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Isocyanate and VOC exposure analysis using Flexane®

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ABSTRACT

Flexane® 80 is a trowelable urethane product used in combination with cleaners and primers to effect rubber conveyor belt repairs. These products are of concern due to the potential for worker exposure to isocyanates and volatile organic compounds (VOCs). Small chamber experiments were used to identify chemicals liberated to the ambient air from each of the Flexane®-related products. A new sample collection method using treated cotton sleeves as a surrogate skin surface to assess potential dermal exposure to isocyanates during mixing and application of the Flexane® product was validated. Six simulations of a worst case scenario were performed by an experienced belt repair technician in a walk-in laboratory exposure chamber. Analysis of air samples from the large chamber simulations did not detect airborne isocyanates. The average airborne VOC concentrations were below established occupational exposure levels. Dermal sleeve samples detected intermittent and low levels of isocyanates from self-application while wearing gloves having surface residues of uncured Flexane®. The data strongly suggest that the normal and intended use of Flexane® putty, and its associated products under worst case or typical working conditions is not likely to result in worker VOC or isocyanate exposure levels sufficient to produce adverse health effects.

1. Introduction

Flexane® 80 (Flexane®) is a trowelable, tear-resistant urethane product produced by ITW Devcon (Danvers, MA). It is available as a 2-part product of putty and hardening agent that, when mixed, cures to form a semi-rigid, flexible compound commonly used to repair heavy-duty conveyor belts in industrial settings such as coal mines. Accessory products are available from Devcon for surface preparation prior to Flexane® application. These products include Cleaner Blend 300 (a cleaning agent), FL-10 (a metal surface primer), and FL-20 (a rubber surface primer).

For the industrial hygienist, the predominant chemical components of interest from a urethane such as Flexane® as well as its associated products are isocyanates and volatile organic compounds (VOCs). Occupational exposures to isocyanates have been a health concern due to the ability of these compounds to act as eye, skin, and respiratory irritants as well as allergic sensitizers in certain individuals (Becher et al., 1996; Boutin et al., 2006; Ceballos et al., 2011; Nakashima et al., 2001; Streicher et al., 1998). Potential worker exposure to isocyanates can occur in industries involved in the manufacture or application of multiple forms of urethane. Factors that may influence isocyanate exposures are application methods, product form (spray, liquid, putty, etc.), environmental conditions, use of protective equipment, local ventilation, and duration of exposure (Creely et al., 2006).

No data have been available for a typical isocyanate and VOC breathing zone or dermal exposure to workers using Flexane® and its associated products to repair a conveyor belt in a coal mine. It is difficult to compare the chemical exposure equivalency of Flexane® putty application to the application of other isocyanate-containing products. Unlike most liquid products, Flexane® has a very thick consistency, reducing the likelihood of unintentional splatter during the application process. Unlike sprayed-on products, Flexane® is applied with a trowel or a similar tool, effectively eliminating the possibility of aerosol generation. In addition, environmental factors may be unique when working in a well-ventilated or cordoned-off area in an underground coal mine.

In a coal mining operation, the environmental conditions in which Flexane® may be used to repair a conveyor belt can be quite variable. Some repairs may take place in confined, underground surroundings (such as a belt haulage way) while other repairs may be at some location outside the underground mine. Though underground belt passages are required to be well ventilated (MHSA, 2001), the use of tarpaulins to control air and dust flow into a repair area may affect the dispersion of any potentially airborne Flexane® constituents. For these reasons, the exposure assessment was designed to quantify airborne exposures under worst-case environmental conditions that might occur in a normal work environment.

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A series of in laboratory tests and work simulations was designed and performed by Bureau Veritas in collaboration with researchers at the Center for Environmental and Occupational Risk Analysis and Management at the University of South Florida in Tampa, Florida. The scenario was designed to balance maximum possible exposure with plausible occupational conditions that could be replicated in a laboratory setting. Thus, the potential exposures produced during this assessment are likely to be greater than any potential exposure typically found in the field. Consequently, it is highly unlikely that any worker would consistently encounter exposure levels produced in this simulation over the course of a working lifetime.

The overall goal of these tests was to quantitatively assess the level of exposure to a worker using Flexane® while performing a typical conveyor belt repair in a coal mine under worst-case exposure conditions. The specific aims were to:

(1) Identify target compounds in Flexane® products capable of being liberated to the ambient air (vaporization);
(2) develop a sensitive and reproducible method to quantify dermal exposure to the isocyanates in Flexane®, and;
(3) quantify the actual exposure levels experienced in a worker's breathing zone and characterize the dermal exposure to isocyanates and VOCs while using Flexane® to repair a rubber conveyor belt under worst-case exposure conditions.

2. Materials and methods

2.1. Materials

Commercially available Flexane® 80 putty and its associated products were obtained from ITW Devcon (Danvers, MA). The curing agent and putty resin were prepackaged as a 1-pound kit. The individual products evaluated are as listed: Cleaner Blend 300; FL-10 Primer; FL-20 Primer (ethyl acetate-based); FL-20 Primer (1,1,1-trichloroethane-based); Flexane® 80 Curing Agent; and Flexane® 80 Putty Resin.

For the purposes of this research, known target compounds were defined as the materials listed on the Material Safety Data Sheet (MSDS) accompanying each of the products (Table 1). Prepolymers of isocyanates were not included in the assessment. The size and low volatility of these prepolymers suggests that they would not likely be released into the air, nor would be likely to diffuse through skin due to the large molecular size limiting uptake during the complex process of partitioning into human sweat, though this has not been verified experimentally. The exposures of particular interest to this assessment are the isocyanate monomers and oligomers. Additionally, chamber air was sampled and analyzed for a wide range of VOCs to identify other compounds potentially liberated during product use.

For any session using a conveyor belt sample, a new section of Goodyear rubber conveyor belt was placed in the center of the chamber at waist-level. The belt section consisted of two 18 in. × 36 in. sections joined by a 36 in. hinged metal belt splice. Sample size was contingent upon the nature of the test use.

2.2. Small chamber tests

Two types of closed chamber test experiments were conducted to identify chemicals released into ambient air during conveyor belt repairs using Flexane® and its related products. Identification of these chemicals provided the target list for sampling and analyzing air samples in the actual belt repair simulation study.

The first set of tests utilized a 1 L glass containers with a Teflon®-lined screw cap top to act as small vessel chambers with which to test each product (Fig. 1). Each product was tested individually in a separate vessel chamber.

Initially, a cellophane membrane was fitted under the screw cap top, which itself was fitted with a sampling port and make up air vent. The cellophane membrane provided a seal between the container's mouth and lid during the equilibrium process, lasting at least 1 h at room temperature (20–21 °C) prior to sampling. After the equilibrium period, the cellophane membrane was punctured to open the sampling port and make up air vent to the air chamber. The screw cap top was then secured to the chamber and the sampling port attached to an external glass-sampling manifold with battery-operated sampling pumps. At the completion of each sampling period, the pumps were checked for calibrated flow rates, the collection media were labeled, and samples were submitted to the laboratory for analysis. For quality control purposes, background air samples were collected within the laboratory over the course of the test and used to detect potential background levels of target compounds. The analytical results were corrected for any background compounds identified.

The second set of tests utilized a Plexiglas glove box chamber (Fig. 2) to measure chemicals liberated from the active process of mixing and applying Flexane® putty resin and curing agent. A section of a new rubber conveyor belt was placed within the chamber,

Table 1
Known target compounds from product MSDS.

Target compounds	CAS No.	Flexane® 80 and related products					
		Cleaner blend 300	Flexane® FL-10 primer	Flexane® FL-20 primer (with 1,1,1-TCA)	Flexane® FL-20 primer (with ethyl acetate)	Flexane® 80 putty curing agent	Flexane® 80 putty resin
Propylene glycol monomethyl ether (PGME)	107-98-2	X					
Propylene glycol monomethyl ether actate (PGMEA)	108-65-6	X					
D-Limonene	5989-27-5	X					
Toluene	108-88-3		X				
Ethyl alcohol	64-17-5		X				
Methyl isobutyl ketone (MIBK)	108-10-1		X				
Isopropyl alcohol	67-63-0		X				
Phenol (from phenolic resin)	108-95-2		X				
Methylene bisphenylisocyanate (MDI)	101-68-8			X	X		X
Oligomers of MDI	9016-87-9						X
1,1,1-Trichloroethane	71-77-6			X			
Ethyl acetate	141-78-6				X		
1,4-Dioxane	13-91-1			X	X		
Methylene bis(4-cyclohexyl isocyanate) (H_2MDI)	5124-30-1						X
Diethyl toluene diamine	68479-98-1					X	