



Isocyanate Exposure Below Analytical Detection When a Paint Brush and Roller Are Used to Apply Moisture-Cure Polyurethane Paint

Carolyn K. Reeb-Whitaker* and Todd M. Schoonover

Safety and Health Assessment and Research for Prevention (SHARP) Program, Washington State Department of Labor & Industries,
243 Israel Road SE Bldg 3, Tumwater, WA 98501, USA

*Author to whom correspondence should be addressed. Tel: +1-360-902-5615; Fax: +1-360-902-5672; e-mail: carolyn.whitaker@lni.wa.gov

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ABSTRACT

Isocyanate exposure is known to be hazardous when polyurethane paints are applied with a spray gun, but less is known of exposure when paint is applied with a paint brush and roller. Concentrations of 1,6-hexamethylene diisocyanate (HDI) monomer and three HDI polymers were assessed when two moisture-cure polyurethane paints containing 31–35% isocyanates were applied with a paint roller and brush. Short-term 15-min samples were taken during paint application in an indoor test environment with no ventilation ($n = 12$); in an outdoor test environment ($n = 11$); and in an outdoor *in situ* assessment ($n = 22$). The outdoor *in situ* assessment involved the painting of a bus shelter and light poles at a public transit station over two night shifts. All isocyanate samples were below analytical detection. The analytical limits of detection for HDI monomer, HDI biuret, HDI isocyanurate, and HDI uretdione were 0.005, 0.84, 0.87, and 0.88 μg , respectively. The finding that isocyanate concentrations were below detection is attributed to the use of paint roller and brush which minimize paint aerosolization and the paint formulation itself which contained <1% of volatile HDI monomer.

KEYWORDS: asthma, coating, LOD, non-detect, negative finding

INTRODUCTION

A public mass transit agency established a maintenance program to paint metal surfaces at bus and light rail stations. The paint system most compatible with the previously painted shelter frames, doors, and light poles was an isocyanate-based moisture-cure primer and paint. The agency was concerned about worker and public exposure to isocyanates, chemicals that

irritate mucus membranes and are well known to cause occupational asthma.

The purpose of this article is to describe isocyanate concentrations when moisture-cure urethane paint containing 35–37% isocyanates was applied with a paint roller and brush. To guide the agency's onsite exposure control plan, airborne isocyanate concentrations were assessed under two scenarios.

The first scenario was an indoor test environment in which isocyanate concentrations were evaluated in an enclosed non-ventilated test room followed by application in an outdoor test setting. The second scenario was the *in situ* application of the paint to an outdoor transit station in the public domain.

METHODS

Data were collected under test conditions in August 2012 and during *in situ* painting in December 2013 and May 2014 in the United States Pacific Northwest Puget Sound Region. The purpose of the test conditions was to inform the exposure control plan for painting at public transit stations. The indoor test condition included a worst-case exposure scenario in which isocyanates were measured in the breathing zone of one painter and at two area stations while seven sheet metal panels (3.1×0.9 m) were painted inside a small room ($12.6 \times 2.3 \times 2.6$ m) without natural nor mechanical ventilation. Outdoor test conditions included the painting of five additional panels and three steel I-beams (3.1×0.25 m) set upright outside to mimic outdoor *in situ* conditions for flat surfaces and light poles.

Following the test conditions, isocyanate concentrations were assessed onsite during two night shifts of painting outdoor structures. On Night 1, two painters painted one three-sided bus shelter on a metal support frame, including upright stanchions and metal rafters. The shelter was tented with plastic and supplied with mechanical ventilation. On Night 2, two painters painted 3 light poles that were not tented but were barred from the public by plastic-wrapped construction fencing.

The paint used in all test conditions was Corothane® I-Aliphatic Moisture Cure Urethane, Safety Black (B65B30) while the paint used onsite was Corothane® I-HS Moisture Cure Urethane, Extra White/Tint Base (B65W51) (The Sherwin-Williams Company, Cleveland, OH, USA). The isocyanate species in these two paint formulations were the same (see Table 1). The formulations did have different color-imparting solids and carrier solvents. Both Corothane® formulations are single part 'moisture cure' paint whereby ambient moisture catalyzes the isocyanates and heat is not needed nor applied to cure the isocyanates. The paint is suitable for use in moist climates such as the Puget Sound Region and less suitable for use in dry

climates. Paint was applied with manually operated knitted polyester roller brushes (15–23 cm with 2 cm nap, Purdy Golden Eagle, Cleveland, OH, USA) and standard paint brushes (13 cm wide).

AIR SAMPLING

Breathing zone and area isocyanate air sampling utilized a dual-stage open-faced sampler calibrated to 2 L min^{-1} and previously published in detail (Reeb-Whitaker *et al.*, 2012). The first filter (PTFE) was field derivitized with 1-(2-methoxyphenyl) piperazine (MOPIP, 1.0 mg ml^{-1} ; Sigma-Aldrich, St. Louis, MO, USA) in reagent grade toluene and analyzed for isocyanate polymers. The second filter (glass fiber) was pre-impregnated with 9-N-methylaminomethyl anthracene (MAMA; Sigma-Aldrich) and diluted in the laboratory with reagent grade methylene chloride before being analyzed for isocyanate monomers.

The Washington State Department of Labor and Industries (L&I) American Board of Industrial Hygiene (ABIH) accredited laboratory performed analytical methods for isocyanate monomer vapor and isocyanate polymer aerosol (Washington State Method L&I 0050, 2011 and Washington State Method L&I 0067, 2011). Analytes included 1,6-hexamethylene diisocyanate (HDI) monomer (CAS 822-06-0), and three HDI polymers: uretdione, biuret, and isocyanurate (CAS 28182-81-2). The analytical methods used high-pressure liquid chromatography with diode array detection and fluorescence detection. The calibration standards included HDI monomer commercial standards as well as diluted HDI polyisocyanate bulk products from Bayer Material Science (Leverkusen, Germany). Quality control was performed to ensure that the standard isocyanate concentrations were within $\pm 15\%$ of the theoretical value. Calibration checks were run before, during, and after all sample analyses. The number of field and laboratory blanks run per sample set was at least 10% of the total number of samples. The limits of detection (LOD) is summarized in Table 1.

Temperature and relative humidity (Rh) were recorded using HOBO data loggers (model H08-004-02, Onset Computer Corporation, Bourne, MA, USA) or using a Traceable® Hygrometer (Control Company, Friendswood, TX, USA). Wind speed was estimated using a rotating vane thermal anemometer (model RVA 501, TSI Instrument, Shoreview, MN, USA).

Table 1. Isocyanate analytical limits of detection and occupational exposure levels

Analyte name	CAS	Limit of detection mass (ug)	Limit of detection concentration (ug m ⁻³) ^a	Limit of detection as a % of STEL	STEL	STEL source
HDI monomer	822-06-0	0.005	0.2	0.1	140	NIOSH REL 10 min ug m ⁻³
HDI uretdione	28182-81-2	0.88	29.3	2.9	1000	OR-OSHA 15 min STEL ug m ⁻³
HDI biuret	28182-81-2	0.84	28.0	2.8	1000	OR-OSHA 15 min STEL ug m ⁻³
HDI isocyanurate	28182-81-2	0.87	29.0	2.9	1000	OR-OSHA 15 min STEL ug m ⁻³

STEL, short-term exposure limit.

^aConcentration estimate based on 30 l volume (2 LPM for 15 min).

RESULTS

All isocyanates were below analytical LOD during the initial test condition in a closed room with no ventilation ($n = 12$, Table 2). Furthermore, all isocyanates were below detection limits in the subsequent outdoor test ($n = 11$) and during outdoor *in situ* station painting ($n = 22$, Table 2).

In reference to the experimental conditions listed in Table 2, the average temperature (range) for the indoor test, outdoor test, Night 1 and Night 2 were respectively as follows: 21°C (21–23°C); 20°C (19–22°C); 8°C (8–8°C); and 26°C (22–29°C). The average relative humidity (range) for the indoor test, outdoor test, Night 1, and Night 2 were: 75% (73–77%); 62% (60–65%); 78% (78–79%); and 35% (32–44%), respectively. Winds were estimated at 5–11 kilometers per hour (kph) during the outdoor test, 13–16 kph on Night 1, and 3–11 kph on Night 2.

DISCUSSION

Isocyanate concentrations were below the analytical LOD and this is primarily attributed to the roller and brush application method which generate low aerosol and therefore low exposure. Additionally, the paint formulation was predominantly comprised of HDI polyisocyanates rather than HDI monomer (<1%) which is more volatile and likely to vaporize. Our findings are similar to other studies that have characterized isocyanate exposure during roller and brush application and documented isocyanate concentrations below detection or at low concentrations. DeNola *et al.* (2010) describe HDI monomeric and polymeric exposure from outdoor brush and roller application of polyurethane paint on a patrol boat to be below the limit of quantitation (LOQ) where the LOQ for HDI monomer was specified at 0.1 µg m⁻³ but the LOQ for HDI polymers was not specified. Coldwell describes polyurethane paint (formulated with isocyanate polymers and a very small fraction of HDI monomer) applied with a roller and brush to car doors resulting in concentrations below an estimated LOD of approximately 0.01 µg NCO m⁻³ (Coldwell and White, 2005). Pronk *et al.* (2006) documents HDI concentrations during application with roller and brush in industrial painting as above detection but low in the range of approximately 0.01–10 µg NCO m⁻³ of HDI.

Exposure to isocyanates is primarily through the inhalation of airborne isocyanate vapor and isocyanate

Table 2. Isocyanate concentrations under test and *in situ* conditions of Corothane® moisture-cure urethane paint application

Item painted	Situation	Location	#Samples	Avg. min (SD)	HDI monomer 822-06-0 ^a 0.10% ^b	HDI Polymer ^c 28182-81-2 ^a 31–35% ^b	<i>p</i> -Toluenesulfonyl isocyanate ^d 4083-64-1 ^a 2–4% ^b
Test condition: indoors, no ventilation							
Test panels	Indoor room	Painter 1	4	16 (3)	nd	nd	na
Test panels	Indoor room	Area 1	4	18 (4)	nd	nd	na
Test panels	Indoor room	Area 2	4	18 (4)	nd	nd	na
Test condition: outdoors							
Panels, columns	Outdoor	Painter 1	3	19 (1)	nd	nd	na
Panels, columns	Outdoor	Area 1	4	17 (1)	nd	nd	na
Panels, columns	Outdoor	Area 2	4	17 (2)	nd	nd	na
In situ, Night 1: outdoor bus shelter with plastic tenting							
Bus shelter	Inside tent	Painter 1	3	23 (2)	nd	nd	na
Bus shelter	Inside tent	Painter 2	3	22 (1)	nd	nd	na
Bus shelter	Outside tent, 5 ft ^e	Area 1	2	37 ^f	nd	nd	na
Bus shelter	Inside tent	Area 2	2	40 ^g	nd	nd	na
In situ, Night 2: outdoor light poles with a barrier fence but no tenting							
Light poles	Inside fence	Painter 1	3	29 (5)	nd	nd	na
Light poles	Inside fence	Painter 2	3	27 (1)	nd	nd	na

Table 2. Continued

Item painted	Situation	Location	# Samples	Avg. min (SD)	HDI monomer 822-06-0 ^a 0.10% ^b	HDI Polymer ^c 28182-81-2 ^a 31–35% ^b	<i>p</i> -Toluenesulfonyl isocyanate ^d 4083-64-1 ^a 2–4% ^b
Light poles	Outside fence, 10 ft ^e	Area 1	3	28 (5)	nd	nd	na
Light poles	Outside fence, 40 ft ^e	Area 2	3	29 (1)	nd	nd	na

^aChemical Abstracts Service (CAS).^bPercent by weight as given on MSDS sheets.^cHDI Polymer includes HDI biuret, HDI isocyanurate, and HDI uretidione.^dAnalytical method could not quantify this isocyanate species.^eDown wind distance from tent or fence.^fRange = 33–41.^gRange = 39–41.

aerosol as well as through skin contact. Isocyanate monomers exist primarily in the vapor phase (Bello *et al.*, 2004), with exposure maximized under the right conditions (HDI monomer vapor pressure = 0.05 mmHg at 20°C). The paint formulation studied here contains a very low fraction of HDI monomer (0.10%, Table 2); thus there is a low reservoir of isocyanate available to naturally vaporize from the paint can, tray, or from uncured applied paint. If a paint formulation has a higher concentration of isocyanate monomer than the Corothane® formulation documented here, isocyanate exposure from roller application may be higher.

While the formulation has a low fraction of isocyanate monomer, it does contain a high fraction of HDI polymers (31–35%) which predominantly exist in the aerosol phase (Bello *et al.*, 2004). With inherently low aerosolization of isocyanate polymers during roller application, exposure is anticipated to be low. As a comparison, two-part automotive polyurethane paints are also formulated high in isocyanate polymers but are typically applied with aerosol-generating high volume low pressure (HVLP) spray guns. The authors have previously used the sampling and analytical methods described here to document very high exposure to HDI polymer when automotive paint formulations are applied with HVLP guns (Reeb-Whitaker *et al.*, 2012). If the Corothane® paint formulation studied here had been applied with a spray gun, isocyanate exposure would be anticipated to be higher.

The primary limitations of this study relate to the sampling method, the available analytical methods, and the attained LOD. It is possible that alternative sampling techniques, such as an impinger or an Institute of Occupational Medicine (IOM) personal inhalable sampler may capture more inhalable isocyanate particles than the dual-stage open-faced sampler used here. The analytical method quantified the HDI monomer and individual HDI polymers but did not quantify the isocyanate *p*-Toluenesulfonyl isocyanate (PTSI, CAS 4083-64-1, $v_p = 0.01$ mm Hg at 25°C, and present at 2–4%). Our exposure assessment is therefore not comprehensive for all of the isocyanate species present and likely an underestimate of the total isocyanate exposure. Future assessments could use an analytical method that quantifies isocyanates as the Total Reactive Isocyanate Group (TRIG, expressed as $\mu\text{g NCO}$).

Regarding LODs, the LOD mass reported here for HDI monomer (0.005 μg , and 0.2 $\mu\text{g m}^{-3}$, Table 1) is

within the LOD range anticipated by other analytical methods such as NIOSH 5525 (0.017 μg HDI) and OSHA 42 (2.3 $\mu\text{g m}^{-3}$ HDI) (NIOSH 2003 and OSHA 1989). The HDI polymer LOD mass reported in this study ranges from 0.84 to 0.88 μg , (Table 1) and is equal to concentrations of approximately 29 $\mu\text{g m}^{-3}$ when sampled at an airflow of 2 liters per minute (LPM) for 15 min; this concentration LOD is in the same range as the HDI polymer LOD range of 1.4 to 37.7 $\mu\text{g m}^{-3}$ reported by Pronk *et al.* (2006).

While this study reports non-detectable airborne isocyanate concentrations, there are additional safety and health factors to consider. First, any of the following may result in higher isocyanate concentrations than that reported here: (i) the paint formulation (isocyanate species and weight fraction), (ii) the presence of heat curing which increases paint volatilization, (iii) paint application with a spray gun, and (iv) insufficient ventilation. Second, skin exposure during roller and brush application should be regarded as hazardous as it may lead to immune sensitization and subsequently to asthma (Redlich, 2010). The use of protective gloves and clothing are needed during paint mixing, application, and clean-up regardless of the anticipated inhalation exposure. Finally, paint solvent exposure and solvent odor should be assessed and managed. Solvent exposure may warrant the use of respiratory protection among workers. In community spaces, strong solvent odor and public perception may influence decisions about workspace containment and ventilation.

CONCLUSION

Isocyanate concentrations were below analytical LOD when a moisture-cure isocyanate based paint was applied with a roller and brush to an outdoor public transit station. Preliminary testing determined that isocyanate concentrations could not be detected in a worst-case exposure scenario where test panels were painted in a non-ventilated room, a confined condition that was designed to maximize potential airborne isocyanate concentrations and their analytical detection. The non-detectable isocyanate concentrations are attributed to the use of roller and brush which generate low aerosol, and to the paint formulation itself which is comprised predominantly of HDI polymers and only a low fraction of volatile HDI monomer. Regardless of the inhalation exposure to isocyanates,

site safety plans need to incorporate protection against skin contact with isocyanates and solvent exposure.

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