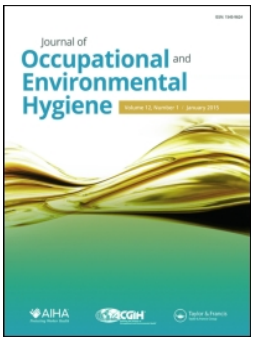

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Center for the Polyurethanes Industry summary of unpublished industrial hygiene studies related to the evaluation of emissions of spray polyurethane foam insulation

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ABSTRACT

Spray polyurethane foam (SPF) insulation is used as thermal insulation for residential and commercial buildings. It has many advantages over other forms insulation; however, concerns have been raised related to chemical emissions during and after application. The American Chemistry Council's (ACC's) Center for the Polyurethanes Industry (CPI) has gathered previously unpublished industrial hygiene air sampling studies submitted by member companies that were completed during an eight-year period from 2007–2014. These studies address emissions from medium density closed cell and low density open cell formulations. This article summarizes the results of personal and area air samples collected during application and post application of SPF to interior building surfaces in both laboratory and field environments. Chemicals of interest included: Volatile Organic Compounds (VOCs), methylene diphenyl diisocyanate (MDI), flame retardants, amine catalysts, blowing agents, and aldehydes. Overall, the results indicate that SPF applicators and workers in close proximity to the application are potentially exposed to MDI in excess of recommended and governmental occupational exposure limits and should use personal protective equipment (PPE) consisting of air supplied respirators and full-body protective clothing to reduce exposure. Catalyst emissions can be reduced by using reactive catalysts in SPF formulations, and mechanical ventilation is important in controlling emissions during and after application.

KEYWORDS
Amine catalyst; blowing agent; flame retardant; MDI; SPF application; spray polyurethane foam

Introduction

The Center for the Polyurethanes Industry member companies have conducted studies related to SPF emissions impacting worker exposure to chemical components, as well as studies addressing post application and long-term indoor air quality concerns for several years. The purpose of this article was to summarize and report results from member companies' previously unpublished studies and offer recommendations to serve as a basis for health and safety determinations related to SPF emissions. All unpublished studies referenced in this article are available as supplemental online only files. While recognizing research studies have been conducted for the past 30 years,[1–3] this article focuses on unpublished industrial hygiene emissions data collected during the eight-year period from 2007–2014, a period of rapid growth for the SPF industry. During this eight-year period, CPI member companies conducted the studies summarized in this article to better understand SPF chemical emissions and the potential impact on workers and building occupants. Studies submitted by CPI and member companies include air sampling results from retrofit and new home construction. Specifically, air sampling was conducted during SPF application to interior walls, attics, basements, crawlspaces, and garages. Air sampling was conducted for several minutes to many hours following SPF application. Although specific SPF formulations differ, those used in the studies included medium-density closed-cell formulations and low density open cell formulations. High-pressure spray equipment commonly used for SPF application was used in each study. Chemicals of interest included Volatile Organic Compounds (VOCs),

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methylene diphenyl diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI), flame retardants, amine catalysts, blowing agents, and aldehydes.

Background

SPF systems consist of two liquid parts commonly referred to as the A-side and B-side. When blended, a solid polyurethane polymer is formed. The A-side, or polymeric methylene diphenyl diisocyanate (PMDI), contains approximately equal amounts of monomeric MDI (4,4-MDI, a two-ring structure) and higher molecular weight oligomers of MDI (three-, four-, and five-ring structures). The B-side is a blend of predominantly polyol, with flame retardants, catalysts, blowing agents, and surfactants.[4]

There are two types of SPF used for building interior application and they are classified according to material density and cell structure. The first type is open cell or low density that has a nominal density of 0.4–0.7 pounds per cubic foot (pcf). It uses water as a blowing agent to react with MDI to form carbon dioxide (CO_2) to form the open cell structure. The second type is a closed cell or medium density foam. It has a nominal density between 1.7–2.3 pcf and uses a fluorocarbon as a blowing agent. The heat caused by the A-side and B-side chemical reaction converts the fluorocarbon liquid to a gas to form the cells. Most of the fluorocarbon is trapped in the closed cells increasing thermal resistance to more than twice that of open cell SPF. Both low-density and high-density formulations are typically applied by high pressure SPF equipment.[5]

During high pressure application, A and B sides are heated and fed separately in a 1:1 ratio to the spray gun at approximately 1000–1500 pounds per square inch (psi), mixing in the spray gun tip just prior to application, forming a fine reactive aerosol that is applied to a substrate. Two component low pressure kits may be used for smaller applications. Kits have separate A- and B- side tanks and produce medium-density closed-cell SPF. A gaseous fluorocarbon blowing agent present in the A and B sides provides approximately 150–200 psi pressure to mix and apply SPF to the substrate.

During the past 30 years, researchers[1–3] have conducted industrial hygiene evaluations during SPF application. Those evaluations have included SPF high-pressure spraying in both interior and exterior applications and have focused on worker exposure to MDI. For example, air sampling studies have been conducted in new construction during SPF application by Bilan et al.,[1] Crespo and Galan,[2] and Lesage et al.[3] The use of mechanical ventilation was not mentioned in any of the studies, therefore it was assumed that passive air flow was used to control emissions. Bilan et al.[1] reported MDI concentrations as high as 0.129 ppm (1.32 mg/m^3) for SPF applicators while the helper's highest MDI concentration was 0.018 ppm (0.18 mg/m^3). Crespo and Galan[2] reported MDI concentrations for the SPF applicators ranging from 0.002 ppm (0.017 mg/m^3) to 0.039 ppm (0.40 mg/m^3). Helper breathing zone concentrations ranged from 0.025–0.308 mg/m3. Lesage et al.[3] determined spray applicator breathing zone MDI concentrations ranged from 0.007 ppm (0.07 mg/m^3) to 0.20 ppm (2.05 mg/m^3). All three researchers concluded that spray foam applicators and most others working in the vicinity of the applicator are likely to be exposed to MDI above the ACGIH TLV-TWA of 0.005 ppm and the OSHA PEL of 0.02 ppm C (Table 1). The MDI results in the other papers described in this report were similar to these three studies. As reported, breathing zone concentrations were generally above recommended and regulatory limits during application.

Sampling and analytical methods

Industrial hygiene data reported in this article was collected using a variety of validated air sampling and analytical methods.[6–10] Those methods are summarized in Appendix 1.

Protective measures

Table 1 is a list relevant occupational exposure limits for chemicals evaluated in this article; however, several chemicals evaluated during the studies lack an OEL and therefore are not listed on Table 1. All workers referenced in the following study summaries who were engaged in the application of spray polyurethane foam or working in close proximity wore appropriate personal protective equipment as described in industry work practice guidance documents published by the CPI.[13] Protective equipment for workers engaged in high pressure SPF application includes the following: NIOSH approved full-face/hood air supplied respirator, chemical-resistant full-body protective clothing and foot coverings, chemical resistant nitrile, butyl, or neoprene gloves. Some manufacturers of low pressure SPF systems suggest fit tested air purifying respirators with safety glasses may be used in place of air supplied respirators for low pressure kit SPF application.

Research study summaries

Laboratory study

A study sponsored by CPI evaluated the effect of cross-draft ventilation on airborne concentrations of specific

Table 1. Occupational Exposure Limits (OELs).

CAS Number	Chemical	Occupational Exposure Limit (OEL)	Type of OEL	OEL Units
101-68-8	Methylene bisphenyl isocyanate	0.02	OSHA Ceiling[a]	ppm
		0.005	ACGIH TLV-TWA[b]	ppm
		50	NL OEL[c]	μg/m³
108-01-0	Dimethylethanolamine (DMEA)	3	Ontario OEL-TWA[d]	ppm
		6	Ontario -STEL	ppm
280-57-9	Triethylenediamine (TEDA)	1	Ontario OEL-TWA	ppm
		3	Ontario -STEL	ppm
149-57-5	2-Ethylhexanoic Acid	5(IFV)[e]	ACGIH TLV-TWA	mg/m³
3033-62-3	Bis (2-dimethylaminoethyl) ether (BDMAEE)	0.05	ACGIH TLV-TWA	ppm
		0.15	ACGIH - STEL	ppm
98-94-2	N,N-dimethylcyclohexylamine (DMCHA)	5	Ontario -STEL	Ppm
75-07-0	Acetaldehyde	25	ACGIH Ceiling	ppm
50-00-0	Formaldehyde	0.75	OSHA PEL	ppm
		2	OSHA STEL	ppm
		0.3	ACGIH Ceiling	ppm
74-40-0	Triethyl Phosphate (TEP)	7.45	AIHA WEEL-TWA[f]	mg/m³
460-73-1	1,1,1,3,3-pentafluoropropane (HFC-245fa)	300	AIHA WEEL -TWA	ppm
811-97-2	1,1,1,2-Tetrafluoroethane (HFC134a)	1,000	AIHA WEEL-TWA	Ppm

[a]OSHA Permissible Exposure Limits[27]
[b]ACGIH Threshold Limit Values[21]
[c]Netherlands Occupational Exposure Limits[18]
[d]Ontario Occupational Exposure Limits[29]
[e]Inhalable fraction and vapor[21]
[f]American Industrial Hygiene Association Workplace Environmental Exposure Levels[16]
Occupational Exposure Limits accessed June 15, 2015

SPF chemical components during application.[14] The study evaluated vapor and particulate emissions from three SPF formulations, prepared for research purposes, by CPI member companies that represented commonly used commercial formulations. These "generic" SPF formulations consisted of a low density high pressure formulation, a medium-density high-pressure formulation, and a low-pressure kit formulation. Research included monitoring of SPF components under controlled conditions to verify airborne concentrations at specified ventilation rates. Air sampling was initially conducted in a 394 cubic foot (11.2 m^3) spray room having ventilation rates ranging from 1–13 Air Changes per Hour (ACH). A ventilation rate of 10 ACH (10.4 ACH actual) was selected as a startingpoint, and the next ventilation rate would be adjusted higher or lower based on the results of the initial air monitoring. The spray time was limited to 15 min for each air sampling session. A set of air samplers were located in the breathing zone of the spray applicator and 2 ft behind the applicator. Air was introduced from one side of the spray room and exhausted at the opposite side such that air moved perpendicular to the sprayer and the stationary air sampling equipment. The initial 10.4 ACH results indicated the air exchange rate had little effect on lowering SPF airborne chemical concentrations during application. For this reason, experiments were next conducted in an adjacent open face, backdraft paint spray booth, capable of operating at much higher ventilation rates. Unlike the spray room that had a range of ventilation rates, the 729 ft^3/21 m^3 spray booth was capable of drawing air at two fan speeds; full speed (7,265 ft^3/min / 206 m^3/min) and half speed (2,828 ft^3/min / 80 m^3/min).

Half speed was determined to be 233 ACH and full speed was 598 ACH. The generic high pressure low density open cell formulation was evaluated at 10.4, 233 ACH, while the high pressure medium density closed cell formulation was evaluated at 10.4, 233, and 598 ACH. The results are summarized in Tables 2–7.

Although the higher air velocities were achievable in the paint spray booth, such velocities and room air exchange rates would be difficult to achieve in a residential or commercial building setting. Lower rates, similar to the 10.4 ACH air exchange rate, would likely be representative of ventilation effectiveness in residential or commercial applications.

10.4 ACH ventilation rate—Air sampling results

The results of personal and area samples listed in Tables 2 and 3 indicate MDI was detected in excess of exposure limits for the high pressure low and medium density formulations during application. A second set of area samples were collected in the spray room 30 min after application to evaluate chemical emissions from the foam after spraying was completed. All post spray MDI concentrations for samples collected beginning 30 minutes after application were below analytical detection limits. The polymeric MDI (pMDI) results listed in Tables 2–4 were similar to the 2, 4-MDI an 4,4-MDI results. The values are listed separately since pMDI is emitted as an aerosol where 2, 4-MDI and 4,4-MDI may be emitted

Table 2. CPI Ventilation Study. Medium-density high-pressure closed-cell formulation - 10.4 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	BDMAEE (ppm)	TMAEEA (ppm)	DAPA (ppm)	TCPP (ppm)	HFC 245fa (ppm)
Spray Applicator Session 1 Morning	13	0.00380	0.02800	0.21	0.630	<0.257	2.31	0.160	182
Stationary sample Session 1 Morning	18	0.00390	0.02500	0.29	1.38	<0.183	3.79	0.290	281
30 min after application	60	<0.00015	<0.00015	<0.0016	<0.039	<0.053	0.14	0.002	<4.91
Spray Applicator Session 2 Afternoon	20	0.00580	0.03700	<0.41	2.51	<0.151	7.67	0.370	365
Stationary sample Session 2 Afternoon	20	0.00480	0.03200	0.36	2.80	<0.141	9.87	0.390	313
30 min after application	53	<0.00016	<0.00016	<0.0016	0.084	<0.083	0.32	0.005	<4.79
Spray Applicator Session 3 Morning	24	0.00330	0.02300	0.33	2.00	<0.119	5.67	0.280	599
Stationary sample Session 3 Morning	24	0.00440	0.02800	0.35	2.63	<0.119	8.80	Invalid	365
30 min after application	45	<0.00021	<0.00021	<0.0021	0.051	<0.058	<0.090	0.0049	<4.92
Spray Applicator Session 4 Afternoon	22	0.00300	0.01900	0.17	2.38	<0.139	7.42	0.370	379
Stationary sample Session 4 Afternoon	24	0.00280	0.01800	0.20	3.20	<0.118	12.48	0.330	309
30 min after application	61	<0.00014	<0.00014	<0.0014	0.440	<0.053	<0.084	0.0061	<4.92
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA		0.05 TLV-TWA 0.15 TLV -STEL				300 TWA AIHA WEEL

Table 3. CPI ventilation study. Low-density high-pressure open-cell formulation - 10.4 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	BDMAEE (ppm)	TMAEEA (ppm)	TMIBPA (ppm)	TCPP (ppm)
Spray Applicator Session 1 Morning	21	0.00380	0.02000	0.18	0.75	0.33	<0.225	0.14
Stationary sample Session 1 Morning	23	0.00090	0.	<0.179	1.37	0.40	<0.222	0.12
30 min after application	60	<0.00016	<0.00016	<0.043	0.18	<0.055	<0.086	0.0036
Spray Applicator Session 2 Afternoon	22	0.00310	0.0170	0.17	1.04	0.40	<0.197	0.17
Stationary sample Session 2 Afternoon	23	0.0010	0.001	<0.122	0.40	<0.125	<0.196	0.16
30 min after application	61	<0.00016	<0.00016	<0.046	1.04	0.24	<0.091	0.0075
Spray Applicator Session 3 Morning	21	0.0020	0.011	0.11	0.90	0.30	<0.220	0.14
Stationary sample Session 3 Morning	21	<0.00046	0.001	<0.198	1.78	0.44	<0.228	0.16
30 min after application	60	<0.00016	<0.00016	<0.047	0.24	<0.055	<0.086	0.0064
Spray Applicator Session 4 Afternoon	20	0.0025	0.013	0.12	1.45	0.41	<0.219	0.22
Stationary sample Session 4 Afternoon	20	0.0052	0.021	0.13	2.42	0.52	<0.263	0.24
30 min after application	61	<0.00016	<0.00016	<0.049	0.16	<0.055	<0.087	0.0039
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA		0.05 TLV-TWA 0.15 TLV-STEL			

Table 4. CPI ventilation study. Low-pressure closed-cell kit formulation - 10.4 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	PMDETA (ppm)	HFC-134a (ppm)	TCPP (ppm)
Spray Applicator Session 1 Morning	30	0.0008	0.0004	<0.102	1.06	11372	0.22
Stationary sample Session 1 Morning	30	0.0005	0.0004	<0.088	1.41	8083	0.16
30 min after application	61	<0.00016	<0.00016	<0.050	0.50	590	0.002
Spray Applicator Session 2 Afternoon	Void	n/a	n/a	n/a	2.71	5009	0.06
Stationary sample Session 2 Afternoon	22	0.0009	<0.00044	<0.140	3.77	7000	0.05
30 min after application	62	<0.00015	<0.00015	<0.050	0.09	188	0.002
Spray Applicator Session 3 Morning	26	0.0010	0.0031	<0.111	2.02	10286	0.04
Stationary sample Session 3 Morning	25	0.0006	0.0014	<0.112	1.01	5963	0.002
30 min after application	61	<0.00015	<0.00015	<0.042	0.07	197	0.0023
Spray Applicator Session 4 Afternoon	24	0.0005	0.0012	<0.0118	1.76	7806	0.0.05
Stationary sample Session 4 Afternoon	23	<0.00042	0.0005	<0.138	2.58	6133	0.030
30 min after application	62	<0.00015	<0.00015	<0.040	0.11	293	0.0034
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA				

in the aerosol or separately as vapo. pMDI was detected during application of the high-pressure systems; however, 30 min post spray results indicate pMDI was not detected. The low-pressure kit pMDI results were below detection limits during application and post application. The lower MDI concentrations observed during the low-pressure application and post application are likely due to reduced aerosol emissions and, secondly, to the premixing of material in the gun prior to spraying. Unlike high-pressure systems, the low-pressure system sprays SPF to the substrate as a partially reacted foam or "froth" resulting in lower MDI emissions.

The amine catalyst results listed in Tables 2–4 indicate a wide range of concentrations ranging from below detection limits to over 9 ppm. Many of the factors that affect MDI emissions also impact amine catalysts. Such factors include the density of the formulation and reaction temperatures. In addition, certain non-reactive or emissive catalysts, such as bis (2-dimethylminoethyl ether (BDMAEE), bis

Table 5. CPI ventilation study. Medium-density high-pressure closed-cell formulation - 233 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	BDMAEE (ppm)	TMAEEA (ppm)	DAPA (ppm)	TCPP (ppm)	HFC 245fa (ppm)
Spray Applicator Session 1 Morning	20	<0.00048	0.0011	0.080	<0.110	<0.151	<0.088	0.018	<15.1
Stationary sample Session 1 Morning	21	0.0035	0.036	0.550	0.290	<0.151	0.43	0.077	22
30 min after application	62	<0.00014	<0.00014	<0.045	<0.038	<0.052	<0.03	<0.00033	<4.92
Spray Applicator Session 2 Afternoon	20	<0.00053	0.0041	<0.120	<0.118	<0.161	<0.094	0.018	25
Stationary sample Session 2 Afternoon	19	0.0035	0.035	0.540	0.190	<0.150	0.028	0.041	31
30 min after application	61	<0.00015	<0.00015	<0.46	<0.040	<0.055	<0.032	<0.00033	<4.79
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA		0.05 TLV-TWA 0.15 TLV -STEL				

Table 6. CPI ventilation study. Low-density high-pressure open-cell formulation - 233 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	BDMAEE (ppm)	TMAEEA (ppm)	TMIBPA (ppm)	TCPP (ppm)
Spray Applicator Session 1 Morning	20	0.00053	0.0064	0.110	<0.123	<0.169	<0.264	0.027
Stationary sample Session 1 Morning	20	0.0023	0.022	0.370	0.270	<0.156	<0.244	0.036
30 min after application	61	<0.0002	<0.0002	<0.046	<0.039	<0.053	<0.083	<0.0003
Spray Applicator Session 2 Afternoon	20	<0.00048	0.0031	<0.151	<0.124	<0.170	<0.266	0.016
Stationary sample Session 2 Afternoon	20	0.0030	0.031	0.450	<0.116	<0.159	<0.249	0.022
30 min after application	60	<0.0002	0.00025	<0.048	<0.039	<0.053	<0.083	<0.0003
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA		0.05 TLV-TWA 0.15 TLV -STEL			

(dimethylaminopropyl) methylamine (DAPA), and pentamethyldiethylene triamine (PMDETA) may be emitted since they do not become bound in the formulation. Other reactive or non-emissive catalysts, such as N,N,N-trimethylaminoethylethanolamine (TMAEEA) are chemically bound to the product and are less likely to become airborne in significant concentrations.

The fire retardant, tris-(1-choro-2-propyl) phosphate (TCPP) was in each of the generic formulations (B-side) in concentrations ranging from 15–30% by weight. The findings presented in Tables 2–4 follow a pattern similar to the other components, with the greatest emissions occurring in the medium-density formulation and the lowest in the low-pressure kit formulation. All concentrations were below 0.5 ppm (8.8 mg/m^3).

The blowing agents HFC-245fa and HFC 134a were present in the medium-density high-pressure system and the low-pressure kit formulation respectively. The

Table 7. CPI ventilation study. Medium-density high-pressure closed-cell formulation - 598 air changes/hour.

Description	Time (min)	2,4-MDI (ppm)	4,4-MDI (ppm)	pMDI (mg/m3)	BDMAEE (ppm)	TMAEEA (ppm)	DAPA (ppm)	TCPP (ppm)	HFC 245fa (ppm)
Spray Applicator Session 1 Morning	19	<0.00045	0.003	<0.108	<0.124	<0.170	<0.099	0.0025	<15.1
Stationary sample Session 1 Morning	20	0.0005	0.007	0.08	<0.106	<0.146	<0.085	<0.0010	<15.1
30 min after application	60	<0.00015	<0.00015	<0.046	<0.038	<0.053	<0.030	<0.00035	<4.55
Spray Applicator Session 2 Afternoon	23	0.0012	0.013	0.17	<0.095	<0.131	<0.076	0.0075	<12.1
Stationary sample Session 2 Afternoon	22	0.0004	0.006	0.08	<0.097	<0.133	<0.077	<0.0010	<12.1
30 min after application	60	<0.0002	<0.0002	<0.047	<0.039	<0.053	<0.031	<0.0004	<4.55
Spray Applicator Session 3 Morning	19	0.0019	0.021	0.27	<0.138	<0.190	<0.110	0.0030	<14.0
Stationary sample Session 3 Morning	22	0.0004	0.005	<0.061	<0.108	<0.148	<0.086	<0.00099	<13.0
30 min after application	62	<0.00017	<0.00017	<0.054	<0.038	<0.052	<0.030	<0.00031	<4.34
Spray Applicator Session 4 Afternoon	19	0.0022	0.025	0.32	<0.127	<0.174	<0.101	<0.0010	<14.0
Stationary sample Session 4 Afternoon	21	0.0006	0.007	0.08	<0.109	<0.149	<0.086	<0.00095	<14.0
30 min after application	61	<0.00014	<0.00014	<0.044	<0.042	<0.058	<0.034	<0.00033	<4.55
Occupational Exposure Limit			0.02 C OSHA 0.005 TLV-TWA		0.05 TLV-TWA 0.15 TLV -STEL				

7% concentration of HFC-245fa in the high-pressure system B-side was substantially lower than the 28% concentration of the HFC-134a in the kit formulation. This concentration difference in the B-side formulations is likely accounts for the large difference in airborne concentrations.

233 ACH and 598 ACH ventilation rates—Air sampling results

The medium-density and low-density high-pressure formulations were evaluated at 233 ACH. The results listed in Tables 5 and 6 indicate 2,4-MDI, 4,4-MDI, and pMDI were detected in both personal and area samples. 30 min post spray application samples were below detection limits. Area sample concentrations for 4,4 MDI for the medium density were 0.0011 ppm and 0.0041 ppm (11 and 42 $\mu g/m^3$) for the applicator and 0.035 ppm and 0.036 ppm (358 $\mu g/m^3$ and 369 $\mu g/m^3$) for the stationary samples. The low-density formulation results were similar with the applicator 4,4-MDI results of 0.0031 ppm and 0.0064 ppm (32 and 66 $\mu g/m^3$) and area sample results of 0.022 ppm and 0.031 ppm (230 and 320 $\mu g/m^3$). Concentrations of MDI emitted from the medium density formulation in the area air sampling device located approximately two feet behind the SPF applicator were significantly higher than the applicator's breathing zone MDI concentrations. Since the applicator was in closer proximity to the source of the MDI emissions, the opposite might be expected. These unanticipated findings, however, were consistent with findings reported by Heitbrink et al.[15] where researchers measured total particulate during paint spray operations in auto repair shops. They determined there is a zone of lower concentration that includes the worker's breathing zone caused by the high-pressure paint application diverting the overspray away to the sides. The researchers concluded that if the spray was directed perpendicular to the air flow, the paint aerosol would be diverted back towards the incoming airstream where it would be re-entrained in the airflow and directed towards the fan or carried back in the direction of the applicator. In this instance, the use of high pressure SPF application coupled with the work practice of beginning the spray at the base of the insert and sprayings to the top forced the aerosol away from the applicator to the upper region of the spray booth where the area air sampling device was located two feet behind the applicator. Similar results were observed for the amine catalysts, TCPP and blowing agent (Tables 5 and 6).

The medium-density high-pressure formulation was also evaluated at 598 ACH (Table 7). 2,4-MDI, 4,4-MDI, and pMDI were detected in both personal and area samples; however, post spray application samples were below detection limits. 4,4-MDI concentrations ranged from 0.003–0.025 ppm (31–260 $\mu g/m^3$) for the applicator and 0.005–0.007 ppm (51–72 $\mu g/m^3$) for the stationary samples. Amine catalysts, TCPP, and blowing agent concentrations were at or below analytical detection limits at the higher ventilation rate. The elevated exhaust ventilation, with the air flow perpendicular to the high-pressure spray, was sufficient to control vapor emissions, however, it was unable to capture and control aerosol emissions. The higher air velocity controlled measured B-side vapor emissions; however, the ventilation had a reduced impact on the MDI-containing aerosol.

At the completion of testing of the generic formulations at the three ventilation rates, it was concluded that as air velocity is increased, chemical concentrations decrease. The results also indicate that there are factors beyond air velocity that impact emissions. Such factors include: chemical characteristics of the formulation (e.g., reactive vs. non-reactive catalyst), the quantity of individual chemicals in the formulation, temperature of the formulation as it is applied, the temperature created during reaction/curing, the density of the formulation, cell structure, and air distribution. These application factors, coupled with many environmental variables related to a residential or commercial site application, make it difficult for workers directly involved in SPF application to be protected though engineering controls exclusively.

Medium-density high-pressure closed-cell SPF formulation application field studies

The application of a commercial high-pressure medium-density formulation was evaluated as the SPF was sprayed in three existing homes. The study involved air sampling of SPF emissions and the impact of ventilation on the retrofit applications. Robert et al.[4] performed industrial hygiene monitoring as SPF was applied to the first floor kitchen addition, attic, basement, and garage. Each spray area was separated from other areas of the house by using polyethylene sheeting and/or plywood. The spray areas were then ventilated using commercially available high volume 110 volt fans and flexible ducts. Chemical emissions evaluated included MDI, amine catalysts, fire retardant, blowing agent, and volatile organic compounds (VOCs).

Airborne concentrations of MDI were below analytical detection limits when ventilation exhaust rates were 2000 cubic feet per minute (CFM) providing air exchange rates between 20–60 ACH. At one stage, a mechanical difficulty resulted in the fan not working properly during SPF application in the garage resulting in a measured MDI concentration of 0.9 ppb (9 $\mu g/m^3$). This malfunction demonstrated the importance of proper mechanical ventilation during SPF application. Area MDI samples collected 1 hour after application found that the concentration of MDI was below detection limits with and without mechanical ventilation.

The fire retardant Triethyl Phosphate (TEP) was also evaluated with concentrations during application ranging from <0.072 mg/m^3 to 6.47 mg/m^3. TEP concentrations 1 hr post application were 0.64 and 1.4 mg/m^3.

Three amine catalysts were evaluated; Dimethylethanolamine (DMEA), Triethylenediamine (TEDA), and N,N,N,-Trimethylaminoethylethanolamine (TMAEEA). DMEA concentrations were the highest ranging from <0.064 ppm to 2.0 ppm. Most DMEA concentrations were in the range of 1–2 ppm; however, all were below the occupational exposure limit (Table 1). TEDA concnetrations were well within acceptable limits ranging from <0.014 ppm to 0.3 ppm and TMAEEA was not detected.

The blowing agent, 1,1,1,3,3-pentafluoropropane (HFC 245fa), was detected in all areas where SPF was applied. Concentrations ranged from a low of 9 ppm (grab sample) to a TWA high concentration of 630 ppm. Although blowing agent concentrations were sometimes above the occupational exposure limit of 300 ppm (Table 1 AIHA WEEL[16]) in work areas, samples collected outside ventilated work areas with a direct-reading indicator (basement, kitchen and attic) were all 75 ppm to non-detect (<50 ppm). Evacuated containers and passive dosimetry did show some emission after spray (2–12 ppm). Six months after SPF application, the second house was monitored using evacuated containers. No blowing agent was detected.

The levels for certain Volatile Organic Compounds (VOCs) were also monitored. Although standards have not been set for VOCs in non-industrial settings, certain common VOCs, such as formaldehyde have been assigned both occupational exposure limits and indoor air quality limits (Table 1).

Smallenberg et al.[17] conducted studies in seven homes where high pressure closed cell systems were sprayed below subfloor in crawlspaces below the living areas of each home. The crawl spaces were mechanically ventilated with fans operating at 2,000–3,000 cfm with air exchange rates ranging from 50–200 ACH. Ventilation was not arranged properly in three of the seven homes such that actual air exchange rates were thought to be poor. Proper ventilation would have included sealing the crawl space access with wood or polyethylene and then positioning ventilation flexible duct to maximize forced ventilation. The poor ventilation described in the study resulted when the flexible duct was positioned 70 cm away from the access to the crawlspace and there was no cover for the access.

Area air sampling was conducted at three locations in each home: the crawlspace area, the area next to the access to the crawlspace, and the nearest living area. The air sampler was positioned inside each crawlspace near the access. When the insulation was applied in two layers, sampling was paused where a period was allowed to cool the foam in between applying the two layers.

Area MDI sample concentrations measured during SPF application in the crawlspace below living spaces ranged from 5.9–770 µg/m^3 (0.0006–0.075 ppm), some exceeding the Netherlands occupational exposure limit of 50 µg/m^3 [18](Table 1). Two hours following SPF application, MDI concentrations were reduced to 5.6 µg/m^3 (0.0006 ppm) where spaces were poorly ventilated, and below detection limits where they were adequately ventilated. The living space concentrations were non-detect with the exception of one measurement of 6 µg/m^3 MDI after 2 hours where the crawlspace was poorly ventilated.

Three amine catalysts Tris-(dimethylaminopropyl) amine, Dimethylethanolamine, and (N,N-dimethylcyclohexylamine) were detected in the same three locations previously described for MDI. Concentrations ranged from above 2000 µg/m^3 (0.38 ppm) during application to 450 µg/m^3 (0.087 ppm) N,N-dimethylcyclohexylamine 30 min after application to non-detect 2 hr after application. The authors noted that these substances can potentially cause significant odor nuisance even at extremely low concentrations.

The flame retardant, TCPP, was detected in area samples during application; however, concentrations were below detection limits 60 to 120 minutes after application. Blowing agents migrated from the foam for longer than other components following application, but concentrations were well below all relevant exposure limits.

Karlovich et al.[19,20] conducted two industrial hygiene surveys during the installation of medium-density closed-cell high-pressure SPF during the renovation or new construction of residential structures. The surveys included an assessment of potential worker exposure to airborne SPF chemicals including MDI/pMDI, HFC 245fa blowing agent (1,1,1,3,3-pentafluoropropane) and amine catalysts. Air monitoring parameters included the determination of airborne concentrations of SPF chemicals in the spray rig, migration of airborne SPF chemicals to other floors, airborne concentrations as a function of distance from the applicator, and airborne concentrations as a function of time (up to 2.5 hr) following the end of application. Mechanical ventilation, such as fans and blowers, were not used to ventilate work areas. In some cases, partially open windows and doors provided passive ventilation during and after application.

The applicator's MDI TWA breathing zone concentration of 71ug/m^3 exceeded the ACGIH TLV-TWA[21] of 51 µg/m^3 in one study.[19] In the second study,[20] MDI 3-hr TWA concentrations were 471 µg/m^3 for the applicator and 189 µg/m^3 for the assistant. pMDI TWA concentrations[20] were also elevated at 572 μg/m^3 for the applicator and 203 μg/m^3 for the assistant. The author noted that MDI and PMDI concentrations should be considered estimates since air flow rates had dropped significantly throughout the air sampling period compared to the flow rates at the start of the sampling periods.[20] Migration of airborne MDI/oligomers to lower floors was observed in both surveys, however, levels were well below the OELs. In one study, MDI was detected only in the first of four consecutive samples collected post-spray on the second floor at 4.7 μg /m^3.[19] All MDI sample concentrations on the other floors were below analytical detection limits (<15 μg/m^3). In the second study, MDI and PMDI were not detected in any post spray samples collected from all floors of the structure.[20]

The amine catalysts, 2-2-((dimethylamine)ethoxy)ethanol, 1,2-dimethylimidozole, and dimethylaminopropyl, hexahydrotriazine were detected in low concentrations (7–15 ppb) in breathing zone samples in one study[19] and below analytical detection limits in the second study.[20] Two catalysts, 2-2-(dimethylamino)ethoxy)ethanol and 1,2-dimethylimidozole, were detected at 10, 20, and 30 ft from the applicator during one study,[19] however, amine catalyst concentrations were below detection limits in all post spray samples in both studies.[19,20]

Airborne concentrations of blowing agent HFC-245fa (1,1,1,3,3-pentafluoropropane) did not exceed the AIHA WEEL of 300 ppm for applicators. Blowing agent results for one study were 148 ppm for the applicator, 56 ppm for the assistant and 22 ppm for the helper.[19] In a second study, a blowing agent concentration of 131 ppm for the applicator and 109 ppm for the helper.[20] Area samples collected in one study[20] indicate 1,1,1,3,3-pentafluoropropane concentrations at 3, 6, and 9 m from the applicator were 108, 108, and 107 ppm, respectively. The author concluded the data suggest the presence of airborne blowing agent at all distances and that the concentrations remained largely unchanged with distance from the applicator. All airborne concentrations of 1,1,1,3,3-pentafluoropropane were well below the AIHA WEEL of 300 ppm.

Low-density high-pressure open cell SPF formulation application field studies

Robert et al.[22] conducted a study to evaluate SPF emissions during high pressure application of a commercial open cell formulation in two homes under construction and under controlled conditions in a laboratory spray booth. Air monitoring was conducted during SPF application and during trimming on freshly sprayed foam as well as foam aged one day to one week following application. Airborne concentrations of MDI, flame retardant, amine catalyst, and total VOCs were evaluated during and after application of spray polyurethane foam in the spray booth and field environments using government and company-validated air sampling methods.

Two homes located in Houston, TX were monitored during January and March of 2014. The first home was sprayed on the second-floor wall areas and parts of the underside of the plywood roof deck. Air monitoring was conducted as a worker followed the sprayer trimming excess foam from the studs and wall cavity to remove protruding foam from the studs and wall cavity to allow wall board to be attached. The second home was a large home (approximately 7,000 square feet) consisting of two floors and a loft area. Monitoring was conducted during application of foam to each floor and during trimming to evaluate potential worker exposure to the SPF components. There was no attempt to mechanically ventilate emissions with engineering controls, however, open doors and windows provided natural ventilation in the house during air monitoring. SPF chemicals monitored included: MDI, Tris-(1-chloro-2-propyl) phosphate (TCPP), total volatile organic hydrocarbons, and amine catalysts Bis-(2-Dimethylaminoethyl) ether (BDMAEE) and N,N,N,-Trimethylaminoethylethanolamine (TMAEEA).

The results of samples collected in the first house indicate area sampling for MDI resulted in concentrations of 0.072 ppb (0.74 μg/m3) and 0.12 ppb (1.2 μg/m3) during SPF application. TCPP samples were lost in shipment therefore could not be analyzed. VOC samples were in the parts per trillion range (ppt), although common construction solvents such as acetone, ethanol, and isopropanol accounted for the trace quantities detected. Personal samples collected for catalyst evaluation on the sprayer and his helper during spraying and trimming resulted in BDMAEE catalyst concentrations ranging from 0.33–0.51 ppm. Unlike BDMAEE, TMAEEA reacts into the foam and therefore was not detected during or after application.

Area sampling for MDI in the second house collected near the sprayer and helper was 2 ppb (20.5 μg/m^3) for 2 ring MDI monomer and 0.55 ppb (6.7 μg/m^3) for 3-ring MDI. TCPP results were 12 ppb (0.11 mg/m3). The other helper, who trimmed 15 ft from the sprayer, did not have a detectable concentration of MDI and the TCPP concentration was 8 ppb (0.09 mg/m^3). VOC concentrations were very low, which could be attributed to common construction glues and sealant solvents. BDMAEE catalyst samples collected during application in the attic areas ranged from 0.52–4.52 ppm. Two personal samples collected during the trimming of fresh SPF were 1.24 and 1.34 ppm. TMAEEA was detected in only two samples as SPF was sprayed in the non-ventilated attic area. All other TMAEEA concentrations were below detection limits.

A second day of industrial hygiene monitoring was conducted in the second house. An area MDI concentration of 1.4 ppb (16 2 μg/m^3) was detected 10–15 ft from the SPF applicator during spray and foam trimming. A TCPP sample collected in the same location resulted in a concentration 3.7 ppb (0.026 mg/m^3) The VOC samples were in the parts per trillion. Again, common construction materials containing solvents were present. BDMAEE catalyst concentrations for personal samples collected during spray application were 0.76 ppm and 1.84 ppm. A personal sample collected during the trimming of foam sprayed 24 hr earlier resulted in a BDMAEE concentration of 0.073 ppm. The author noted that the BDMAEE concentrations appeared to be uniform throughout the house as an area sample collected in the central area of the second floor during the trim operation also resulted in a BDMAEE concentration of 0.073 ppm. TMAEEA concentrations were all below analytical detection limits.

To evaluate BDMAEE catalyst emissions during trimming activities detected during the Houston air sampling study, an air monitoring was completed in a laboratory spray booth. Panels, approximately 3 ft × 4 ft (1 m × 1.2 m) were sprayed with the same open cell formulation and placed in a ventilated spray booth. The mechanical ventilation was not in operation during the experiments. Air monitoring was conducted during a 30-min period as the panels were cut and scraped to simulate a worst-case scenario. Both aged foam sprayed 5 days previously and foam sprayed 4 hr prior to sampling were tested on two separate days. Area samples were gathered for MDI and TVOC. Personal samples were obtained for TCPP and BDMAEE. Wipe samples were also gathered for free MDI on the surface of the foam.

The authors note the trimmer's exposure to MDI and TCPP was minimal, although breathing zone BDMAEE ranged from 0.07–0.36 ppm. The BDMAEE results do not represent full shift exposures; however, they indicate the potential for excessive exposure to unprotected workers during trimming operations for both fresh foam and foam sprayed five days prior to trimming.

Brennan[23] conducted industrial hygiene monitoring as a high-pressure low-density open-cell formulation was applied to new residential construction. Post-application area samples were collected at 2 hr and 19 hr following spray application. Air samples were collected in the SPF application areas as well as the adjacent hallways. The home was tested without any mechanical ventilation present. Area samples were also collected to assess possible migration. Four samples (2 for MDI and 2 for the catalyst) were taken approximately 2 hr after spraying, and 16 samples (8 for MDI and 8 for the catalyst) were taken approximately 19 hr after spraying. All of the 2-hr post-application area air samples for MDI and the catalyst were collected over a 30-min time period. One of the two catalyst area samples collected at 2 hr following spray application resulted in a concentration of 0.045 ppm BDMAEE. All samples for MDI collected 2 hr and 19 hr after spray foam application were non-detectable.

The author reported at 2 hr post-spray BDMAEE was detected, but below detection limits at 19 hr. All catalyst concentrations were below occupational exposure limits and all MDI concentrations, 2 hr and 19 hr following spray foam application were below the analytical detection limit. Data from this study is consistent with the common industry practice of waiting 24 hr after completing the spray foam application before re-entry.

Karlovich et al.[24–26] conducted three industrial hygiene surveys during the installation of low-density open-cell high-pressure SPF during the renovation or new construction of residential structures. The surveys investigated a number of items, including potential worker exposures to airborne SPF chemicals (MDI/pMDI and amine catalysts), airborne concentrations of SPF chemicals in the spray rig, migration of airborne SPF chemicals to other floors, airborne concentrations as a function of distance from the applicator, and airborne concentrations as a function of time (up to 3 hr) following the end of application. No mechanical ventilation such as fans or blowers were used to ventilate work areas. In some cases, partially open windows and doors provided passive ventilation during and after application.

Key findings from the studies are as follows: worker air monitoring data indicated airborne MDI concentrations exceeded the ACGIH TLV-TWA of 0.005 ppm (51 μg/m^3) and the short-term OSHA Ceiling Limit[27] of 0.02 ppm (200 μg/m^3) for the majority of applicators and also for helpers when they conducted some amount of spraying. (TWA) MDI personal samples collected in the breathing zone of the SPF applicator during indoor application ranged from 44–86 μg/m^3. TWA helper/applicator exposure concentrations ranged from 22–144 μg/m^3.

Airborne concentrations of one amine catalyst, BDMAEE (a non-reactive catalyst) exceeded the ACGIH TLV-TWA for both applicator and helper in one survey.[26] In one instance, airborne MDI concentrations exceeded the 8-hr and short-term OELs at distances up to 6 m from the applicator.[25] The airborne level of BDMAEE exceeded the ACGIH TLV-TWA at up to 9 m in one survey.[26]

Except for one sample, airborne MDI/oligomers were not detected in post-spray samples collected from all floors of the structures. MDI was identified in one post spray sample at 4.7 μg/m^3 (0.0005 ppm) in the third of four consecutive samples collected on the third floor, approximately 2 hr following the end of spraying. The other three samples collected at this location, at intervals beginning 15 min post spray and ending 3 hr post spray, were below the analytical Limit of Quantitation (LOQ) of 0.1 µg/sample.[25] Airborne amine catalysts were identified in post-spray samples in one survey only;[26] the level of DMAEE exceeded the ACGIH TLV-TWA. As previously stated, BDMAEE is a non-reactive catalyst. Airborne concentrations of SPF chemicals in the spray rig were either non-detectable or at low levels well below the OELs.[25,26]

Discussion

Health and safety considerations related to SPF application and post application continue to be of great interest to those potentially impacted by SPF emissions. This article summarizes several previously unpublished papers submitted by CPI member companies for the purpose of sharing industrial hygiene study results and conclusions. SPF formulations were evaluated during and after application to interior surfaces. Included were laboratory and field studies representing environmental conditions encountered in retrofit and new construction.

The results indicate applicators of both open-cell and closed-cell high-pressure systems are potentially exposed to SPF emissions in excess of occupational exposure limits during application.[4,14,17,19,20,22–26] The data collected during the studies suggest that workers spraying high-pressure SPF systems and those in close proximity (10–15 ft) should use PPE consisting air-supplied respiratory protection and full-body protective clothing.[19,20,24–26] Ventilation and isolation were key to reducing the migration of chemicals and therefore non-applicator worker exposure. In one study, the author stated workers can work unprotected outside contained and ventilated SPF sprayed areas provided the containment is ventilated at rate of 60 ACH or greater.[4] Workers may also return to SPF sprayed areas one hour after application provided that same ventilation rate is maintained.[4] The results of a crawlspace SPF application study concluded traces of MDI could be detected in living spaces 2 and 8 hr after application if the crawlspace was not properly ventilated. The authors recommended at a rate of at least 30 ACH for crawl space application.[17,28] B-side components were a greater concern for open cell formulations. In particular, emissive/non-reactive amine catalysts such as BDMAEE continue to emit in concentrations in excess of the occupational exposure limit 24 hr after application.[20] Foam trimming was determined to be a source for worker exposure to emissive catalysts while non-emissive catalyst, such as TMAEEA, were below detection limits during trimming activities.[22]

Conclusions

SPF applicators and helpers have potential exposure to A- and B-side chemicals in excess of occupational exposure limits. Industry work practice guidance reflected in CPI materials continues to recommend appropriate PPE for workers spraying SPF insulation.[13] Air-supplied respiratory protection, protective clothing, and gloves continue to be recommended for applicators and helpers. SPF formulations containing reactive amine catalysts, as opposed to non-reactive catalysts, can help reduce airborne concentrations of amine catalysts during and following spraying. Ventilation is key to SPF application and re-entry times for trade workers and building occupants. Based on the studies cited in this article, ventilation rates for high-pressure systems ranging from 30 ACH to 205 ACH, in combination with enclosures to isolate the spray work area, appear to effectively control the migration of emissions to other areas of the building during application. CPI recommends consulting the product manufacturer regarding re-entry of trade workers and re-occupancy of building residents to the work area following interior application of SPF.

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Appendix 1: Air sampling and analytical methods

MDI

Two methods were used for research projects summarized in this article. Both methods for MDI collection use a derivatizing agent which serves to stabilize the reactive isocyanate group by forming a urea derivative with them. The first, which is a preferred method for the ease of field sampling, makes use of a treated glass fiber filter. Samples are collected by drawing a known volume of air through a glass fiber filter coated with 1.0 mg of 1-(2-pyridyl) piperazine (1-2PP) which is contained in an open-face cassette. Samples are extracted with 90/10 (v/v) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by high-performance liquid chromatography (HPLC) using an ultraviolet (UV) or fluorescence detector (OSHA 47).[6] The second method traps diisocyanates in a bubbler solution containing toluene and a nitro reagent (0.0002 M p-nitrobenzyl-N-n-propylamine). The reagent reacts readily with diisocyanates to form a stable UV absorbing urea derivative that is easily chromatographed by high-pressure liquid chromatography. A 13 mm coated glass fiber filter follows the impinger to collect any unreacted aerosol (OSHA 18).[6] Smallenberg[3] collected MDI samples by impinger filled with 10 ml 0.01 M dibutylamine (DBA) containing solution followed by DBA coated 13 mm glass fiber filter followed by analysis by LC-MS/MS. Although the use of the impinger method can be challenging in the field, it is the preferred method for accurately measuring MDI in SPF aerosols since the reacting droplets that enter the impinger are dissolved in solution with the derivatizing agent, facilitating rapid and complete reaction. In the case of coated filters, the aerosol droplet which is trapped on the filter, must spread out and wet the filter in order to come into complete contact with the derivatizing agent.

Triethyl phosphate (TEP) / Tris-(1-choro-2-propyl) phosphate (TCPP)

The fire retardant TEP is collected on an XAD-7 OVS tube (glass fiber filter, 13-mm; XAD-7, 200 mg/100 mg) per NIOSH Method 5523[7] while TCPP is collected on an XAD-2 OVS tube (270 mg front and 140 mg backup separated by a PUF plug). TEP and TCPP are analyzed by gas chromatography with a nitrogen phosphorus detector per ICL-IP Method Number CG024-1.[8]

Amine catalysts

Amine catalysts samples are collected on XAD-2 sorbent material (generally with 400 mg front section followed by a 200 mg back-up section). Samples are solvent desorbed and analyzed by gas chromatography using a NPD detector according to Bayer Material Science Industrial Hygiene Method 2.10.3.[9]

Volatile organic hydrocarbon (VOC) EPA method to-15

The air sample is drawn into a specially-prepared stainless steel evacuated canisters. Flow rates can be adjusted to change the sample duration from several minutes to several hours. The captured gases/vapors are analyzed gas chromatography/mass spectroscopy (GC/MS).[10]

1,1,1,3,3-pentafluoropropane (HFC-245fa) and 1,1,1,2-Tetrafluoroethane (HFC-134a)

There are two methods that were used to measure airborne HFC-245fa and HFC-134a. These include diffusive air samplers and active air sampling.

Diffusive air samplers are small badges containing a solid sampling media, such as charcoal, which can be clipped to an employee's clothing for personal monitoring of halocarbons. Area monitoring can be performed using these samplers if sufficient air flow is present in the workplace. Samples are analyzed by GC according to a modified OSHA Method 7.[6]

Active air samples for halocarbon evaluation are collected by drawing air through tubes containing activated charcoal (400 mg and 800 mg) with calibrated air pumps. Samples are then analyzed by GC-FID using a modified NIOSH Method 2516.[7]