



In-Depth Survey Report

Spray Polyurethane Foam Chemical Exposures during Spray Application

All About Kids, Crestwood, KY

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Abstract

The American Resource and Recovery Act of 2009 promoted green jobs and energy efficiency. Spray polyurethane foam (SPF) installation is a green job. SPF is a highly-effective and widely used insulation and air sealant material. However, exposures to its key ingredient, isocyanate, and other SPF chemicals in vapors, aerosols, and dust during and after installation can cause asthma, sensitization, lung damage, occupational asthma, and skin and eye irritation. Past studies have shown sprayers' exposures to methylene diphenyl diisocyanate (MDI) to range from 7.0 to 205 $\mu\text{g}/\text{m}^3$, (OSHA PEL=200 $\mu\text{g}/\text{m}^3$ as a fifteen minute ceiling limit) indicating the need to better understand exposure during SPF installation. Studies characterizing both MDI exposure as well as exposures to the other chemicals present in SPF are limited. This survey was conducted to determine the extent of exposure to the 4,4'-methylene diphenyl diisocyanate (MDI) monomer, isocyanate functional group (NCO) monomer, NCO oligomer, total NCO, pentamethyl-dipropylene-triamine, tris-(1-chloroisopropyl-2) phosphate (TCPP), triethylphosphate, ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, tetraethylene glycol, and 1,1,1,3,3-pentafluoropropane, all found in SPF.

Air sampling was conducted to characterize the chemical exposures to compounds present during SPF installation during three work shifts. Personal breathing zone air samples were collected for MDI, NCO monomer, and NCO oligomer. The mean MDI concentration for the sprayer was 10.1 $\mu\text{g}/\text{m}^3$ ranging from 4.85 to 18.7 $\mu\text{g}/\text{m}^3$. The helpers' mean MDI concentration was 2.86 $\mu\text{g}/\text{m}^3$, ranging from 0.18 to 7.89 $\mu\text{g}/\text{m}^3$. None of these measurements exceeded the NIOSH TWA REL of 50 $\mu\text{g}/\text{m}^3$. Area air samples were collected for: MDI; NCO monomer; NCO oligomer; total NCO; an amine catalyst (pentamethyldipropylene triamine); two flame retardants (TCPP and triethyl phosphate); glycols (ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol and tetraethylene glycol); and blowing agent (1,1,1,3,3-pentafluoropropane).

These air sample results showed the presence of all of the chemical compounds sampled for except the glycols. Based on concentrations found in the personal breathing zone air sample results the sprayer should use supplied-air full-face respirators and wear coveralls, head and foot covers, and chemical resistant gloves. The helper should use air-purifying full-face respirators and wear coveralls, head and foot covers, and chemical resistant gloves. The results from the samples collected from the perimeter area indicated that all workers should wear personal protective equipment (PPE) (i.e. full-face respirator, coveralls, head and foot covers, and gloves) at all

times while in the work area and those workers without the proper PPE should remain outside of the work area.

Based on these sampling results, an engineering control research study should be conducted to reduce exposures to the chemicals found in SPF when it is being installed. The sampling results indicate that MDI as well as chemical compounds found in the B-component side are present and need to be removed from the spraying area.

Introduction

Background for Control Technology Studies

The National Institute for Occupational Safety and Health (NIOSH) is the primary Federal agency engaged in occupational safety and health research. Located in the Department of Health and Human Services, it was established by the Occupational Safety and Health Act of 1970. This legislation mandated NIOSH to conduct a number of research and education programs separate from the standard setting and enforcement functions carried out by the Occupational Safety and Health Administration (OSHA) in the Department of Labor. An important area of NIOSH research deals with methods for controlling occupational exposure to potential chemical and physical hazards. The Engineering and Physical Hazards Branch (EPHB) of the Division of Applied Research and Technology has been given the lead within NIOSH to study the engineering aspects of health hazard prevention and control.

Since 1976, EPHB has conducted a number of assessments of health hazard control technology on the basis of industry, common industrial process, or specific control techniques. Examples of these completed studies include the foundry industry; various chemical manufacturing or processing operations; spray painting; and the recirculation of exhaust air. The objective of each of these studies has been to document and evaluate effective control techniques for potential health hazards in the industry or process of interest, and to create a more general awareness of the need for or availability of an effective system of hazard control measures.

These studies involve a number of steps or phases. Initially, a series of walk-through surveys is conducted to select plants or processes with effective and potentially transferable control concept techniques. Next, in-depth surveys are conducted to determine both the control parameters and the effectiveness of these controls. The reports from these in-depth surveys are then used as a basis for preparing technical reports and journal articles on effective hazard control measures. Ultimately, the information from these research activities builds the data base of publicly available information on hazard control techniques for use by health professionals who are responsible for preventing occupational illness and injury.

Background for this Study

The American Resource and Recovery Act of 2009 promoted green jobs and energy efficiency. The use of spray polyurethane foam (SPF) as an insulation material has increased with the promotion of green jobs^[1]. Because of its insulating properties SPF is a highly-effective and widely used insulation and air sealant material. However, exposure to its key ingredients (isocyanates, and other SPF chemicals in vapor, aerosol, and dust form) during and after installation can cause asthma, sensitization, lung damage, occupational asthma, and skin and eye irritation. SPF is a two-component system with an A-side containing 4,4'-diphenylmethane diisocyanate (MDI) and a B-side containing polyols such as ethylene glycol, amine

catalyst, blowing agents, and flame retardants. The current industry standard for protecting workers from the chemical compounds present in SPF is primarily the use of administrative controls (i.e. job rotation) and personal protective equipment (PPE). Typically the SPF sprayer will wear a full-face air-supplied respirator with chemical protective coveralls (e.g. Tyvek) and chemical protective gloves (e.g. nitrile) when spraying. The helper will usually wear either a half- or full-face air purifying respirator and may or may not wear other PPE. Workers in surrounding areas do not wear PPE.

MDI exposures referenced in the literature^[2,3,4] indicate that the sprayer's exposure to MDI range from 7.0 to 205 $\mu\text{g}/\text{m}^3$. The OSHA permissible exposure limit (PEL) for MDI is 200 $\mu\text{g}/\text{m}^3$ as a fifteen minute ceiling limit and the NIOSH REL is 50 $\mu\text{g}/\text{m}^3$. Clearly these data suggest that engineering controls to remove aerosol from the work area should be researched. The concentrations of MDI were shown to decrease with distance from the source in another study.^[4] Very limited data on the concentrations of the other chemicals present in SPF are currently available. This study gathered exposure data to other components (e.g. polyols, amine catalysts, blowing agents, and flame retardants) of the SPF process.

To better control exposures during and after SPF application, a more complete understanding of the exposures is needed. The following activities are currently underway to address exposures and potential engineering controls:

- Conduct three field surveys to determine the extent of exposure to the chemical compounds present in SPF. Area samples will be collected for MDI, oligomers, polyols, amine catalysts, blowing agents, and flame retardants near and away from the spray source. Personal breathing zone (PBZ) samples will be collected on the sprayers and sprayer helpers.
- During field surveys, collect area samples to quantify any potential exposure levels 24 hours after the spraying has ceased.
- Develop and evaluate engineering controls to reduce exposures to the various compounds present during SPF application.

This report presents the results from the first field survey conducted during SPF operations at "All About Kids" in Crestwood, KY.

Building and Process Description

An existing Wal-Mart facility (46,000 ft²) was being renovated into a recreational facility, All About Kids, by Lichtefeld Inc., Louisville, KY. Lichtefeld had subcontracted to Bio-Foam Insulation System of Kentucky the application of SPF insulation to the facility's ceiling. The sprayers for Bio-Foam used a two component system manufactured by BioBased Insulation. Component-A, 2001 NB, was a polymeric mixture of MDI and Component-B, 2001 NB(s), was a polyol blend with an amine catalyst.

Occupational Exposure Limits and Health Effects

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH investigators use mandatory and recommended occupational exposure limits (OELs) when evaluating chemical, physical, and biological agents in the workplace.

Generally, OELs suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the exposure limit.

Combined effects are often not considered in the OEL. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus can increase the overall exposure. Finally, OELs may change over the years as new information on the toxic effects of an agent become available.

Most OELs are expressed as a Time Weighted Average (TWA) exposure. A TWA exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

In the U.S., OELs have been established by Federal agencies, professional organizations, state and local governments, and other entities. The U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) establishes Permissible Exposure Limits (PELs) ^[5], legally enforceable occupational exposure limits in workplaces covered under the Occupational Safety and Health Act. NIOSH Recommended Exposure Levels (RELs) are based on a critical review of the scientific and technical information available on the prevalence of health effects, the existence of safety and health risks, and the adequacy of methods to identify and control hazards ^[6]. RELs have been developed using a weight of evidence approach and formal peer review process. Other OELs that are commonly used and cited in the U.S. include the Threshold Limit Values (TLVs)[®] recommended by the American Conference of Governmental Industrial Hygienists (ACGIH)[®], a professional organization ^[7]. ACGIH TLVs are considered voluntary guidelines for use by industrial hygienists and others trained in this discipline “to assist in the control of health hazards.” Workplace Environmental Exposure Levels (WEELs) are recommended OELs developed by the American Industrial Hygiene Association (AIHA) and have been established for some chemicals “when no other legal or authoritative limits exist” ^[8].

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or

serious physical harm [Occupational Safety and Health Act of 1970, Public Law 91–596, sec. 5(a)(1)]. Thus, employers are required to comply with OSHA PELs. Some hazardous agents do not have PELs, however, and for others, the PELs do not reflect the most current health-based information. Thus, NIOSH researchers encourage employers to consider the other OELs in making risk assessment and risk management decisions to best protect the health of their employees. NIOSH researchers also encourage the use of the traditional hierarchy of controls approach to eliminate or minimize identified workplace hazards. This includes, in preferential order, the use of: (1) substitution or elimination of the hazardous agent, (2) engineering controls (e.g., local exhaust ventilation, process enclosure, dilution ventilation) (3) administrative controls (e.g., limiting time of exposure, employee training, work practice changes, medical surveillance), and (4) personal protective equipment (e.g., respiratory protection, gloves, eye protection, hearing protection).

The OSHA PEL for MDI (found in Component-A) is established as a 15 minute ceiling concentration of $200\text{ }\mu\text{g}/\text{m}^3$ (0.02 parts per million (ppm)). The ACGIH TLV and the NIOSH REL for MDI are established as a ten-hour TWA of $50\mu\text{g}/\text{m}^3$ (0.005 ppm).^[6,7] NIOSH also has set a ten minute ceiling REL of $200\mu\text{g}/\text{m}^3$ (0.02 ppm) for MDI.⁶ Although there are no specific exposure limits for individual oligomers of MDI, several countries, e.g., the United Kingdom, Ireland, New Zealand, and Australia have set limits for all isocyanates based on total NCO of $20\text{ }\mu\text{g}$ (NCO)/ m^3 .^[8] OSHA and NIOSH have not established a PEL or REL for ethylene glycol which is found in Component-B of the SPF formulation. ACGIH has established a $100\text{ mg}/\text{m}^3$ ceiling limit for ethylene glycol.^[7] The amine catalysts found in the component B of the SPF may be sensitizers and irritants that can cause blurry vision (halo effect).^[8] Flame retardants, such as halogenated compounds, are persistent bio accumulative and toxic chemicals. Russia has established an OEL STEL for triethyl phosphate of $2\text{ mg}/\text{m}^3$.^[9] Blowing agents, such as 1,1,1,3,3-pentafluoropropane, are mildly irritating to the eyes and lungs and an OEL of 300 ppm as an 8-hour TWA has been established by AIHA.^[7]

Methodology

Bulk samples were collected for Component-A containing the MDI and Component-B containing the glycols, amine catalysts, flame retardants, blowing agents, and organic solvents. In order to identify the chemicals present in the SPF formulation bulk liquid direct injection of $0.5\text{ }\mu\text{L}$ into a gas chromatograph–mass spectrometer (GC-MS) was done.

PBZ samples were collected on the sprayer and sprayer helper using a 37mm glass fiber filter cassette impregnated with 1-(9-anthracenylmethyl) piperazine (MAP) connected to an air sampling pump calibrated at a flow rate of 1.0 liter per minute (Lpm). Once the air sampling was completed, the glass fiber filter was removed from the filter cassette holder, placed in a wide-mouthed jar containing 5 milliliters (ml) of 1×10^{-4} MAP in acetonitrile, and refrigerated for sample preservation. Analysis for MDI monomer, functional isocyanate monomers, and functional

isocyanate oligomers was performed according to NIOSH Manual of Analytical Methods (NMAM) method 5525.^[10]

Area samples were also collected for MDI using glass fiber filters impregnated with the MAP agent. In addition area samples were collected for MDI using impingers containing 15 ml of 1×10^{-4} MAP in butyl benzoate. Impinger samples were also analyzed using NIOSH NMAM method 5525.

Area samples were collected for glycols such as ethylene glycol and propylene glycol, amine catalysts, flame retardants (tris-(1-chloro-2-propyl) phosphate and triethyl phosphate), blowing agents (1,1,1,3,3,-pentafluoropropane), and organic vapors (acetone). Area air samples were collected inside the building near the SPF application on five separate tripods fitted with pump mounting brackets to hold the pumps and attach the sampling media. The samples were collected approximately five feet above the ground. Two of the tripods used for collecting the area air samples were placed 10 feet to the left and to the right of the sprayer. They were moved when the sprayer moved. Two tripods were placed approximately 50 feet to the right and to the left of the sprayer. One tripod was placed in a room adjacent to the spraying activities.

Area samples were collected for glycols on XAD-7 OSHA Versatile Sampler (OVS) tubes at a sampling flow rate of 2.0 Lpm. Once the air sampling was completed, the samples were capped, refrigerated, and analyzed according to NIOSH NMAM method 5523.^[10]

Area samples were collected for amine catalysts on XAD-2 OVS tubes at a sampling flow rate of 2.0 Lpm. Once the air sampling was completed, the samples were capped, refrigerated, and analyzed according to Bayer Material Science Environmental Analytics Laboratory method 2.10.3.^[11] Area samples were also collected for flame retardants on XAD-2 OVS tubes at a sampling rate of 2.0 Lpm. Once air sampling was completed, the samples were capped, refrigerated, and analyzed according to a BVNA internal method.

Area samples were collected for blowing agent, 1,1,1,3,3-pentafluoropropane, on two charcoal tubes in series at an air sampling flow rate of 20 mL per minute. Once air sampling was completed, the samples were capped, refrigerated, and analyzed according to NIOSH MNAM method 1300.^[10]

Results

Air sampling was conducted on three shifts. During each shift, the sprayer was applying SPF to the ceiling of the rehab building using a scissor jack as shown in Figure 1.



Figure 1: Sprayer applying SPF to the ceiling using a scissors lift

Bulk samples for the components A and B used to produce the SPF at this job site were collected and qualitatively analyzed for chemical composition using a Hewlett-Packard model HP6890A gas chromatograph with an HP5973 mass selective detector (GC-MSD), operated under electron ionization (EI) conditions, scanning 30-400 amus. Major peaks identified in Component-B included pentafluoropropane, triethyl phosphate, diethylene glycol, triethylene glycol, tris(2-chloroisopropyl)phosphate, and a number of amine compounds, namely pentamethyldipropylene triamine, 3,5-diethyl-2,4-diaminotoluene, and tris(3-dimethylaminopropyl)amine. Results of peaks identified are shown in Table 1. These results were used to determine what compounds to have analyzed on the area air samples collected.

Table 1: Bulk Sample Analysis of Component-B

Number	Identified Chemical Compound
1	1,1,1,3,3-Pentafluoropropane
2	Ethylene glycol
3	1,4-Dioxane
4	Propylene glycol
5	Methyl trioxocane
6	Diethylene glycol
7	Diethylene glycol monomethyl ether
8	Diethylene glycol monovinyl ether
9	Alkyl cyclohexanamine
10	Dipropylene glycol
11	Triethyl phosphate (MW = 182, CAS 78-40-0)
12	Triethylene glycol
13	Triethylene glycol monomethyl ether
14	Polyglycols, unidentified
15	Pentamethyldipropylene triamine (MW = 201, CAS 3855-32-1)
16	Tetraethylene glycol
17	Dodecanethiol
18	3,5-Diethyl-2,4-diaminotoluene (MW = 178, CAS 2095-02-5)
19	Isomer of #18 (MW = 178)
20	Tris(3-dimethylaminopropyl)amine (MW = 272, CAS 33329-35-0)
21	Tris(2-chloroisopropyl)phosphate
22	Bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate
23	Bis(3-chloro-1-propyl)(1-chloro-2-propyl)phosphate
24	Dimethyl-1-hexadecanamine

PBZ samples were collected on the sprayer and helper using glass fiber filters treated with MAP and analyzed for MDI monomer, isocyanate functional group (NCO) monomer, and NCO oligomer. A total of six samples were collected over three work shifts and these results are shown in Table 2.

Table 2: MDI and Isocyanate Results (Glass Fiber Filter)

Sample Date	Worker Description	Sample Time (minutes)	MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
6/27/2012	Sprayer 1	310	18.7	6.12	1.00	7.12
6/27/2012	Helper 1	306	7.89	2.53	0.30	2.83
6/28/2012	Sprayer 1	279	6.80	2.22	0.31	2.53
6/28/2012	Helper 1	301	0.50	0.16	0.05	0.21
6/29/2012	Sprayer 2	168	4.85	1.54	0.29	1.83
6/29/2012	Helper 2	166	0.18	0.06	0.13	0.19

OSHA PEL for MDI Monomer = $200 \mu\text{g}/\text{m}^3$ as 15 min. ceiling

NIOSH REL = $50 \mu\text{g}/\text{m}^3$ TWA

Sprayer 1 sampled on the first work shift had the highest personal exposure to MDI monomer at $18.7 \mu\text{g}/\text{m}^3$. A leak had developed in the line that feeds Component-A to the spray gun which took some time to repair. Also the spraying was conducted in an area with little air movement, potentially contributing to this high exposure. MDI monomer exposure concentrations for the sprayer ranged from 4.85 to $18.7 \mu\text{g}/\text{m}^3$ and 0.18 to $7.89 \mu\text{g}/\text{m}^3$ for the helper over the three shifts sampled. The mean concentration of the MDI monomer for the three shifts was $10.1 \mu\text{g}/\text{m}^3$ for the sprayers and $2.86 \mu\text{g}/\text{m}^3$ for the helpers. None of the PBZ sample results exceeded the NIOSH TWA REL to MDI monomer of $50 \mu\text{g}/\text{m}^3$. PBZ results for NCO monomers and oligomers for the sprayers and helpers are also shown in Table 2. An isocyanate is a compound with a chemical structure of $\text{R}-\text{N}=\text{C}=\text{O}$ and a compound that has two NCO groups is known as a di-isocyanate. MDI is a di-isocyanate. An oligomer is a molecule that consists of a few monomer units, in contrast to a polymer that, at least in principle, consists of a nearly unlimited number of monomers. Dimers, trimers, and tetramers are oligomers. NCO monomer and oligomer results are listed in Table 2 because they better represent the exposure hazard. The United Kingdom's OEL for MDI is $20 \mu\text{g (NCO)}/\text{m}^3$.^[8] None of the personal sample results (for sprayers or helpers) exceeded this OEL.

Area samples were collected by mounting the sample equipment on tripods and placing them throughout the work area. Based on results from the bulk sample analysis area samples were collected for: an amine catalyst, pentamethyldipropylene triamine; flame retardants, tris-(1-chloropropyl) phosphate (TCPP) and triethyl phosphate; a blowing agent, 1,1,1,3,3-pentafluoropropane; glycols, ethylene, diethylene, propylene, triethylene, and tetraethylene; and MDI using both, glass fiber filter and impingers methods. Two tripods were placed 10 feet from the sprayer (left and right of the sprayer), two tripods were placed 50 feet from the sprayer (left and right of the sprayer), and one tripod was placed in a

room adjacent to the spraying area. All samples collected on the tripods were collected at approximately five feet above the ground, the breathing zone height.

A total of 15 MDI glass fiber filter samples were collected during three work shifts. The results for MDI monomer, NCO monomer, and NCO oligomer concentrations are listed in Appendix A and summarized in Table 3.

Table 3: Summary of Mean MDI and Isocyanate Results (Glass Fiber Filter)

Tripod Number	Tripod Location	Mean MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
1	10' from sprayer, left side	2.06	0.67	0.15	0.82
2	10' from sprayer, right side	3.72	1.23	0.29	1.51
3	50' from sprayer, left side	1.96	0.63	0.14	0.77
4	50' from sprayer, right side	1.82	0.58	0.13	0.71
5	Adjacent room	1.50	0.49	0.10	0.59

OSHA PEL for MDI Monomer = $200 \mu\text{g}/\text{m}^3$ as 15 min. ceiling

NIOSH REL = $50 \mu\text{g}/\text{m}^3$ TWA

All area samples collected had detectable concentrations of MDI monomer, NCO monomer, and NCO oligomer except one sample collected during the third work shift in the room adjacent to the spray area. The highest sample result of $7.79 \mu\text{g}/\text{m}^3$ was collected on tripod 2 (close to the spray) during the first work shift. The tripods closest to the sprayer (tripods 1 and 2) had the highest mean concentrations of MDI monomer, NCO monomer, and NCO oligomer when compared to tripods 3, 4, and 5 (located 50 feet on either side of the sprayer and in an adjacent room). This indicates that MDI exposures are higher near the sprayer and decline further away from the spray area which may indicate that MDI does not seem to migrate far from the spraying area.

Fifteen impinger samples were also collected alongside the glass fiber filter samples for MDI, NCO, and NCO oligomer. Impinger samples were collected for comparison to the glass fiber filter samples. Impinger samples tend to have better collection efficiencies than the glass fiber filters because they prevent the loss of isocyanates

to curing reactions by trapping, dissolving, and derivatizing the isocyanate aerosol. The results of the impinger sampling are shown in Appendix B and are summarized in Table 4. Table 5 shows the results of the side by side method comparison (glass fiber method vs. impinger method).

Table 4: Summary of Mean MDI and Isocyanate Results (Impinger)

Tripod Number	Tripod Location	Mean MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Mean Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
1	10' from sprayer, left side	19.25	6.50	3.07	9.57
2	10' from sprayer, right side	30.36	10.12	4.76	14.88
3	50' from sprayer, left side	11.60	3.92	1.47	5.39
4	50' from sprayer, right side	15.91	5.19	1.95	7.14
5	Adjacent room	2.55	0.87	0.66	1.53

OSHA PEL for MDI Monomer = $200 \mu\text{g}/\text{m}^3$ as 15 min. ceiling

NIOSH REL = $50 \mu\text{g}/\text{m}^3$ TWA

Eleven out of the 15 impinger samples collected had detectable concentrations of MDI, NCO, and NCO oligomer. The highest MDI concentration measured was $83.3 \mu\text{g}/\text{m}^3$, which exceeded the NIOSH REL of $50 \mu\text{g}/\text{m}^3$. This sample was collected on a tripod near the sprayer. As with the glass fiber filters, the mean MDI concentrations were higher in the locations closer to the sprayer when compared to those collected away from the spraying area. The four non-detectable samples were collected on tripods 3, 4, and 5 (located 50 feet on either side of the sprayer and in an adjacent room).

Table 5: Comparison of Glass Fiber MDI Monomer, NCO Monomer, NCO Oligomer, and Total NCO Concentration Results to Impinger MDI Monomer, NCO Monomer, NCO Oligomer, and Total NCO Concentration Results

Tripod Number	Sample Time (minutes)	Glass Fiber MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Impinger MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Glass Fiber NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Impinger NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	Glass Fiber NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Impinger NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Glass Fiber Total NCO Conc. ($\mu\text{g}/\text{m}^3$)	Impinger Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
1	300	4.99	53.0	1.63	17.9	0.26	5.63	1.89	23.5
2	304	7.79	83.3	2.61	27.8	0.41	9.02	3.02	36.8
3	304	5.20	16.7	1.69	5.69	0.25	2.08	1.94	7.77
4	301	4.91	15.9	1.57	5.19	0.23	1.95	1.80	7.14
5	298	2.82	4.98	0.92	1.69	0.18	0.66	1.10	2.35
1	349	0.97	4.57	0.31	1.57	0.07	0.51	0.38	2.08
2	369	0.54	4.51	0.17	1.52	0.05	0.49	0.22	2.01
3	378	0.44	6.46	0.14	2.15	0.05	0.85	0.19	3.00
4	396	0.35	<0.01	0.11	<0.003	0.03	<0.10	0.14	<0.10
5	400	0.18	0.12	0.06	0.04	0.04	<0.10	0.10	0.04
1	225	0.21	0.22	0.07	0.07	0.11	<0.18	0.18	0.07
2	212	2.84	3.29	0.9	1.08	0.4	<0.20	1.30	1.08
3	201	0.23	<0.01	0.07	<0.01	0.13	<0.19	0.20	<0.19
4	189	0.19	<0.02	0.06	<0.01	0.14	<0.22	0.20	<0.22
5	171	<0.03	<0.02	<0.01	<0.01	0.08	<0.23	0.08	<0.23

OSHA PEL for MDI Monomer = $200 \mu\text{g}/\text{m}^3$ as 15 min. ceiling

NIOSH REL = $50 \mu\text{g}/\text{m}^3$ TWA

The mean of the difference between the impinger samples and the glass fiber samples is $10.7 \mu\text{g}/\text{m}^3$, with a 95% confidence interval of -1.26 to 22.8. The paired t-test resulted in a two-tailed P value of 0.08, indicating the difference between the two sampling methods was not statically significant at 95% confidence. A correlation coefficient value of 0.83 was determined, meaning there is a correlation between the two sampling methods. Similar findings were seen by Schaeffer et al ^[12]. The mean percent difference between the impinger results and the filter results is 54% indicating that the impingers collection efficiency is 54% higher than that for the filters.

Results for the air samples collected for amine catalyst, pentamethyldipropylene triamine, are listed in Appendix C and summarized in Table 6. A total of 15 samples were collected during the three shifts sampled.

Table 6: Summary of Mean Alkyl Amine Catalyst Results

Tripod Number	Location	Mean Pentamethyl-dipropylene-triamine ($\mu\text{g}/\text{m}^3$)
1	10' from sprayer, left side	13.1
2	10' from sprayer, right side	15.7
3	50' from sprayer, left side	19.6
4	50' from sprayer, right side	12.3
5	Adjacent room	43.1

No OELs established

All samples collected for pentamethyldipropylene triamine were above the limit of detection (LOD) of $1.00 \mu\text{g}/\text{m}^3$ and ranging from 1.36 to $90.5 \mu\text{g}/\text{m}^3$. Unlike the MDI results, high concentrations of pentamethyldipropylene triamine were also found in samples collected on tripods away from the sprayer and in the adjacent room (see Table 6 and Appendix C). The highest concentration of $90.5 \mu\text{g}/\text{m}^3$ was collected on the tripod located in the adjacent room (see Appendix C).

There were two flame retardants present in the Component-B, tris-(1-chloroisopropyl-2)-phosphate (TCPP) and triethyl phosphate. A total of 15 air samples were collected and analyzed for these compounds. The results of this analysis are listed in Appendix D and summarized in Table 7.

Table 7: Summary of Mean Organophosphate Flame Retardants Results

Tripod Number	Tripod Location	Mean Tris-(2-chloroisopropyl) phosphate ($\mu\text{g}/\text{m}^3$)	Mean Triethylphosphate ($\mu\text{g}/\text{m}^3$)
1	10' from sprayer, left side	7.2	121.5
2	10' from sprayer, right side	12.5	168.9
3	50' from sprayer, left side	7.1	165.5
4	50' from sprayer, right side	4.6	97.1
5	Adjacent room	7.8	170.8

No OELs established

All samples collected for the two flame retardants had concentrations above the LOD with detection limits for TCPP and triethyl phosphate of 0.20 and $0.10 \mu\text{g}/\text{m}^3$, respectively. The sample results for TCPP ranged from 3.36 to $19.6 \mu\text{g}/\text{m}^3$, with the highest results measured on tripod 2, near the sprayer. The sample results for triethyl phosphate ranged from $35.2 \mu\text{g}/\text{m}^3$ to $289 \mu\text{g}/\text{m}^3$, with highest concentration measured away from the sprayer on tripod 3 (located 50 feet to the

left of the sprayer). As was the case for the amine catalyst, the two flame retardants were dispersed through the work area. High concentrations were found in samples collected away from the sprayer and in adjacent rooms as well as near the sprayer (see Table 7 and Appendix D).

Polyglycols were also present in Component-B. A total of 15 air samples were collected and analyzed for ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, and tetraethylene glycol. The results of these analyses are listed in Appendix E and summarized in Table 8.

Table 8: Summary of Mean Glycol Results

Tripod Number	Tripod Location	Mean Ethylene glycol ($\mu\text{g}/\text{m}^3$)	Mean Diethylene glycol ($\mu\text{g}/\text{m}^3$)	Mean Propylene glycol ($\mu\text{g}/\text{m}^3$)	Mean Triethylene glycol ($\mu\text{g}/\text{m}^3$)	Mean Tetraethylene glycol ($\mu\text{g}/\text{m}^3$)
1	10' from sprayer, left side	<15	<23	<18	<117	<176
2	10' from sprayer, right side	<15	<23	<18	<117	<176
3	50' from sprayer, left side	<15	<23	<18	<117	<176
4	50' from sprayer, right side	<15	<23	<18	<117	<176
5	Adjacent room	<15	<23	<18	<117	<176

ACGIH TLV for ethylene glycol = 100 mg/m^3 as a 10-minute ceiling

All the samples collected for the polyols were below the LOD, except for one, which had detectable levels of all measured glycols. The LODs for those compounds are of 15 $\mu\text{g}/\text{m}^3$, 23 $\mu\text{g}/\text{m}^3$, 18 $\mu\text{g}/\text{m}^3$, 117 $\mu\text{g}/\text{m}^3$, and 176 $\mu\text{g}/\text{m}^3$, respectively. The detectable concentration measured was 20 $\mu\text{g}/\text{m}^3$ of diethylene glycol collected on tripod 1 near the sprayer.

Fifteen samples were collected for the blowing agent used in Component-B (1,1,1,3,3-pentafluoropropane). Appendix F contains the sample results for the blowing agent, and Table 9 shows the summary results.

Table 9: Summary of Mean Blowing Agent Results

Tripod Number	Tripod Location	Mean 1,1,1,3,3-pentafluoropropane (ppm)
1	10' from sprayer, left side	2.52
2	10' from sprayer, right side	2.49
3	50' from sprayer, left side	0.04
4	50' from sprayer, right side	1.81
5	Adjacent room	1.86

AIHA OEL = 300 ppm TWA

All samples collected for 1,1,1,3,3-pentafluoropropane were above the LOD of 0.01 $\mu\text{g}/\text{m}^3$ except for one, tripod 3 away from the sprayer. These samples ranged from 0.03 to 4.12 ppm, with the highest concentration measured on tripod 1 near the sprayer. The blowing agent results showed similar patterns to the MDI results in that the highest results were collected near the sprayer, and the results were lower at greater distances from the sprayer.

Personal Protective Equipment

The sprayers wore the following personal protective equipment while spraying SPF: Tyvek coveralls with a hood, gloves, shoe covers, and a full-faced air purifying respirator using organic vapor and total particulate cartridges. The helper wore a half-faced respirator with organic vapor and total particulate cartridges.

The Material Safety Data Sheet (MSDS) for BioBased® A-Component^[13] and 2001NB B-Component^[14] by BioBased Insulation Component-A provides the following recommendations for exposure control/personal protection:

- Engineering Controls: Provide local exhaust ventilation sufficient to keep vapors below safe exposure limits.
- Hygiene Measures: Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Appropriate techniques should be used to remove the potentially contaminated clothing. Contaminated work clothing should not be allowed out of the workplace. Wash contaminated clothing before reusing.
- Personal Protective Equipment
 - o Skin Protection: Wear chemical resistant gloves. Suitable materials include nitrile rubber, butyl rubber, and neoprene. Thin latex disposable gloves should be avoided for repeated or long term use. Protective clothing should be selected and used in accordance with "Guidelines for the selection of Chemical Protective Clothing" published by ACGIH. Use of rubber footwear or overshoes is recommended.
 - o Eye Protection: Wear chemical safety goggles and/or chemical safety goggles with face shield for liquid transfer operations.

- o Respiratory Protection: Not required for properly ventilated areas. In areas where vapors and/or mists are present but the concentration is unknown, use of an air supplied respirator or an approved MSHA/NIOSH positive-pressure respirator is recommended. Air purifying respirators equipped with organic vapor cartridges and a HEPA (P100) particulate filter may be used under certain conditions when a cartridge change-out schedule has been developed in accordance with the OSHA respiratory protection standards (29 CFR 1910.134).
- o Additional Recommendations: A safety shower and eye wash should be available. Consult your supervisor or SOP for special handling instructions.

Based on the MSDS recommendations and the air sampling results, the sprayers should wear full-face air-supplying respirators to assure proper respiratory protection. The helper should wear a full-faced air-purifying respirator to protect their eyes from the irritating chemical compounds found in the SPF components. In addition, the helpers should wear protective clothing to protect their skin from chemical exposure.

Recommendations

Air samples collected during the three shifts of SPF installation demonstrated that detectable concentrations of chemical compounds found in SPF were present in the air samples collected during spraying. Protective clothing including coverall, gloves, and foot covers and respirators are needed for all workers in the spraying operations. Based on these results, which only represent the findings from this location, local exhaust ventilation should be used to control and reduce the SPF exposures to the sampled compounds, and in particular MDI, NCO monomer, and NCO oligomer. The sprayer should be using an air supplied respirator instead of air purifying. The helper should use air-purifying full-face respirators and wear coveralls, head and foot covers, and chemical resistant gloves. If air purifying respirators are used, they need to be full-faced and the air purifying cartridges should be changed based on a schedule determined by OSHA Respiratory Protection e-Tool and an OSHA Standard Interpretation letter concerning isocyanates provide guidance on cartridge change-out schedules and respirator selection.^[15]

A respiratory protection program was not observed during our survey. A respiratory protection program is required by OSHA (Standard 29 CFR 1910.134) when using respirators. Included in the program should be the following elements:

- Respirator selection logic^[16]
- Medical clearance process
- Quantitative respirator fit testing done annually
- Annual training to ensure the competence of respirator users
- The proper cleaning, inspecting, maintenance and storing of respirator

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Appendices

Appendix A: Glass Fiber MDI and Isocyanate Results

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
6/27/2012	1	10' from sprayer, left side	300	4.99	1.63	0.26	1.89
6/27/2012	2	10' from sprayer, right side	304	7.79	2.61	0.41	3.02
6/27/2012	3	50' from sprayer, left side	304	5.20	1.69	0.25	1.94
6/27/2012	4	50' from sprayer, right side	301	4.91	1.57	0.23	1.80
6/27/2012	5	Adjacent room	298	2.82	0.92	0.18	1.10
6/28/2012	1	10' from sprayer, left side	349	0.97	0.31	0.07	0.38
6/28/2012	2	10' from sprayer, right side	369	0.54	0.17	0.05	0.22
6/28/2012	3	50' from sprayer, left side	378	0.44	0.14	0.05	0.19
6/28/2012	4	50' from sprayer, right side	396	0.35	0.11	0.03	0.14
6/28/2012	5	Adjacent room	400	0.18	0.06	0.04	0.10
6/29/2012	1	10' from sprayer, left side	173	0.21	0.07	0.11	0.18
6/29/2012	2	10' from sprayer, right side	211	2.84	0.90	0.4	1.30
6/29/2012	3	50' from sprayer, left side	199	0.23	0.07	0.13	0.20
6/29/2012	4	50' from sprayer, right side	188	0.19	0.06	0.14	0.20
6/29/2012	5	Adjacent room	168	<0.03	<0.01	0.08	0.08

Appendix B: Impinger MDI and Isocyanate Results

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	MDI Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Monomer Conc. ($\mu\text{g}/\text{m}^3$)	NCO Oligomer Conc. ($\mu\text{g}/\text{m}^3$)	Total NCO Conc. ($\mu\text{g}/\text{m}^3$)
6/27/2012	1	10' from sprayer, left side	300	53.0	17.9	5.63	23.5
6/27/2012	2	10' from sprayer, right side	300	83.3	27.8	9.02	36.78
6/27/2012	3	50' from sprayer, left side	304	16.7	5.69	2.08	7.77
6/27/2012	4	50' from sprayer, right side	301	15.9	5.19	1.95	7.14
6/27/2012	5	Adjacent room	298	4.98	1.69	0.66	2.35
6/28/2012	1	10' from sprayer, left side	348	4.57	1.57	0.51	2.08
6/28/2012	2	10' from sprayer, right side	254	4.51	1.52	0.49	2.01
6/28/2012	3	50' from sprayer, left side	378	6.46	2.15	0.85	3.00
6/28/2012	4	50' from sprayer, right side	392	<0.01	<0.01	<0.10	<0.10
6/28/2012	5	Adjacent room	399	0.12	0.04	<0.10	0.04
6/29/2012	1	10' from sprayer, left side	225	0.22	0.07	<0.18	0.07
6/29/2012	2	10' from sprayer, right side	212	3.29	1.08	<0.20	1.08
6/29/2012	3	50' from sprayer, left side	201	<0.01	<0.01	<0.19	<0.19
6/29/2012	4	50' from sprayer, right side	189	<0.02	<0.01	<0.22	<0.22
6/29/2012	5	Adjacent room	171	<0.02	<0.01	<0.23	<0.23

Appendix C: Alkyl Amine Catalyst Results

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Pentamethyl- dipropylene- triamine ($\mu\text{g}/\text{m}^3$)
6/27/2012	1	10' from sprayer, left side	265	16.5
6/27/2012	2	10' from sprayer, right side	303	12.3
6/27/2012	3	50' from sprayer, left side	304	9.08
6/27/2012	4	50' from sprayer, right side	301	6.13
6/27/2012	5	Adjacent room	299	90.5
6/28/2012	1	10' from sprayer, left side	348	1.36
6/28/2012	2	10' from sprayer, right side	369	20.3
6/28/2012	3	50' from sprayer, left side	376	25.4
6/28/2012	4	50' from sprayer, right side	396	10.0
6/28/2012	5	Adjacent room	400	12.5
6/29/2012	1	10' from sprayer, left side	277	21.2
6/29/2012	2	10' from sprayer, right side	134	14.5

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Pentamethyl- dipropylene- triamine ($\mu\text{g}/\text{m}^3$)
6/29/2012	3	50' from sprayer, left side	200	24.4
6/29/2012	4	50' from sprayer, right side	188	20.7
6/29/2012	5	Adjacent room	170	26.4

Appendix D: Organophosphate Flame Retardants Results

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Tris-(2-chloroisopropyl) phosphate ($\mu\text{g}/\text{m}^3$)	Triethylphosphate ($\mu\text{g}/\text{m}^3$)
6/27/2012	1	10' from sprayer, left side	297	6.06	40.4
6/27/2012	2	10' from sprayer, right side	304	19.6	62.2
6/27/2012	3	50' from sprayer, left side	304	4.45	36.3
6/27/2012	4	50' from sprayer, right side	302	3.36	35.2
6/27/2012	5	Adjacent room	218	13.0	200
6/28/2012	1	10' from sprayer, left side	349	8.41	157
6/28/2012	2	10' from sprayer, right side	369	11.0	257
6/28/2012	3	50' from sprayer, left side	377	12.0	289
6/28/2012	4	50' from sprayer, right side	396	5.94	139
6/28/2012	5	Adjacent room	400	5.08	145
6/29/2012	1	10' from sprayer, left side	226	7.05	167
6/29/2012	2	10' from sprayer, right side	211	6.87	187
6/29/2012	3	50' from sprayer, left side	200	4.96	171
6/29/2012	4	50' from sprayer, right side	188	4.53	117
6/29/2012	5	Adjacent room	170	5.40	168

Appendix E: Glycol Results

Sample Date	Tripod Number	Tripod Location	Sample Time (min.)	Ethylene glycol ($\mu\text{g}/\text{m}^3$)	Diethylene glycol ($\mu\text{g}/\text{m}^3$)	Propylene glycol ($\mu\text{g}/\text{m}^3$)	Triethylene glycol ($\mu\text{g}/\text{m}^3$)	Tetra-ethylene glycol ($\mu\text{g}/\text{m}^3$)
6/27/2012	1	10' from sprayer, left side	297	<15	20	<18	<117	<176
6/28/2012	1	10' from sprayer, left side	348	<15	<23	<18	<117	<176
6/29/2012	1	10' from sprayer, left side	226	<15	<23	<18	<117	<176
6/27/2012	2	10' from sprayer, right side	300	<15	<23	<18	<117	<176
6/28/2012	2	10' from sprayer, right side	369	<15	<23	<18	<117	<176
6/29/2012	2	10' from sprayer, right side	211	<15	<23	<18	<117	<176
6/27/2012	3	50' from sprayer, left side	308	<15	<23	<18	<117	<176
6/28/2012	3	50' from sprayer, left side	377	<15	<23	<18	<117	<176
6/29/2012	3	50' from sprayer, left side	199	<15	<23	<18	<117	<176
6/27/2012	4	50' from sprayer, right side	302	<15	<23	<18	<117	<176
6/28/2012	4	50' from sprayer, right side	396	<15	<23	<18	<117	<176

Sample Date	Tripod Number	Tripod Location	Sample Time (min.)	Ethylene glycol (µg/m ³)	Diethylene glycol (µg/m ³)	Propylene glycol (µg/m ³)	Triethylene glycol (µg/m ³)	Tetra- ethylene glycol (µg/m ³)
6/29/2012	4	50' from sprayer, right side	188	<15	<23	<18	<117	<176
6/27/2012	5	Adjacent room	298	<15	<23	<18	<117	<176
6/28/2012	5	Adjacent room	399	<15	<23	<18	<117	<176
6/29/2012	5	Adjacent room	170	<15	<23	<18	<117	<176

Appendix F: Blowing Agent Results

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	1,1,1,3,3- pentafluoropropane (ppm)
6/27/2012	1	10' from sprayer, left side	300	1.05
6/27/2012	2	10' from sprayer, right side	299	1.09
6/27/2012	3	50' from sprayer, left side	298	<0.01
6/27/2012	4	50' from sprayer, right side	306	0.78
6/27/2012	5	Adjacent room	306	0.29
6/28/2012	1	10' from sprayer, left side	338	2.40
6/28/2012	2	10' from sprayer, right side	368	2.57
6/28/2012	3	50' from sprayer, left side	377	0.03
6/28/2012	4	50' from sprayer, right side	394	1.65
6/28/2012	5	Adjacent room	401	2.01
6/29/2012	1	10' from sprayer, left side	231	4.12
6/29/2012	2	10' from sprayer, right side	212	3.80
6/29/2012	3	50' from sprayer, left side	200	0.04
6/29/2012	4	50' from sprayer, right side	191	2.98
6/29/2012	5	Adjacent room	172	3.28



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