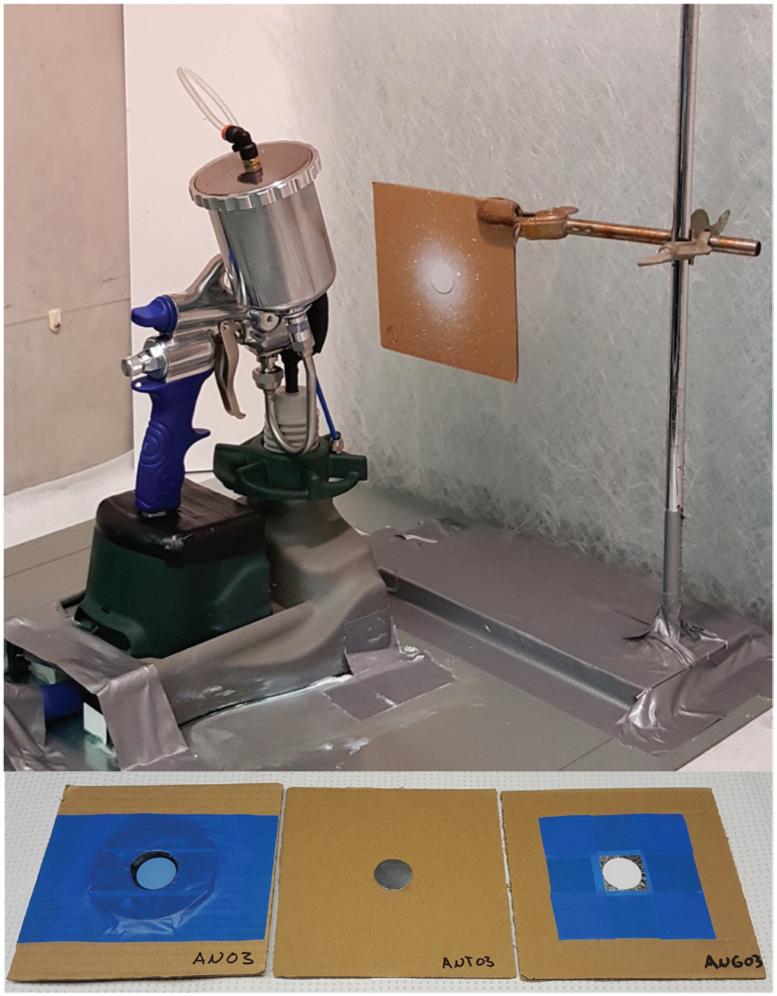

Figure 1. (Top) Coating application was conducted using a fixed-position spray gun and an 8-s spray interval to minimize loading variability from spray gun stroke speed, number of passes, and nozzle distance. (Bottom–left to right) Permeation test cells, aluminum thickness blanks, and gravimetric loading filters were individually mounted on 15.24 × 15.24 cm single-walled corrugated cardboard panels to facilitate the efficient collection of solid test media and simplify clean-up.

spray gun disassembly and cleaning, requiring the adjustment of spray gun settings between batches. A coating thickness of ~0.08 mm [3.0 mils (1 mil = 0.001 in.)] was found to provide consistent coverage without excessive run-off with both coatings. A computer-based timer with audible alarm was used to indicate the beginning and end of each spray interval and to monitor elapsed time for solid media collection.

Permeation/penetration sample collection

The solid collection media was removed from each test cell at pre-established times following coating application. Collection times ranged from 5 to 120 min and included 3 replicate samples at each time point. A total of 16 samples were collected with each batch of test cells to include 15 permeation/penetration samples and one field blank. An initial time point of 5 min was selected based upon breakthrough during similar studies with isocyanate-containing clear coats (Ceballos *et al.*, 2011, 2014b). An end point of 120 min was chosen based upon the tack-free times (i.e. surface cure) of each coating. Detailed sample collection and desorption procedures were conducted as described in Mellette *et al.* (2018).

Gravimetric loading and thickness samples

Eight gravimetric loading samples were sprayed with each batch of test cells. Average loading and the percent coefficient of variation (%CV) were used to quantitatively assess the homogeneity of coating and compare loading variability with similar studies (Ceballos *et al*., 2011, 2014b). 37-mm polytetrafluoroethylene (PTFE) filters (Polyflon PTFE fiber filters; Toyo Roshi International Inc., Los Angeles, CA, USA) were mounted using pre-punched aluminum foil with a 2.54-cm diameter opening identical to the area of the test cell window. PTFE filters were pre-and post-conditioned in a desiccant chamber for 24 h. Gravimetric loading filters were cured at room temperature for 72 h post application in accordance with the coating cure times. Gravimetric measurements were conducted in an environmental chamber using an analytical balance (Model XP26; Mettler-Toledo, LLC, Columbus, OH, USA) with a 0.001-mg resolution.

Eight aluminum blanks (Part no.: L400021-RD-1000 [25.4 mm × 0.81 mm]; Rose Metal Products Inc., Springfield, MO, USA) were used to visually monitor coating application and determine the average dry coating thickness for each batch of test cells. Each blank was premeasured using a dial caliper and remeasured after 72 h of coating application. Both the loading filters and blanks were mounted centered on cardboard panels similar to each test cell (see Fig. 1).

Isocyanate direct-loading samples and theoretical protection factors

A total of 10 PTFE filters (5 per coating type) were sprayed directly with each coating to determine the amount of isocyanate deposited under conditions of unprotected skin exposure. Direct loading data were used to establish theoretical 'protection factors' for each coating and garment combination. These theoretical protection factors (PFs) describe the ratio between isocyanate surface loading under the test conditions and the expected amount of isocyanate permeation or penetration on the inside of each garment. Theoretical PFs were calculated using the following equation:

$$PF = \frac{L_o}{L_i}$$

where PF is the theoretical protection factor (unitless); L_o is the expected isocyanate surface loading at 0.08-mm (3.0 mils) coating thickness (ng cm^{-2}) using the average values for direct loading with each type of coating; L_i is the maximum cumulative isocyanate permeation or penetration (ng cm^{-2}) for each garment and coating combination at 0.08-mm (3.0 mils) coating thickness.

These theoretical PFs are limited by the testing conditions and do not account for seams, stitching, and zippers as a route of penetration or worker variability. Minimum protection factors (MPF) for each coating type have been established using direct loading data and the cumulative permeation/penetration threshold as described in 'Permeation data analysis'.

Sample analysis and quality control

25-mm glass fiber filters impregnated with a 1-(9-anthracenylmethyl)piperazine reagent were used to collect isocyanate samples as described in Mellette *et al.* (2018). The normalized limits of detection (LOD) for each quantifiable species of isocyanate were as follows: 0.04 ng cm^{-2} 4,4′-MDI; 0.01 ng cm^{-2} 2,4′-MDI; 0.01 ng cm^{-2} 2,2′-MDI; 0.39 ng cm^{-2} MDI trimer; 0.05 ng cm^{-2} 1,6-HDI; and 19.62 ng cm^{-2} HDI isocyanurate. These values correspond to ~0.03 (MDI) ng^{-1} isocyanate (MDI trimer)/sample. There were no other isocyanate species detected in the test cell samples or bulk materials.

One field blanks per batch of test cells was analyzed for quality assurance. No blank corrections were made due to the very low level of contamination detected (i.e. ≤0.01 ng/sample). Test cell disassembly and cleaning were conducted as described in Mellette *et al.* (2018).

Permeation data analysis

It was not possible to completely differentiate between the processes of permeation and penetration during this study. However, some indicators of penetration were observed by tint and by the detection of higher molecular weight oligomers on garment samples. To simplify discussion, chemical movement through highly impermeable materials (i.e. gloves) has been referred to as 'permeation', whereas chemical movement through porous materials (i.e. breathable clothing) has been referred to as 'penetration'. These descriptions represent the most likely means of chemical transfer.

Permeation/penetration at each time point has been reported as the accumulated mass of isocyanate measured on the collection media. The results from each sample were divided by the cross-sectional area of the exposed filter to normalize data by unit area (ng cm^{-2}). Total isocyanate (reported as 'isocyanate or NCO') was defined as the sum of each detectable isocyanate species present in the tested coating (primer: 4,4′-MDI, 2,4′-MDI, and 2,2′-MDI, MDI trimer; finish coating: 1,6′-HDI monomer and HDI isocyanurate). Simple substitution of the LOD/$\sqrt{2}$ was used for each censored data point (Hewett and Ganser, 2007).

Additional normalization was performed by dividing permeation/penetration data by the average mass of dry coating (mg) to allowed for consistent comparison of permeation results across separate batches of test (Ceballos *et al.*, 2011, 2014b). Normalized data from each coating were then multiplied by the mass of dry coating associated with a typical coat of 0.08-mm (3.0 mils) thickness (primer = 76.49 mg; finish coating = 97.67 mg). Final data have been presented as 'ng NCO/cm^2 @ 0.78 [3.0 mils] of dry coating' to correspond with the manufacturer's recommended coating thickness and is believed to present a worst-case scenario for surface contamination due to spray painting overspray.

Simple linear regression analysis was conducted to determine the rate of permeation or penetration and the 95% confidence interval for each regression line over the 120-min test period. Permeation and penetration rates were compared with the ASTM F739 and ISO 6529 normalization permeation rate of 0.1 μg cm^{-2} min^{-2} as a threshold for minimum acceptable permeation resistance. Analysis of covariance was performed to compare garment permeation/penetration rates for statistically significant differences (IBM SPSS Statistics, v. 25, Armonk, NY, USA) at a threshold of 0.05.

A cumulative permeation/penetration mass of 1.0 μg cm^{-2} was also used as a threshold for acceptable garment penetration by isocyanate. This cumulative threshold was based upon clinical patch testing data with 4,4′-MDI (Mäkelä *et al.*, 2014) and is believed to provide a more protective measure of garment effectiveness that considers the sensitizing capacity of isocyanates.

Results

Disposable glove permeation

The thin latex [0.076 mm (3.0 mils)] and nitrile gloves [0.078 mm (3.1 mils)] were tested for isocyanate permeation with both coating formulations. The MDI isomers from the zinc-rich primer (MDI-based: 4,4′-MDI, 2,4′-MDI, and 2,2′-MDI. 4,4′-MDI) were the only isocyanate species found to permeate through the glove materials at a detectable level. Similarly, the HDI monomer (HDI-based: 1,6′-HDI) from the aliphatic finish coating was the only species found to permeate through the glove materials at a detectable level. None of the higher molecular weight oligomers (MDI trimer and HDI Isocyanurate) from either coating were found to permeate though the glove materials despite their high concentrations in the bulk coatings. HDI biuret was not detected in the test chemical. Zinc-rich primer and glove permeation data by individual MDI species have been included for additional reference as Supplementary Figure 3 (available at *Annals of Work Exposures and Health* online).

Disposable glove permeation rates, breakthrough detection times, and maximum cumulative isocyanate permeation for both glove materials are presented in Table 3. The latex gloves showed the highest rate of total isocyanate permeation (primer: 27.38 ng NCO cm^{-2} min^{-1}; finish coat: 7.39 ng NCO cm^{-2} min^{-1}) and detectable breakthrough within the first 5 min of contact with both coatings. Although, the nitrile gloves showed detectable isocyanate permeation during the first 5 min of contact with the zinc-rich primer (1.89 ng NCO cm^{-2} min^{-1}), they did not show detectable isocyanate permeation until after 15 min with the aliphatic finish coating (1.26 ng NCO cm^{-2} min^{-1}). Permeation data and regression analysis for each glove material have been presented in Fig. 2.

Protective clothing penetration

The Tyvek coverall [0.105 mm (4.1 mils)], PP/PE coverall [0.116 mm (4.6 mils)], and heavyweight cotton t-shirt [0.382 mm (15.0 mils)] were tested for isocyanate penetration with both coating formulations. Although only MDI monomers from the zinc-rich primer (MDI-based) were detected in coverall samples, low concentrations of the higher molecular weight MDI trimer were detected on samples from the very porous cotton t-shirt. Higher oligomeric isocyanate species from the aliphatic finish coating (HDI-based) were not detected in any of the clothing samples. Zinc-rich primer and coverall penetration data by individual MDI species have been included for additional reference as Supplementary Figure 4 (available at *Annals of Work Exposures and Health* online).

Clothing penetration rates, breakthrough detection times, and maximum cumulative isocyanate penetration for each clothing material have been presented in Table 3. The Tyvek coverall was penetrated by isocyanate from the zinc-rich primer within the first 5 min (3.47 ng NCO cm^{-2} min^{-1}) and after 15 min with the HDI-based aliphatic finish coating (0.87 ng NCO cm^{-2} min^{-1}). The PP/PE coverall was penetrated by both coatings within the first 5 min (primer: 0.08 ng NCO cm^{-2} min^{-1}; finish coating: 1.27 ng NCO cm^{-2} min^{-1}). The cotton t-shirt was rapidly penetrated by the zinc-rich primer (146.65 ng NCO cm-2 min-1) within the first 5 min but was penetrated more gradually by isocyanates from the aliphatic finish coating (4.64 ng NCO cm^{-2} min^{-1}). Penetration of the cotton t-shirt by the green primer was visually observed on the collection media. Penetration data and regression data for each clothing material have been presented in Fig. 2.

Isocyanate direct-loading samples and theoretical PFs

PTFE filters sprayed directly with both coatings were analyzed for isocyanate loading to assess the amount

Table 3. Total isocyanate permeation/penetration rate (ng NCO cm^{-2} min^{-1}), breakthrough detection time, and protection factor by garment and coating type, normalized to 0.08-mm (3.0 mils) dry coating.

Garment type	Zinc-rich primer (MDI-based)[a]					Aliphatic finish coating (HDI-based)[b]				
	Maximum cumulative permeation[c] (ng cm^{-2})	Theoretical protection factor[d]	Linear regression			Maximum cumulative permeation[c] (ng cm^{-2})	Theoretical protection factor[d]	Linear regression		
			Breakthrough detection (min)	Permeation rate[c] (ng cm^{-2} min^{-1})	S[e]			Breakthrough detection (min)	Peremation rate[c] (ng cm^{-2} min^{-1})	S[d]
Disposable gloves										
Latex	3146.48	6	≤5	27.38	303.79	1014.42	69	≤5	7.39	66.01
Nitrile	300.44	64	≤5	1.89	57.62	203.40	343	≤30	1.26	25.70
Clothing										
Tyvek	472.00	41	≤5	3.47	106.51	101.63	685	≤15	0.87	7.15
PP/PE[f]	17.92	1073	≤5	0.08	4.72	190.53	366	≤5	1.27	13.82
Cotton shirt	1748.76	11	≤5	146.65[g]	276.45[g]	593.32	117	≤5	4.64	31.89

[a]Concentration values equal the sum of detectable analytes, to include 4,4′-MDI, 2,4′-MDI, 2,2′-MDI, and MDI trimer.
[b]Concentration values equal the sum of detectable analytes, to include 1,6-HDI and HDI isocyanurate.
[c]Refers to permeation with highly impermeable materials (i.e. gloves) and penetration with porous materials (i.e. breathable clothing).
[d]Theoretical protection factor = isocyanate direct loading concentration (ng cm^{-2})/maximum cumulative permeation (ng cm^{-2}).
[e]S = Standard error of regression.
[f]PP/PE = Polypropylene/polyethylene coverall.
[g]Zinc-rich primer penetrated the cotton t-shirt rapidly with an average penetration rate of 146.65 ng cm^{-2} min^{-1} between 0 and 5 min (see Fig. 2). Standard error of the mean has been presented for the three data points at 5 min.

of isocyanate deposited under conditions of unprotected skin exposure. The zinc-rich primer showed an average isocyanate loading of 19.23 µg isocyanate cm^{-2} @ 0.08 mm (3.0 mils) coating thickness with a range of 14.34–21.90 µg cm^{-2}. Loading samples for the aliphatic finish coating showed an average isocyanate loading of 69.65 µg cm^{-2} @ 0.08 mm (3.0 mils) coating thickness and a range of 45.50–70.06 µg cm^{-2}.

As previously described, theoretical PFs have been calculated for each coating and garment combination and are provided in Table 3. MPF of at least 20 for the zinc-rich primer and 70 for the aliphatic finish coating are recommended based upon the average isocyanate content of each coating. Theoretical PFs from the latex gloves (primer PF: 6; finish coating PF: 69) did not meet the MPF for either coating.

Dry coating loading and thickness samples

The variation of dry coating loading within each batch of spray cells ranged from 3.8 to 18.7%CV with the zinc-rich primer and 3.4 to 8.4%CV with the aliphatic finish coating. When comparing variation across all batches (i.e. the combined samples for each coating type), an average loading of 93.97 mg (15.7%CV) was measured with the zinc-rich primer and 74.09 mg (7.9%CV) with the aliphatic finish coating. The average dry coating thickness for each coating was 0.071 mm (2.8 mils) with the zinc-rich primer and 0.68 mm (2.7 mils) with the aliphatic finish coat. The applied thicknesses for both coatings were within the range of recommended coverage provided by the manufacturer. A complete summary of loading and thickness data has been provided in Table 4.

Discussion

Disposable glove permeation

Nitrile gloves were found to provide significantly greater resistance to permeation from isocyanates when compared to the disposable latex gloves. A statistically significant difference was found between the gloves' permeation rates when tested with both coatings (primer: $F = 174.77$, $P < 0.000$; finish coat: $F = 103.81$, $P < 0.000$), indicating that the nitrile gloves were significantly more protective then latex. The data indicated that, on average, the nitrile gloves were 14.5 times more protective than latex against the zinc-rich primer and 5.9 times more protective against the aliphatic finish coating. In addition, the nitrile material delayed detectable isocyanate permeation until after 5 min of contact with the aliphatic finish coating. Cumulative permeation results also indicate that the latex gloves were an ineffective barrier against these coatings, as demonstrated

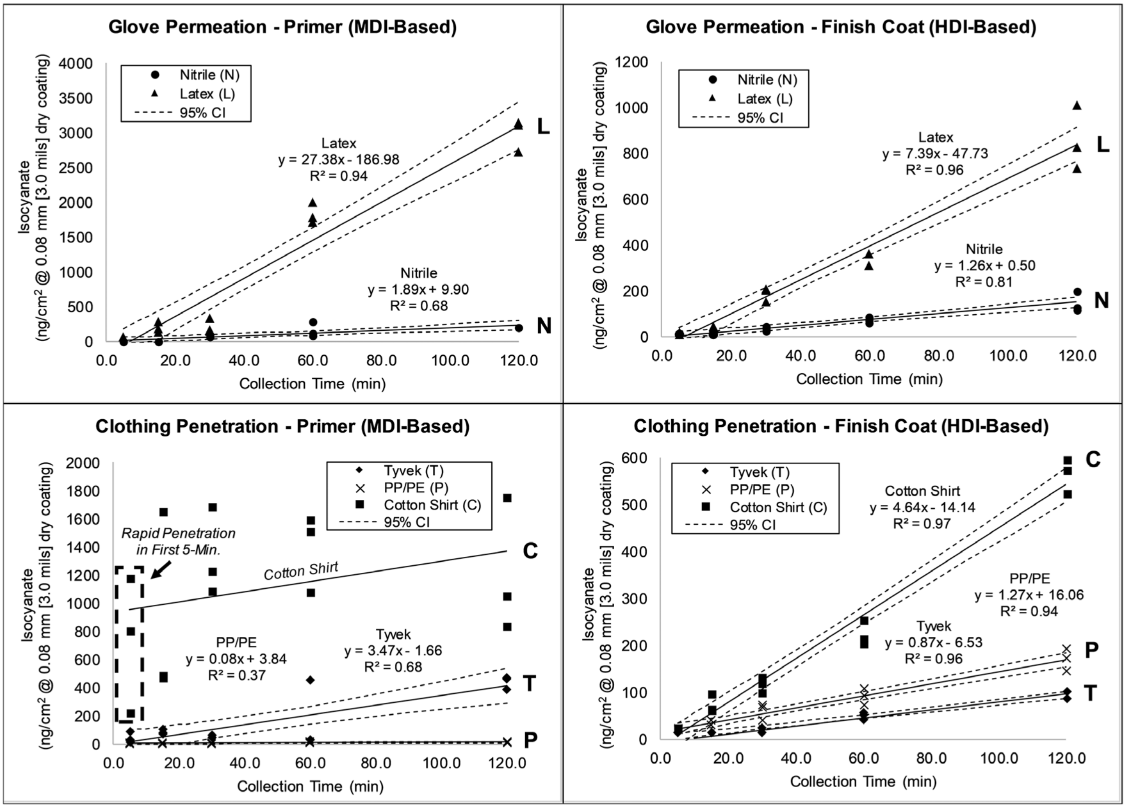

Figure 2. Isocyanate permeation data and regression analysis are presented for latex and nitrile gloves with the zinc-rich primer (top left) and aliphatic finish coating (top right), and for Tyvek coveralls, PP/PE coveralls, and a heavy-duty cotton t-shirt with the zinc-rich primer (bottom left) and aliphatic finish coating (bottom right). All data have been normalized by the exposed filter area and mass of dry coating and presented as 'ng NCO cm^{-2} at 0.08-mm (3.0 mils) dry coating'. Higher oligomeric forms of isocyanate from the primer (i.e. MDI trimer) only penetrated the cotton t-shirt. HDI isocyanurate from the aliphatic finish coating did not penetrate any of the garment materials, likely due to the high viscosity of the mixture.

Table 4. Average loading and thickness sample results by garment and coating type.

Garmenttype	Material	Zinc-rich primer		Aliphatic finish coating	
		Average loading dried coating[a] [mg (%CV)]	Average thickness dried coating[b] [mm (mils)]	Average loading dried coating[a] [mg (%CV)]	Average thickness dried coating[b] [mm (mils)]
Glove	Latex	93.50 (18.7%)	0.082 (3.2)	72.19 (3.4%)	0.068 (2.7)
Glove	Nitrile	79.31 (5.8%)	0.069 (2.7)	74.05 (6.8%)	0.076 (3.0)
Coverall	Tyvek	83.47 (5.5%)	0.054 (2.1)	76.08 (8.4%)	0.062 (2.5)
Coverall	Polypropylene	101.79 (6.7%)	0.077 (3.0)	68.17 (5.4%)	0.063 (2.5)
Shirt	Cotton	111.78 (3.8%)	0.074 (2.9)	79.97 (5.0%)	0.072 (2.8)
Total averages by coating type[c]		93.97 (15.7%)	0.071 (2.8)	74.09 (7.9%)	0.068 (2.7)

[a]Loading measurements of dry coating were obtained by spraying eight PTFE filters with independent batches of test cells for each coating/garment combination. Filters were analyzed using gravimetric analysis.

[b]Thickness measurements of dry coating were obtained by spraying eight aluminum stamping blanks with independent batches of test cells for each coating/garment combination. Thickness was measured using a dial caliper with a 0.001 in resolution.

[c]Total averages for loading and thickness measurements from all samples within each coating group.

by their exceedance of the established cumulative permeation threshold of 1.0 ug cm^{-2}. Nitrile gloves provided and effective barrier against isocyanates and were well below the established thresholds for permeation rate and cumulative permeation with both coatings.

A comparison of glove permeation by coating type shows that permeation rate may largely be dependent upon the monomeric isocyanate content of each coating. This was demonstrated by the more rapid permeation of the latex material by the zinc-rich primer (containing nearly 92% monomeric isocyanate), despite the primer's lower total isocyanate content when compared to the aliphatic finish coating (containing only 19% monomeric isocyanate). Higher molecular weight isocyanate oligomers (i.e. MDI trimer and HDI isocyanurate) did not permeate either glove material at a detectable level despite their high concentrations in both coatings. This is consistent with Fick's second law and the process of diffusion which occurs randomly due to Brownian motion and favors lower-mass molecules (Anna, 2011; Sun and Pan, 2011; Tro, 2011).

It is also important to note that the permeation of these materials could have been significantly influenced by the solvent composition and the viscosity of each coating. Both coatings contained a high percentage of solvents with poor-to-moderate permeation and degradation ratings [i.e. primer: trimethylbenzenes (≤14%); finish coat: methyl *n*-amyl ketone (≤10%), Ethyl 3-ethoxypropionate (≤5%), xylenes (≤3%), cyclohexanone (≤2.1%)]. These ratings indicate that there is a potential for rapid breakthrough with both latex and nitrile materials (Forsberg *et al.*, 2014).

Protective clothing penetration

Interesting differences in penetration resistance to each coating were identified between the Tyvek and PP/PE coveralls. Although the PP/PE coverall was 43 times more protective than the Tyvek coverall against the zinc-rich primer, the Tyvek coverall was slightly more protective (1.5 times) against the aliphatic finish coating. The differences in protective coverall permeation rates were statistically significant with both the zinc-rich primer (F = 25.97, P < 0.000) and aliphatic finish coating (F = 9.88, P = 0.005). The Tyvek coverall also delayed isocyanate penetration by the aliphatic finish coating until after 5 min of exposure.

The exact reasons for these differences in penetration are not completely understood but are most likely due to the physical structure of each material, rather than their similar thermoplastic polyolefins composition. It is believed that the low-viscosity primer (0.48 cm^2 s^{-1}) may have more readily permeated the Tyvek's PE fiber matrix than the multiple laminate layers and highly dispersed microporous structure of the PP/PE membrane. In addition, the zinc particles in the primer were roughly the same diameter as the pores observed in the PP/PE membrane (~10 µm) and may have helped to reduce coating penetration. Neither breathable coverall material was penetrated by oligomeric forms of isocyanate present in the bulk coatings. Despite these significant differences, both protective coverall materials provided and effective barrier against isocyanates and were well below the established thresholds for penetration rate and cumulative penetration with both coatings.

The cotton t-shirt was less effective than both coveralls and was readily penetrated by isocyanate from the lower viscosity zinc-rich primer during the first 5 min of exposure. Although the cotton provided adequate protection against the higher viscosity aliphatic finish coating, it exceeded the established threshold for penetration rate by 147% and the cumulative penetration threshold by 178%. Despite the low level of protection provided by the cotton t-shirt, it did provide some resistance and should be considered for use only as a secondary barrier under loose fitting protective coveralls.

Homogeneity of coating application

As an alternative to robotic spray equipment, which is expensive and not readily available, this study also evaluated the effectiveness of a fixed-position spray application technique to minimize coating variability during application. This method demonstrated a significant reduction in variability within each batch of test cells when compared to standard manual spray application. Gravimetric loading results for dry coating showed that the variability within batches was mostly from 3.8 to 6.7%CV with the primer and 3.4 to 8.4%CV with the finish coating. This was well below manual spray variability from a similar study (Ceballos *et al.*, 2011: 8.8–14.9%CV) and reasonably consistent with robotic spray application (Ceballos *et al.*, 2014b: 1.9–6.7%CV) even with the higher solids content and viscosity of the anticorrosion coatings. One batch of test cells with zinc-rich primer did demonstrate a higher variability that was inconsistent with other batches (18.7%CV).

Loading variability across all batches with the zinc-rich primer was higher than expected at 15.7%CV. Although higher than desired, this amount of variability was still less than the 20% variability typically encountered during manual spray painting (Ceballos *et al.*, 2014b). The higher variability between test-cell batches was likely due to differences in spray consistency experienced between spray sessions after spray gun cleaning and reassembly. A lack of continuous agitation to help maintain particle suspension in the coating binder may have also contributed to inconsistencies with the homogeneity of coating application.

Conclusions and recommendations

Nitrile gloves consistently demonstrated a superior resistance to these isocyanate-containing coatings. This has been demonstrated during this study with complex polyurethane coatings and during previous research with automotive clear coats and spray polyurethane foam (SPF) insulation (Ceballos *et al.*, 2014b; Mellette *et al.*, 2018). Similarly, latex gloves have shown consistently poor performance and should be discouraged from use in industrial coatings (Ceballos *et al.*, 2011, 2014b; Mellette *et al.*, 2018). Although the thin nitrile gloves tested during this study provided sufficient resistance, these gloves are susceptible to tearing from the mechanical forces and sharp edges found in construction trades. We highly recommend the use of thicker nitrile gloves whenever possible, and, appropriate for the physical work environment. It may also be possible to use this data to draw general conclusions about the suitability of combination gloves (e.g. nitrile-coated cotton glove). These gloves are commonly used in the construction industry but were not tested directly due to thickness constraints with the test apparatus.

Although both coverall materials provided sufficient resistance to isocyanate penetration, the PP/PE coverall provided more consistent resistance to both coatings. The heavyweight cotton t-shirt did not provide adequate protection against isocyanate permeation during contact with the zinc-rich primer, but should be considered for use as an undergarment with protective coveralls to provide a secondary barrier to penetration. During future studies, testing of other types of standard work clothing should also be considered (e.g. tighter woven coveralls and work clothing).

The use of a fixed-position spray application techniques provided consistent and reproducible results within independent batches of permeation test cells. These improvements to coating consistence were achieved even with the use of higher solids coating formulations. Additional measures are still necessary to reduce the variability between batches to ensure consistent coating application between test sessions. One recommendation to improve spray performance and consistency is the use of continuous agitation to improve spray consistency and prevent settling of suspended solids. In addition, a wet-film thickness gauge should be used to provide a more robust quantitative measure of wet coating thickness during pre-spray calibration procedures.

Supplementary Data

Supplementary data are available at *Annals of Work Exposures and Health* online.

Funding

This research was supported by CPWR: The Center for Construction Research and Training (CPWR) through NIOSH Cooperative Agreement Number U60-OH009762.

Disclaimer

Its contents are solely the responsibility of the authors and do not necessarily represent the official views of CPWR or NIOSH.

References

Anna DH, American Industrial Hygiene Association, editors. (2011) *The occupational environment: its evaluation, control and management*. 3rd edn. Fairfax, VA: American Industrial Hygiene Association.

ASTM F739. (2012) *Standard test method for permeation of liquids and gases through protective clothing materials under conditions of continuous contact*. West Conshohocken, PA: ASTM International.

Bello D, Herrick CA, Smith TJ *et al.* (2007) Skin exposure to isocyanates: reasons for concern. *Environ Health Perspect*; **115**: 328–35.

Bello D, Streicher RP, Woskie SR. (2002) Evaluation of the NIOSH draft method 5525 for determination of the total reactive isocyanate group (TRIG) for aliphatic isocyanates in autobody repair shops. National Institute for Occupational Safety and Health. *J Environ Monit*; **4**: 351–60.

Bello D, Woskie SR, Streicher RP *et al.* (2004) Polyisocyanates in occupational environments: a critical review of exposure limits and metrics. *Am J Ind Med*; **46**: 480–91.

Bureau of Labor Statistics. (2018) Painters, construction and maintenance: Occupational Outlook Handbook: U.S. Bureau of Labor Statistics. Available at https://www.bls.gov/ooh/construction-and-extraction/painters-construction-and-maintenance.htm. Accessed 30 April 2019.

Ceballos D, Reeb-Whitaker C, Glazer P *et al.* (2014a) Understanding factors that influence protective glove use among automotive spray painters. *J Occup Environ Hyg*; **11**: 306–13.

Ceballos DM, Sasakura M, Reeb-Whitaker C *et al.* (2014b) Testing of glove efficacy against sprayed isocyanate coatings utilizing a reciprocating permeation panel. *Ann Occup Hyg*; **58**: 50–9.

Ceballos DM, Yost MG, Whittaker SG *et al*. (2011) Development of a permeation panel to test dermal protective clothing against sprayed coatings. *Ann Occup Hyg*; **55**: 214–27.

Cochrane SA, Arts JH, Ehnes C *et al*. (2015) Thresholds in chemical respiratory sensitisation. *Toxicology*; **333**: 179–94.

Daftarian HS, Lushniak BD, Reh CM *et al*. (2002) Evaluation of self-reported skin problems among workers exposed to toluene diisocyanate (TDI) at a foam manufacturing facility. *J Occup Environ Med*; **44**: 1197–202.

Engfeldt M, Isaksson M, Zimerson E *et al*. (2012) Several cases of work-related allergic contact dermatitis caused by isocyanates at a company manufacturing heat exchangers. *Contact Dermatitis*; **68**: 175–80.

Federal Highway Administration. (2017) *National Bridge Inventory: Deficient Bridges by Highway System 2017*. Washington, DC: U.S. Department of Transportation. Available at https://www.fhwa.dot.gov/bridge/nbi/no10/defbr17.cfm. Accessed 30 April 2019.

Forsberg K, Van den Borre A, Henry NW *et al*. (2014). *Quick selection guide to chemical protective clothing*. 6th edn. Hoboken, NJ: Wiley.

Harari H, Bello D, Woskie S *et al*. (2016) Development of an interception glove sampler for skin exposures to aromatic isocyanates. *Ann Occup Hyg*; **60**: 1092–103.

Hewett P, Ganser GH. (2007) A comparison of several methods for analyzing censored data. *Ann Occup Hyg*; **51**: 611–32.

ISO 6529. (2013) *Protective clothing—protection against chemicals—determination of resistance of protective clothing materials to permeation by liquids and gases*. Geneva, Switzerland: International Organization for Standardizatio.

Kieć-Świerczyńska M, Świerczyńska-Machura D, Chomiczewska-Skóra D, *et al*. (2014) Occupational allergic and irritant contact dermatitis in workers exposed to polyurethane foam. *Int J Occup Med Environ Health*; **27**: 196–205.

Kirk RS, Mallet WJ. (2018) *Highway bridge conditions: issues for congress* (No. R44459). Washington, DC: Congressional Research Service.

Knudsen OØ, Forsgren A. (2017) *Corrosion control through organic coatings*. 2nd edn. Corrosion technology. Boca Raton, FL: CRC Press, Taylor & Francis Group.

Larsen TH, Gregersen P, Jemec GB. (2001) Skin irritation and exposure to diisocyanates in orthopedic nurses working with soft casts. *Am J Contact Dermat*; **12**: 211–4.

Lockey JE, Redlich CA, Streicher R *et al*. (2015) Isocyanates and human health: multistakeholder information needs and research priorities. *J Occup Environ Med*; **57**: 44–51.

Mäkelä EA, Henriks-Eckerman ML, Ylinen K *et al*. (2014) Permeation tests of glove and clothing materials against sensitizing chemicals using diphenylmethane diisocyanate as an example. *Ann Occup Hyg*; **58**: 921–30.

Mellette MP, Bello D, Xue Y *et al*. (2018) Testing of disposable protective garments against isocyanate permeation from spray polyurethane foam insulation. *Ann Work Expo Health*; **62**: 754–64.

Pianoforte K. (2018). Industrial coatings market. Coatings World. Available at https://www.coatingsworld.com/issues/2018-06-01/view_features/industrial-coatings-market-. Accessed 30 April 2019.

Redlich CA. (2010) Skin exposure and asthma: is there a connection? *Proc Am Thorac Soc*; **7**: 134–7.

Redlich CA, Herrick CA. (2008) Lung/skin connections in occupational lung disease. *Curr Opin Allergy Clin Immunol*; **8**: 115–9.

Rom WN, Markowitz S, editors. (2007) *Environmental and occupational medicine*. 4th edn. Philadelphia, PA: Wolters Kluwer/Lippincott Williams & Wilkins.

Sun G, Pan N, editors. (2011) *Functional textiles for improved performance, protection and health*. Woodhead Publishing Series in Textiles. Philadelphia, PA: Woodhead, Cambridge.

Tro NJ. (2011) *Chemistry: a molecular approach*. 2nd edn. Upper Saddle River, NJ: Pearson Prentice Hall.