



## In-Depth Survey Report

---

### **Spray Polyurethane Foam Chemical Exposures during Spray Application**

**Priority 1, Cincinnati, Ohio**

David Marlow and Joseph DeCapite

---

Division of Applied Research and Technology  
Engineering and Physical Hazards Branch  
EPHB Report No. 005-166  
Priority 1 Insulation,  
Cincinnati, Ohio

April 2017

DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Centers for Disease Control and Prevention  
National Institute for Occupational Safety and Health



**Sites Surveyed: Residence on 8020 Bloom Rd., Cincinnati, OH;  
Bishop Hall, Miami University, Oxford, OH; and Old Fire House on  
3678 Heekin Ave., Cincinnati, OH**

**NAICS Code:**

**Survey Dates: 10/02/2012; 10/25/2012; and 10/31/2012**

**Surveys Conducted By: David Marlow and Joseph DeCapite**

**Employer Representatives Contacted: Barry Kirby**

## **Disclaimer**

Mention of any company or product does not constitute endorsement by NIOSH. In addition, citations to websites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these websites. All Web addresses referenced in this document were accessible as of the publication date.

# Table of Contents

Disclaimer .....	3
Abstract .....	5
Introduction .....	1
Background for Control Technology Studies .....	1
Building and Process Description .....	2
Occupational Exposure Limits and Health Effects .....	2
Methodology .....	8
Results .....	10
Recommendations .....	14
References .....	15

## Abstract

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. 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) 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. Past studies have shown that sprayers' exposures to MDI can range from 7.0 to 205  $\mu\text{g}/\text{m}^3$ , exceeding the OSHA permissible exposure limit (200  $\mu\text{g}/\text{m}^3$  as a 15 minute ceiling limit). No air sampling has been conducted to assess both MDI exposure as well as exposures to the other chemicals present in SPF. This survey was conducted to more fully evaluate worker exposures during the application of SPF.

Air sampling was conducted to characterize the chemical exposures during spray polyurethane foam installation at three different sites. Personal breathing zone air samples were collected for MDI, isocyanate functional group (NCO) monomer, and NCO oligomer. The mean MDI concentration for the sprayers was 47.4  $\mu\text{g}/\text{m}^3$  ranging from 7.98 to 105  $\mu\text{g}/\text{m}^3$ . The helper mean MDI concentration for the sprayer was 6.27  $\mu\text{g}/\text{m}^3$  ranging from 0.33 to 9.74  $\mu\text{g}/\text{m}^3$ . The mean concentration for MDI for the sprayers was 47.4  $\mu\text{g}/\text{m}^3$ , approaching the NIOSH TWA REL of 50  $\mu\text{g}/\text{m}^3$ . 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). These air samples showed the presence of all the chemical compounds sampled.

Based on concentrations found in the personal breathing zone air sample results the sprayer and helpers should use supplied-air 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. The sampling results indicate that MDI as well as chemical compounds found in the B-component side are present in 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.<sup>[1]</sup> 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) 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), chemical protective gloves (e.g. nitrile) and foot covers 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.

Studies have shown that short term MDI exposures for sprayers have ranged from 7.0 to 205  $\mu\text{g}/\text{m}^3$ .<sup>[2,3,4]</sup> NIOSH has recommended that TDI exposure be limited to 0.005 ppm (0.005 mg/m<sup>3</sup>) as a TWA for up to a 10-hour workday during a 40-hour workweek, with a ceiling concentration of 0.02 ppm (0.2 mg/m<sup>3</sup>) for any 10-minute period [NIOSH 1978]. The concentrations of MDI were shown to decrease with distance from the source in another study.<sup>[4]</sup> Very limited data on the concentrations of the other chemicals present in SPF are currently available. This study gathered exposure data on MDI, (NCO) monomer, and NCO oligomer as well as to other components of the SPF process (e.g. polyols, amine catalysts, blowing agents, and flame retardants).

## **Building and Process Description**

Air sampling was conducted at three sites on three different days. Site #1 was a residential renovation and foam was sprayed on 400 ft<sup>2</sup> exterior facing walls. Site #2 was Bishop Hall at Miami University, which was under renovation, and foam was sprayed on 2700 ft<sup>2</sup> exterior facing walls. Site #3 was an old firehouse being renovated into an office building and foam was sprayed on 2200 ft<sup>2</sup> exterior facing walls. These spray installations were done by Priority 1 Construction Service, Inc. from Cincinnati, Ohio. The sprayers for Priority 1 used a two component system manufactured by Dow Chemical Company. Component-A, Dow 3019 isocyanate, was a polymeric mixture of MDI and Component-B, Styrofoam™ SPF MX 2030 polyol, was a polyol blend with 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 also have a recommended short term exposure limit (STEL) or a ceiling value 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) establish Permissible Exposure Limits (PELs) <sup>[5]</sup>, 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 <sup>[6]</sup>. 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) <sup>®</sup> recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) <sup>®</sup>, a professional organization <sup>[7]</sup>. 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” <sup>[8]</sup>.

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 ceiling concentration of  $200 \mu\text{g}/\text{m}^3$  (0.02 parts per million (ppm)). The ACGIH TLV and the NIOSH REL for MDI are established as a eight (ACGIH) or ten (NIOSH) hour TWA of  $50 \mu\text{g}/\text{m}^3$  (0.005 ppm).<sup>[6,7]</sup> NIOSH also has set a ceiling REL of  $200 \mu\text{g}/\text{m}^3$  (0.02 ppm) for MDI.<sup>6</sup> 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  $20 \mu\text{g}$  (NCO)/ $\text{m}^3$ . 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.<sup>[7]</sup> The amine catalysts (such as benzyldimethylamine, tertiary amine catalyst, or triethylenediamine) found in the component B of the SPF may be sensitizers and irritants that can cause blurry vision (halo effect).<sup>[8]</sup> Flame retardants, such as halogenated compounds, are persistent, bioaccumulative, and toxic chemicals. 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.<sup>[7]</sup>

## Methodology

In order to identify the chemicals present in the SPF formulation bulk liquid direct injection of  $0.5 \mu\text{L}$  into a gas chromatograph–mass spectrometer (GC-MS) was done. 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.

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  $1 \times 10^{-4}$  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.<sup>[9]</sup>

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  $1 \times 10^{-4}$  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 MNAM method 5523.<sup>[10]</sup>

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.<sup>[11]</sup> 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.<sup>[12]</sup>

## Results

Bulk samples of the two components used to produce SPF, Component-A and Component-B, were collected and analyzed for chemical composition using a Hewitt-Packard model HP6890A gas chromatograph with an HP5973 mass selective detector (GC-MSD), operated under EI conditions, scanning 30-400 amu. 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 qualitative results were used to determine what compounds to sample for in the air samples.

Table 1

## Bulk Sample Qualitative Analysis of Component B Chemical Composition

Number	Identified Chemical Compound
1	1,1,1,3,3-Pentafluoropropane
2	Dimethylethanolamine
3	Propylene glycol
4	1-Methyl-imidazole
5	Diethylene glycol
6	Methyl styrene
7	N,N-dimethylcyclohexanamine (CAS 98-94-2)
8	Dipropylene glycol
9	C <sub>6</sub> H <sub>14</sub> O <sub>3</sub> isomer, 2-(2-hydroxypropoxy)-1-propanol
10	Bromoether compound
11	4-Morpholineethanol
12	2,2'-oxybis[N,N-dimethyl]ethanamine
13	Triethyl phosphate
14	2-Ethylhexanoic acid
15	p-Methyl benzyl alcohol
16	Triethylene glycol
17	Di- or Triethylene glycol monomethyl ether
18	Polyglycols, unidentified
19	Bis-(dimethylaminopropyl)amine
20	Triethanolamine
21	Tetradecane
22	Methyl p-(hydroxymethyl)benzoate
23	Tribromobenzene
24	Tris(3-dimethylaminopropyl)amine (MW=272, CAS 33329-35-0)
25	Tris(2-chloroisopropyl)phosphate
26	Bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate
27	Methyl benzoic acid, 2-methoxyethyl ester
28	Tetrabromobenzene
29	Chlorophosphate compound
30	Brominated compound
31	Low molecular weight oligomers of the polyol production

Personal breathing zone (PBZ) air samples using glass fiber filters treated with MAP were collected on the sprayers and helpers and analyzed for MDI monomer, isocyanate functional group (NCO) monomer, and NCO oligomer. A total of 11 samples were collected over three days and these results are shown in Table 2.

Table 2

Glass Fiber MDI and Isocyanate Results							
Sample Date	Location	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. ( $\mu\text{g}/\text{m}^3$ )
Day 1	Residence	Sprayer #1	70	105	35.1	4.35	39.5
Day 1	Residence	Sprayer #2	68	8.39	2.80	<1.03	2.80
Day 1	Residence	Helper #1	68	9.74	3.29	<1.00	3.29
Day 2	University	Sprayer #2	211	30.7	10.2	0.39	10.6
Day 2	University	Helper #2	40	2.70	0.91	<1.72	0.91
Day 2	University	Helper #3	35	0.33	0.11	<1.94	0.11
Day 3	Firehouse	Sprayer #1	115	101	33.5	5.87	39.4
Day 3	Firehouse	Sprayer #1	145	7.98	2.73	<0.47	2.73
Day 3	Firehouse	Sprayer #2	137	31.4	10.2	3.21	13.4
Day 3	Firehouse	Helper #4	74	9.41	3.09	<0.94	3.09
Day 3	Firehouse	Helper #4	116	9.44	3.00	1.03	4.03

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

A total of six PBZ air samples were collected on the sprayers with a mean MDI concentration of  $47.4 \mu\text{g}/\text{m}^3$  and ranging from  $7.98$  to  $105 \mu\text{g}/\text{m}^3$ . Sprayer#1 had the highest exposure measured on a worker to MDI monomer at  $105 \mu\text{g}/\text{m}^3$  on Day 1. Much of the spraying during this sampling period was in a small room (8 ft. x 15 ft. x 8 ft.) with no ventilation. The second highest MDI concentration was also measured on Sprayer #1 on Day 3 with a concentration of  $101 \mu\text{g}/\text{m}^3$ . This sample was collected at the firehouse renovation site while spraying the inside of a bell tower (8 ft. x 8 ft. x 30 ft.). Both of these samples exceeded the NIOSH REL and ACGIH TLV of  $50 \mu\text{g}/\text{m}^3$ . A total of 5 PBZ air samples were collected on helpers during the three days of sampling. The mean MDI concentration found for the helper was  $6.27 \mu\text{g}/\text{m}^3$  and range of  $0.33$  to  $9.74 \mu\text{g}/\text{m}^3$ . Also shown in Table 2 are PBZ results for isocyanate functional groups (NCO) monomers and oligomers for the sprayers and helpers. An isocyanate contains the formula of  $\text{R-N}=\text{C}=\text{O}$  and a compound that has two NCO (such as MDI) is known as 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, trimer, 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 total NCO is  $20 \mu\text{g (NCO)}/\text{m}^3$ . [13] Two of

the sprayers' results exceeded this OEL. Sprayer #1 total NCO on day 1 was 39.5  $\mu\text{g NCO}/\text{m}^3$  and on day 3 it was 39.4  $\mu\text{g NCO}/\text{m}^3$ .

Area air samples were collected on tripods placed throughout the work area. Based on results from the bulk sample analysis on each tripod, air samples were collected for: the amine catalysts, N,N-dimethylcyclohexanamine and tris(3-dimethylaminopropyl)amine; flame retardants, tris(1-chloropropyl-2) phosphate (TCPP), and triethyl phosphate; a blowing agent, 1,1,1,3,3-pentafluoropropane; diethylene glycol; and MDI using both glass fiber filter treated with MAP and impingers containing 15 ml of  $1 \times 10^{-4}$  M MAP in butyl benzoate. Tripods (Tripods #1 and #2) were placed in areas approximately 10 ft. on the left and right sides of the spraying operation. These two tripods were moved along the sprayer in order to stay near the spraying operations.

A total of 14 MDI glass fiber filter samples were collected during three days of sampling. The results for MDI monomer, NCO monomer, and NCO oligomer concentrations are listed in Table 3.

Table 3

Area Air 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. ( $\mu\text{g}/\text{m}^3$ )
Day 1	1	10' from sprayer, left side	67	15.7	5.13	1.34	6.47
Day 1	2	10' from sprayer, right side	65	22.6	7.52	1.96	9.48
Day 2	1	10' from sprayer, left side	212	2.48	0.86	<0.32	0.86
Day 2	2	10' from sprayer, right side	209	5.59	1.96	<0.33	1.96
Day 2	3	50' from sprayer, left side	196	0.60	0.20	<0.35	0.20
Day 2	4	50' from sprayer, right side	42	0.46	0.15	<1.68	0.15
Day 3	1	10' from sprayer, left side	186	6.12	2.09	0.76	2.85
Day 3	1	10' from sprayer, left side	186	14.3	4.69	1.02	5.71
Day 3	2	10' from sprayer, right side	183	8.31	2.86	0.99	3.85
Day 3	2	10' from sprayer, right side	187	8.64	2.80	0.66	3.46
Day 3	3	50' from sprayer, left side	182	3.50	1.18	<0.38	1.18
Day 3	3	50' from sprayer, left side	190	7.22	2.42	0.67	3.09
Day 3	4	50' from sprayer, right side	180	0.88	0.29	<0.39	0.29
Day 3	4	50' from sprayer, right side	191	10.9	3.64	1.25	4.89

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 air glass fiber samples collected had detectable concentrations of MDI monomer and NCO monomer. The MDI concentrations collected on the tripods ranged from 0.46 to 22.6  $\mu\text{g}/\text{m}^3$ , with a mean concentration of 7.02  $\mu\text{g}/\text{m}^3$ . The highest sample result, 22.6  $\mu\text{g}/\text{m}^3$ , was collected on tripod #2 on Day 1.

Collected alongside the glass fiber filter samples were 10 impinger samples analyzed for MDI, NCO, and NCO oligomer. Impinger samples were collected for comparison to the glass fiber filter samples. Impinger samples have better collection efficiencies than the glass fiber filters because they prevent loss of isocyanates to curing reactions by trapping, dissolving, and derivatizing the isocyanate aerosol. <sup>[14]</sup> Listed in Table 4 are the results of the impinger samples.

Table 4

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. ( $\mu\text{g}/\text{m}^3$ )
Day 1	#1	10' from sprayer, left side	67	76.4	25.9	0.86	26.8
Day 1	#2	10' from sprayer, right side	65	78.1	26.0	0.93	26.9
Day 2	#1	10' from sprayer, left side	212	63.8	21.4	4.42	25.8
Day 2	#2	10' from sprayer, right side	209	356	117	20.3	137
Day 2	#3	50' from sprayer, left side	196	12.4	4.05	0.69	4.74
Day 2	#4	50' from sprayer, right side	145	3.62	1.16	0.09	1.25
Day 3	#1	10' from sprayer, left side	371	44.2	14.3	0.81	15.1
Day 3	#2	10' from sprayer, right side	370	37.8	12.6	0.76	13.4
Day 3	#3	50' from sprayer, left side	372	9.19	3.15	0.16	3.31
Day 3	#4	50' from sprayer, right side	371	3.16	1.05	0.09	1.14

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 10 impinger samples collected had detectable concentrations of MDI, NCO, and NCO oligomer. The highest MDI concentration measured was 78.1  $\mu\text{g}/\text{m}^3$ , which exceeded the NIOSH REL of 50  $\mu\text{g}/\text{m}^3$ . This sample was collected on a tripod near the sprayer. As was seen with the glass fiber filters the MDI concentrations were highest on the tripods that were near the sprayer when compared to those collected away from the sprayer.

The glass fiber filters and impinger samples were collected side by side on the tripods for comparison of the two sample methods. Shown in Table 5 are the results of this side by side comparison.

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	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	15.7	76.4	5.13	25.9	1.34	0.86	6.47	26.8
#2	22.6	78.1	7.52	26.0	1.96	0.93	9.48	26.9
#1	2.48	63.8	0.86	21.4	<0.32	4.42	0.86	25.8
#2	5.59	356	1.96	117	<0.33	20.3	1.96	137
#3	0.60	12.4	0.20	4.05	<0.35	0.69	0.20	4.74
#4	0.46	3.62	0.15	1.16	<1.68	0.23	0.15	1.39
#1	10.2	44.2	3.39	14.3	0.89	0.81	4.28	15.1
#2	8.48	37.8	2.83	12.6	1.00	0.76	3.83	13.4
#3	5.40	9.19	0.70	3.15	0.43	0.16	1.13	3.31
#4	6.06	3.16	2.02	1.05	0.74	0.09	2.76	1.14

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 MDI concentration of impinger samples minus mean MDI concentration of glass fiber samples is  $60.7 \mu\text{g}/\text{m}^3$ , with a 95% confidence interval of -14.18 to 135. The paired t-test results was a two-tailed P value of 0.10, indicating the difference between the two sampling method was not statically significant at 95% confidence. A correlation coefficient value of 0.10 was determined, showing a weak correlation between the two sampling methods.

Results for the air samples collected for amine catalysts, tris (3-dimethylaminopropyl) amine and dimethylcyclohexylamine, are shown in Table 6. A total of 10 samples were collected during the three days sampled.

Table 6

Alkyl Amine Catalyst Results					
Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Dimethylcyclohexylamine ( $\mu\text{g}/\text{m}^3$ )	Tris-(3-dimethylaminopropyl) amine ( $\mu\text{g}/\text{m}^3$ )
Day 1	Tripod #1	10' from sprayer, left side	67	0.10	<0.37
Day 1	Tripod #2	10' from sprayer, right side	65	0.07	<0.38
Day 2	Tripod #1	10' from sprayer, left side	161	<0.01	0.89
Day 2	Tripod #2	10' from sprayer, right side	198	<0.01	<0.13
Day 2	Tripod #3	50' from sprayer, left side	119	<0.01	<0.21
Day 2	Tripod #4	50' from sprayer, right side	145	<0.01	<0.18
Day 3	Tripod #1	10' from sprayer, left side	371	2.01	0.19
Day 3	Tripod #2	10' from sprayer, right side	370	2.01	0.13
Day 3	Tripod #3	50' from sprayer, left side	372	1.46	<0.07
Day 3	Tripod #4	50' from sprayer, right side	371	1.78	0.12

No OELs established

Six of the 10 air samples collected for dimethylcyclohexylamine were detectable ranging from 0.07 to 2.01  $\mu\text{g}/\text{m}^3$  with a limit of detection of 0.01  $\mu\text{g}/\text{m}^3$ . All four of the non-detectable dimethylcyclohexylamine were collected during the second day of air sampling at Bishop Hall. Four of the 10 air sampling results for tris-(3-dimethylaminopropyl) amine had detectable concentrations ranging from 0.12 to 0.89  $\mu\text{g}/\text{m}^3$ .

There were two flame retardants present in the B-side, tris-(1-chloroisopropyl-2)-phosphate (TCPP) and triethyl phosphate. A total of 10 air samples were collected and analyzed for these compounds. The results are listed in Table 7.



Table 7

Organophosphate Flame Retardants Results					
Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Tris-(1-chloropropyl-2) phosphate ( $\mu\text{g}/\text{m}^3$ )	Triethylphosphate ( $\mu\text{g}/\text{m}^3$ )
Day 1	Tripod #1	10' from sprayer, left side	67	0.36	8.10
Day 1	Tripod #2	10' from sprayer, right side	65	0.40	8.39
Day 2	Tripod #1	10' from sprayer, left side	107	1.48	0.002
Day 2	Tripod #2	10' from sprayer, right side	209	2.23	0.001
Day 2	Tripod #3	50' from sprayer, left side	45	0.20	0.001
Day 2	Tripod #4	50' from sprayer, right side	145	0.20	0.001
Day 3	Tripod #1	10' from sprayer, left side	371	0.07	9.47
Day 3	Tripod #2	10' from sprayer, right side	370	0.06	9.39
Day 3	Tripod #3	50' from sprayer, left side	372	0.03	7.63
Day 3	Tripod #4	50' from sprayer, right side	371	0.05	7.83

No OELs established

All samples collected for the two flame retardants had detectable concentrations with detection limits for TCP and triethyl phosphate being  $0.03 \mu\text{g}/\text{m}^3$ , and  $0.001 \mu\text{g}/\text{m}^3$ , respectively. The sample results for TCP ranged from  $0.03$  to  $2.23 \mu\text{g}/\text{m}^3$ , with highest result measured on tripod #2, near the sprayer. The sample result for triethyl phosphate ranged from  $0.001 \mu\text{g}/\text{m}^3$  to  $9.47 \mu\text{g}/\text{m}^3$ , with highest concentration measured near the sprayer on tripod #2.

Diethylene glycol was also present in the B-side. A total of 10 air samples were collected and analyzed for diethylene glycol. The results of these analyses are listed in Table 8.

Table 8

Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	Diethylene glycol ( $\mu\text{g}/\text{m}^3$ )
10/02/2012	Tripod #1	10' from sprayer, left side	67	<0.04
10/02/2012	Tripod #2	10' from sprayer, right side	65	0.76
10/25/2012	Tripod #1	10' from sprayer, left side	212	<0.01
10/25/2012	Tripod #2	10' from sprayer, right side	186	<0.01
10/25/2012	Tripod #3	50' from sprayer, left side	196	<0.01
10/25/2012	Tripod #4	50' from sprayer, right side	32	1.70
10/31/2012	Tripod #1	10' from sprayer, left side	371	0.17
10/31/2012	Tripod #2	10' from sprayer, left side	370	0.18
10/31/2012	Tripod #3	50' from sprayer, left side	372	0.22
10/31/2012	Tripod #4	50' from sprayer, right side	370	0.21

No OELs established

Six of the 10 of the samples collected had detectable concentrations of ethylene glycol ranging from 0.18 to 1.70  $\mu\text{g}/\text{m}^3$  with detection limits of 5  $\mu\text{g}/\text{m}^3$ . The blowing agent used in the B-side was 1,1,1,3,3-pentafluoropropane. A total of 10 samples were collected for 1,1,1,3,3,-pentafluoropropane. Listed in Table 9 are the results of the samples.

Table 9

Blowing Agent Results				
Sample Date	Tripod Number	Tripod Location	Sample Time (minutes)	1,1,1,3,3-pentafluoropropane (ppm)
Day 1	Tripod #1	10' from sprayer, left side	67	1.28
Day 1	Tripod #2	10' from sprayer, right side	65	107
Day 2	Tripod #1	10' from sprayer, left side	212	0.06
Day 2	Tripod #2	10' from sprayer, right side	210	0.20
Day 2	Tripod #3	50' from sprayer, left side	197	0.09
Day 2	Tripod #4	50' from sprayer, right side	195	0.05
Day 3	Tripod #1	10' from sprayer, left side	372	<0.01
Day 3	Tripod #2	10' from sprayer, right side	372	63.5
Day 3	Tripod #3	50' from sprayer, left side	358	77.8
Day 3	Tripod #4	50' from sprayer, right side	369	79.0

AIHA OEL = 300 ppm TWA

Nine of the 10 samples collected for 1,1,1,3,3-pentafluoropropane had detectable concentration with the detectable concentrations ranging from 0.05 to 79.0 parts per million (ppm), with highest concentration measured on tripod #3 away from the sprayer.

## Personal Protective Equipment

The sprayers during all three days 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. On the third day of sampling, there were two sprayers; one sprayer wore a full-face air purifying respirator and the other sprayer wore a full-face air-supplied respirator. The helper during all three days wore a half-face respirator with organic vapor and total particulate cartridges. Some of the helpers wore Tyvek coveralls and some did not.

The use of respirators is the least preferred method of controlling worker exposures. Respirators should not be used as the primary control for routine operations, but NIOSH recognizes that they may be used during situations such as implementation of engineering controls, some short-duration maintenance procedures, and emergencies. Only the most protective respirators should be used for situations involving exposures to isocyanates that have poor warning properties, are potent sensitizers, or may be carcinogenic. These respirators include any self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive-pressure mode, and any supplied-air respirator with a full facepiece operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive-pressure mode. Whenever there is potential for exposure to diisocyanates, even concentrations below the NIOSH REL, NIOSH recommends that employees be supplied with supplied-air respiratory protection. (Negative pressure air-purifying respirators are not recommended since diisocyanates have poor odor warning properties.)<sup>[15]</sup>

Any respiratory protection program must, at a minimum, meet the requirements of the OSHA respiratory protection standard [29 CFR 1910.134]. Respirators must be certified by NIOSH and MSHA according to 30 CFR or by NIOSH (effective July 19, 1995) according to 42 CFR 84. A complete respiratory protection program should include (1) regular training and medical evaluation of personnel, (2) fit testing, (3) periodic environmental monitoring, (4) periodic maintenance, inspection, and cleaning of equipment, (5) proper storage of equipment, and (6) written standard operating procedures governing the selection and use of respirators. The program should be evaluated regularly.

In addition, employers should provide protective clothing, gloves, and footwear that is impervious to isocyanate--containing compounds. The protective clothing should either be disposed or laundered after each use (e.g., at the end of the work shift).

<sup>[15]</sup> The gloves should be elbow-length and made of an isocyanate-resistant material. Workers should wear protective clothing such as chemical goggles, Tyvek suits, boots or shoe covers chemically resistant gloves (including butyl rubber, polyethylene, chlorinated polyethylene, ethyl vinyl alcohol laminate). The MSDS ([http://www.easterninsulation.com/pdfs/MSDS\\_Biobased\\_A\\_Component\\_October\\_20\\_2010.pdf](http://www.easterninsulation.com/pdfs/MSDS_Biobased_A_Component_October_20_2010.pdf) and [http://www.easterninsulation.com/pdfs/MSDS\\_2001\\_NB\\_Biobased\\_Insulation\\_B\\_Component\\_Jan\\_28\\_11.pdf](http://www.easterninsulation.com/pdfs/MSDS_2001_NB_Biobased_Insulation_B_Component_Jan_28_11.pdf)) provides examples of acceptable glove barrier material including: viton, neoprene, polyvinyl chloride ("PVC" or "vinyl"), nitrile/butadiene rubber ("nitrile" or "NBR"). Also, workers should follow good personal hygiene practices including: not eating or storing food in the work area and washing hands before smoking or eating.

## Recommendations

Air samples collected during the three shifts of SPF installation demonstrated that detectable concentration of chemical compounds found in SPF were present in the air samples collected during spraying. Protective clothing including coverall, gloves, and foot covers and respirator are needed for all workers working in the spraying operations. Based on these results, which only represent the findings from this location, engineering controls 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 and helper should be using an air supplied respirator instead of air purifying. If air purifying respirators are used they need to be full-faced and the air purifying cartridges should be change based schedule determined by the OSHA Respiratory Protection e-Tool ([https://www.osha.gov/SLTC/etools/respiratory/change\\_schedule.html](https://www.osha.gov/SLTC/etools/respiratory/change_schedule.html)) and an OSHA National Emphasis Program Directive concerning isocyanates provide guidance on cartridge change-out schedules and respirator selection.<sup>[16]</sup>

A respiratory protection program was not observed during our survey. Respirator 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 <sup>[17]</sup>
- 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

## References

1. 75 Fed. Reg. 182 [2010]. Department of Labor, Bureau of Labor Statistics, Summary of comments: notice of comments received and final definition of green jobs.
2. Crespo, J., and J. Galan [1999]. Exposure to MDI during the process of insulating building with spray polyurethane foam. *Ann. Occup. Hyg.* 43:415-419.
3. Bilan, R.A., W.O. Hafliðson, and D.J. McVittie [1989]. Assessment of isocyanate exposure during the spray application of polyurethane foam. *Am. Ind. Hyg. Assoc. J.* 50:303-306.
4. Lesage, J., J. Stanley, W.J. Karoly, and F.W. Lichtenberg [2007]. Airborne methylene diphenyl diisocyanate associated with the application of spray polyurethane foam in residential construction. *J. Occup. And Environ. Hyg.* 4:2, 145-155.
5. CFR [2003]. 29 CFR 1910.134. Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
6. NIOSH [1978]. Criteria for a Recommended Standard: Occupational Exposure to Diisocyanates. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 78-215.
7. ACGIH [2015]. 2015 TLVs® and BEIs®: threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
8. ACC [2011]. Polyurethane Amine Catalysts: Safe Handling Guidelines. Center for the Polyurethanes Industry. American Chemistry Council (ACC). [<http://polyurethane.americanchemistry.com/Resources-and-Documents-Library/3852.pdf>]. Date accessed March 2016.
9. NIOSH [1994]. Isocyanates, Total (MAP): Method 5525 (supplement issued 3/15/2003). In: Schlecht, P.C. & O'Connor, P.F. Eds. NIOSH Manual of Analytical Methods (NMAM). 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
10. NIOSH [1994]. Glycols: Method 5523. In: NIOSH Manual of Analytical Methods (NMAM®). In: Schlecht, P.C. & O'Connor, P.F. Eds. NIOSH Manual of Analytical Methods (NMAM). 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
11. Bayer Material Science Environmental Analytics Laboratory Method 2.10.3 - Determination of Aliphatic Amine Catalysts in Air by Sampling with a XAD-2 Sorbent Tube and Analysis by Capillary Gas Chromatography.
12. NIOSH [1994]. Ketones I: Method 1300 (supplement issued 5/15/96). In: Schlecht, P.C. & O'Connor, P.F. Eds. NIOSH Manual of Analytical Methods

- (NMAM). 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
13. Health and Safety Executive [1999]. Occupational exposure limits.
  14. Schaeffer, J.W., L.M. Sargent, D.R. Sandfort, and W.J. Brazile [2013]. A comparison of two sampling methods for the detection of airborne methylene bisphenyl diisocyanate. *J. Occup. And Environ. Hyg.* 10(4) 213-221.
  15. NIOSH [2004]. A Summary of Health Hazard Evaluations: Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2004-116.
  16. OSHA [2013]. National Emphasis Program-Occupational Exposure to Isocyanates. CPL 03-00-017. June 20, 2013. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration. [https://www.osha.gov/OshDoc/Directive\\_pdf/CPL\\_03-00-017.pdf](https://www.osha.gov/OshDoc/Directive_pdf/CPL_03-00-017.pdf)
  17. NIOSH [2004]. NIOSH Respirator Selection Logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2005-100.



**Delivering on the Nation's promise:  
Safety and health at work for all people  
through research and prevention.**

To receive NIOSH documents or other information about occupational safety and health topics, contact NIOSH at

1-800-CDC-INFO (1-800-232-4636)

TTY: 1-888-232-6348

E-mail: [cdcinfo@cdc.gov](mailto:cdcinfo@cdc.gov)

or visit the NIOSH Web site at [www.cdc.gov/niosh](http://www.cdc.gov/niosh)

For a monthly update on news at NIOSH, subscribe to NIOSH eNews by visiting [www.cdc.gov/niosh/eNews](http://www.cdc.gov/niosh/eNews)

**SAFER • HEALTHIER • PEOPLE**