

CPI Ventilation Research Project for Estimating Re-Entry Times for Trade Workers Following Application of Three Generic Spray Polyurethane Foam Formulations

RICHARD WOOD, CIH

*Air Products and Chemicals, Inc.
7201 Hamilton Blvd
Allentown, PA 18195*

ABSTRACT

The Center for the Polyurethanes Industry (CPI) Ventilation Research Task Force conducted experiments to evaluate and determine the decay rate of specific chemical vapor following SPF application. The purpose of the study was to estimate the time required to restrict unprotected trade workers, such as plumbers, electricians, dry wall installers, etc. from the work area to minimize their exposure. Emissions from CPI generic high pressure medium density, high pressure low density SPF, and a low pressure, 2 component kit formulations were evaluated in a ventilated room operating at a ventilation rate of 10 Air Changes per Hour (ACH) and lowered to 1 ACH after 3 hours to evaluate decay rates for a 12 hour period. Chemical ingredients selected for evaluation represent those typically present in SPF formulations. Substances evaluated include: Methylene diphenyl diisocyanate (MDI), amine catalysts, blowing agents, and flame retardants. This paper will discuss the experimental protocol, report results of the air sampling study, and provide recommendations.

INTRODUCTION/BACKGROUND

The determination of trade worker re-entry time following the application of SPF in residential and commercial buildings has traditionally been estimated by SPF manufacturers. Frequently decisions related to the time required for airborne concentrations of SPF chemical components to fall to within acceptable levels have been based on qualitative information such as comfort and odor. Other factors considered have included building volume, mechanical and natural ventilation. This research focused on the evaluation and impact of SPF emissions on healthy adults working an average 8 to 10 hour work day. Emissions data collected following SPF application was used to determine chemical degradation times to estimate the time required for workers to safely re-enter and work without respiratory protection.

The CPI re-entry research builds on the Phase 1 and 2 work completed during the CPI Ventilation Research Project. During Phase 1 of that study three (3) generic SPF formulations were developed to represent those currently available in the SPF marketplace. The generic formulations included a low density high pressure formulation, a medium density high pressure formulation, and a low pressure kit formulation. During Phase 2 of the study generic formulations were to be sprayed at three ventilation rates (10 Air Changes per Hour (ACH), 233 ACH, and 598 ACH) while the spray applicator was monitored for airborne SPF chemical components. Fixed area samples were also collected during application and 30 minutes following application. Although the medium density formulation was evaluated at 10.4 ACH, 233 ACH and 598 ACH, all three generic formulations were evaluated only at the 10.4 ACH rate. Since worker exposure data was available for the SPF application of the 3 generic formulations at 10.4 ACH, the CPI Ventilation Task Force selected the 10.4 ACH ventilation rate as the starting point for the re-entry research. Once completed, the ventilation research and re-entry research could be compared to provide a complete view of the time required from application to re-entry for each generic formulation at the 10.4 ACH ventilation rate. The 10.4 ACH ventilation rate represents minimal air flow, similar to natural ventilation, such as open doors/windows or perhaps a bathroom fan. The results of the Phase 2 Ventilation study indicated 10.4 ACH was insufficient to control SPF emissions during application.

Table 1 : Generic SPF Formulations		
Low Density (1/2 pound) High Pressure SPF Formulation	Medium Density (2 pound) High Pressure SPF Formulation	Low Pressure (2 Component) Kit Formulation
A-side		
100% pMDI	100% pMDI	92.5% pMDI Blowing Agent 134a (7.5%)
B-side		
Polyether Polyol (34%)	Aromatic Polyester Polyol (36.39%) Aromatic Amino Polyether Polyol (33.61%)	Polyester Polyol (23%) Polyether Polyol (23%)
NPE Emulsifier (11.9%)		
Blowing agent Water (20%)	Blowing agent HFC-245fa (6.97%) Water (2.53%)	Blowing Agent 134a (17%)
Fire Retardant Tris-(1-chloro-2-propyl) phosphate (TCPP) (25.2%)	Fire Retardant Tris-(1-chloro-2-propyl) phosphate TCPP (15.91%)	Fire Retardant Tris-(1-chloro-2-propyl) phosphate TCPP (30%)
Silicone Surfactant (1.0)	Silicone Surfactant (1.0)	Silicone Surfactant (2%)
Catalyst Bis (2-Dimethylaminoethyl) ether (BDMAEE) (0.9%) Tetramethyliminobispropylamine (TMIBPA) (3.0%) N,N,N-Trimethylaminoethylethanolamine (TMAEEA) (4.0%)	Catalyst Bis (2-Dimethylaminoethyl) ether (BDMAEE) (0.7%) Bis (dimethylaminopropyl) methylamine (DAPA) (2.59%) N,N,N-Trimethylaminoethylethanolamine (TMAEEA) (0.3%)	Catalyst Pentamethyldiethylene triamine (5%) (ethylhexanoic, 2-, potassium salt/ Oxybisethanol, 2,2')

Research Protocol for SPF Re-Entry Study

Knowledge and experience related to the selection and use of mechanical ventilation to control emissions during and following SPF application varies widely among contractors. Consequently, contractors often rely on government required personal protective equipment for spray applicators and helpers while mechanical ventilation may be used to supplement PPE and reduce emissions in surrounding areas of the building. Due to variations in the use of effective mechanical ventilation, this study has been designed to represent a feasible worst case scenario for residential or commercial SPF application. It is thought that the majority of contractors will use barriers and portable exhaust ventilation as recommended by EPA and the SPF industry; however, it is plausible that some will remove the portable ventilation at the end of the day/project, so that it can be used at another location the following day. This would be especially true for small retrofit projects. The protocol selected for this study was designed to reflect this scenario. Exhaust ventilation is supplied to the work area during application and is removed several hours later when the contractor leaves the site and other trade workers arrive to provide other services. To simulate this scenario, the generic formulations were sprayed for a 15 minute period at 10 ACH. The ventilation continued to operate at 10 ACH for 3 hours following application, but was then reduced to 1 to 2 ACH for the remaining test period to represent minimal passive ventilation that would be expected from an open door or windows.

Emissions from the generic high pressure low density, high pressure medium-density SPF, and a low pressure, 2 component kit formulations were evaluated in a ventilated room operating at an air exchange rate of 10 Air Changes

per Hour (ACH) and 1-2 ACH. Chemical ingredients selected for evaluation represent those typically present in SPF formulations. Substances evaluated included:

- Methylene diphenyl diisocyanate (MDI),
- Amine catalysts,
- Blowing agents other than water
- Flame retardants

Facilities, Equipment, and Application

Area air monitoring was conducted while generic formulations were applied to test panels inside a ventilated spray room. The ventilated spray room was designed to meet the following specifications:

1. The dimensions of the spray room are approximately 8 ft. x 8ft x 8ft. Make-up air was supplied to the room and it is exhausted through an 8ft x 8ft filter bank on the opposite wall of the room.
2. The spray substrate consisted of 2x4 inch studs, 7 feet in height, spaced 16 inches apart, providing 2 cavities lined with cardboard inserts for SPF application. The total size of the spray structure was approximately 3 ft. x 7 ft. representing a typical wall cavity.

The SPF applicator sprayed the generic high pressure formulations using a Graco Fusion Air Purge 01 round tip spray gun. The generic low pressure kit formulation was sprayed using manufacturer supplied spray equipment. SPF was applied under the following conditions:

1. Ambient air temperature of 75°- 80°F with 50% relative humidity.
2. Samples were sprayed using manufacturer recommended pressure.
3. The system was heated to the manufacturer recommended temperature.
4. Samples were sprayed while maintaining a 12 to 24 inch distance from the substrate being sprayed.
5. When SPF application was completed, inserts were removed and stacked in the room. The cardboard inserts were then replaced and SPF application continued.
6. A 3 ft. by 7 ft. area was sprayed in one pass at a nominal thickness of:
 - 2 in for medium density (2 lb.) SPF
 - 4 in for low density (1/2 pound) SPF.
 - 2 in for low pressure kit SPF.
7. The amount of foam used (lbs.) and the densities of the foams sprayed were recorded.

Test Protocol

Air sampling for the chemical ingredients selected for evaluation were conducted by a third-party contractor according to applicable sampling and analytical protocols:

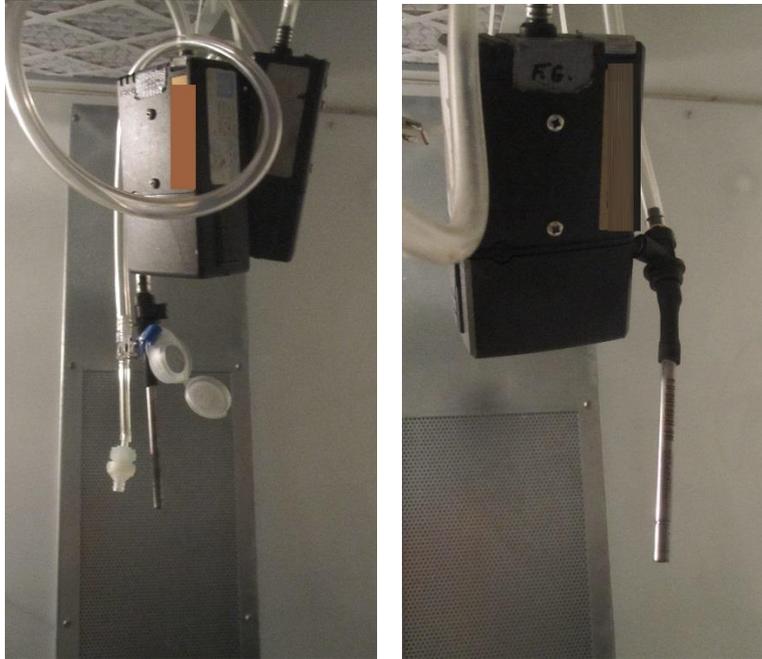
1. Two (2) sessions of area sampling were conducted for each SPF formulation (low density high pressure SPF, medium density high pressure SPF, and low pressure kit SPF) following application to the spray substrate.
2. SPF formulations were applied for 15 minutes for each air sampling test.
3. SPF formulations were applied at the target ventilation rate of 10 ACH. Actual ventilation rates varied for each two day air sampling session.
4. Following application, sprayed inserts remained in the ventilated spray room with ventilation operating at 10ACH
5. The air samplers were located near the center of the room, approximately 6 feet off the floor. Following the monitoring session, samples were submitted to a several qualified laboratories for analysis.
6. Air sampling was conducted according to the following schedule:
 - a. Hour 1 - Air sampling was initiated one hour after application.
 - b. Hour 2 - At the completion of Hour 1 sampling, air samplers were replaced with a second set of air samplers.

- c. Hour 3 – At the completion of Hour 2 sampling, ventilation was reduced from 10 ACH to a target rate of 1 ACH. The ventilation rate continued to operate at 1 ACH for one hour. Air sampling was not conducted during Hour 3 so that the ventilation could stabilize.
- d. Hour 4 – At Hour 4, a third set of air samplers were placed in the ventilated room. The ventilation rate continued at 1 ACH.
- e. Hour 8 – At Hour 8 a fourth set of air samplers were placed in the ventilated room.
- f. Hour 12 – At hour 12, a fifth set of air samplers were placed in the ventilated room. Ventilation continued at 1 ACH.

Sample Methodology

Table 2: Air Sampling and Analytical Methodology for Select SPF Constituents.				
CAS #	Analyte	Analytical Method	Flow Rate	Sampling media
101-68-8	2,4 MDI and 4,4 - MDI	Modified OSHA 47 High performance liquid chromatography (HPLC) using an ultraviolet (UV) or fluorescence detector	1.0 lpm	13 mm glass fiber filter coated with 1.0 mg of 1-(2-pyridyl)piperazine (1-2PP) extracted with 90/10 (v/v) acetonitrile/dimethyl sulfoxide (ACN/DMSO)
460-73-1	1,1,1,3,3-Pentafluoropropane	Modified OSHA 7 (diffusive sampler)		Diffusive sampler Assay Technology
811-97-2	1,1,1,2-Tetrafluoroethane	Bayer: ASTM Draft Method WK40293 Thermal desorption/GC/MS	0.25 lpm	Multi-sorbent tubes
13674-84-5	Tris-(1-chloro-2-propyl) phosphate (TCPP)			
3033-62-3	Bis (2-Dimethylaminoethyl) ether			
6711-48-4	Tetramethyliminobispropylamine			
2212-32-0	N,N,N-Trimethylaminoethylethanolamine			
3855-32-1	Bis (dimethylaminopropyl) methylamine			
3030-47-5	Pentamethyldiethylene triamine			

Figure 1



Example of air sampling configuration for generic formulations

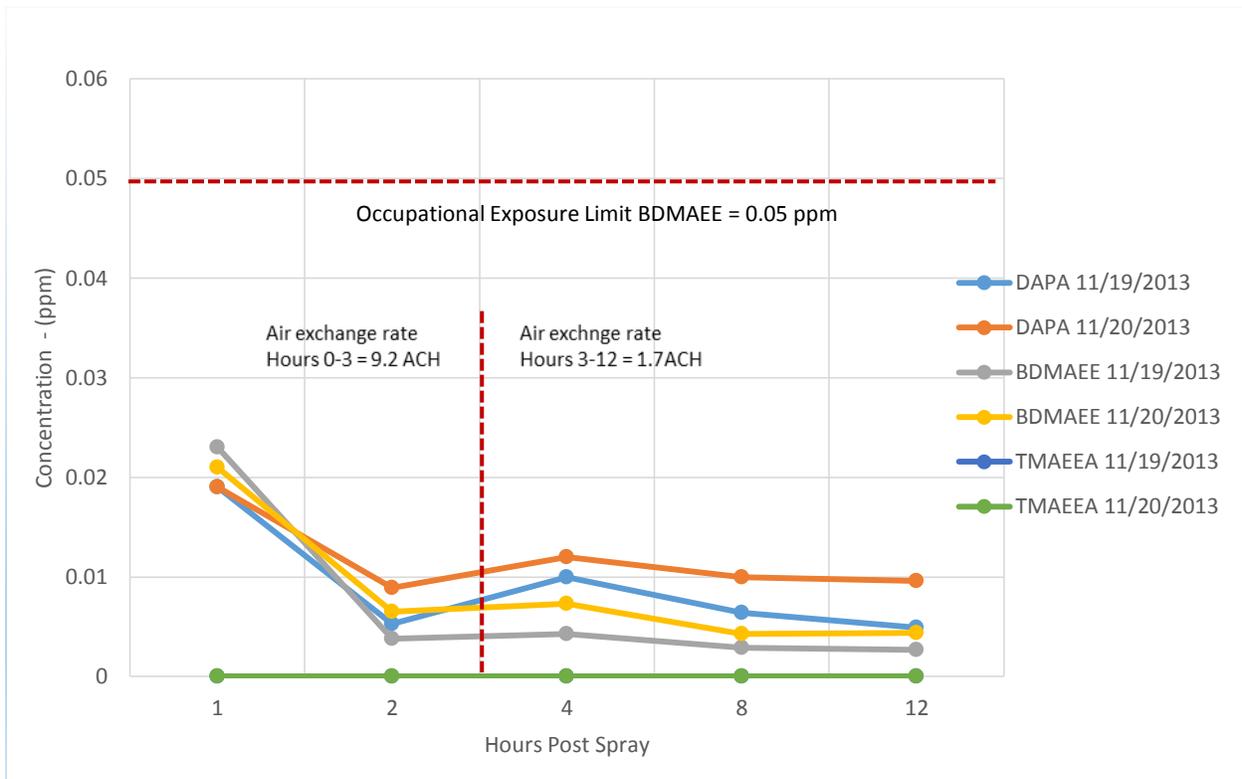
Results of Air Sampling – Generic High Pressure Medium Density Formulation

Samples were collected at a measured ventilation rate of 9.2 ACH at one and two hours after SPF application. Beginning 3 hours after application, the ventilation rate was reduced to a measured air exchange rate of 1.7 ACH. Air samples were again collected at 4, 8, and 12 hours after application at 1.7 ACH. The “A-Side” MDI vapor was monitored during hours 1, 2, and 4 only since no detectable concentrations of MDI were expected throughout the 12 hour study period. The “B-Side” components were monitored at each target hour. All samples were collected for 20 minutes with the exception of MDI. MDI samples were collected for 60 min to meet acceptable analytical detection limits. Sample times bracketed each target hour, for example, 20 minute samples began 10 minutes before the hour and ended 10 minutes after the hour.

Air samples were collected prior to spraying the generic formulations to measure potential background concentrations of the SPF components. Field blanks were also submitted following each round of testing. Analysis of background and field blank samples indicated small amounts of SPF components in two samples; however, the quantities were considered insignificant.

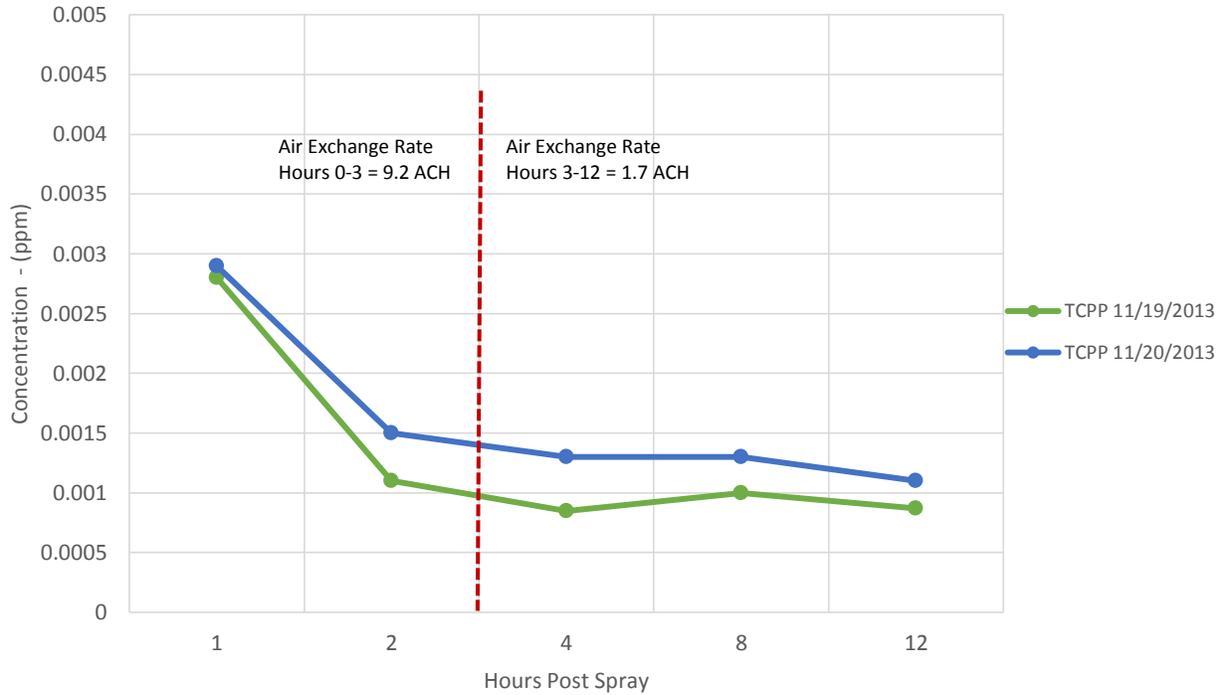
The results of analysis are listed in Appendix 1 and displayed in graphical form in Figures 2 - 4. There were no measureable airborne concentrations of either 2,4-MDI or 4,4-MDI in the samples collected 1, 2 and 4 hours after application. MDI aerosol and vapor has been shown to present during spray application of the generic medium density formulation, however, it was not detected after 1 hour following application. The detection limits ranged from 0.00014 to 0.00016 ppm which is significantly below the occupational exposure limit of 0.005 ppm for 4,4-MDI.

Figure 2
Amine Catalyst
Generic Medium Density High Pressure Formulation



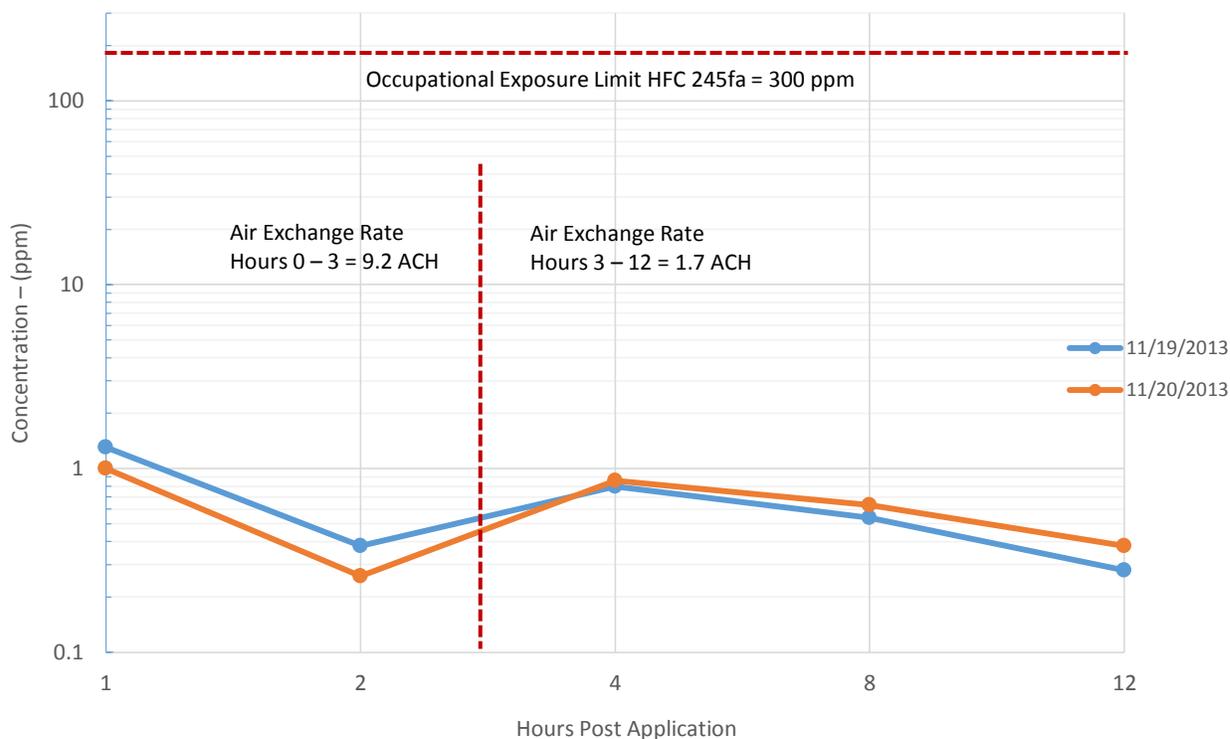
Amine catalyst concentrations listed in Appendix 1 ranged from below detection limits to 0.023 ppm. Figure 2 displays the data in graphical form and includes the occupational exposure limit (OEL) for BDMAEE, as a point of reference. BDMAEE is the only amine catalyst in the generic formulation that has been assigned an OEL. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned BDMAEE a Threshold Limit Value of 0.05 ppm, as an 8 hr. time-weighted average concentration (TLV-TWA). The highest concentration measured during the two day study was approximately ½ the recommended value. This occurred within 1 hour following application. The concentration continued to decrease during the second hour and increased slightly during the fourth hour after the ventilation had been lowered to 1.7 ACH. TMAEEA, a non-emissive catalyst, was not detected in any of the samples; however, it must be noted that the reported TMAEEA values are semi-quantitative since the compound degrades due to the thermal desorption during sample analysis. DAPA, an emissive catalyst, followed emission patterns similar to BDMAEE. Concentrations decreased from the first to the second hour as the ventilation rate equaled 9.2 ACH. At the fourth hour following SPF application, concentrations of the catalysts, BDMAEE and DAPA increased or remained the same at 1.7 ACH. Concentrations then generally remained steady or decreased slightly from hour 4 through 12.

Figure 3
Tris-(chloro-2-propyl) phosphate (TCPP)
Generic Medium Density High Pressure Formulation



TCPP concentrations ranged from below 1 ppb to 3 ppb (Appendix 1/Figure 3). Concentrations were highest one hour after application, dropping in half by the second hour. At hours 4 through 12 concentrations remained at approximately 1 ppb at the reduced air exchange rate of 1.7 ACH. There are no published OELs for TCPP, however, emissions from the closed cell generic formulation were negligible.

Figure 4
HFC-245fa
Generic Medium Density High Pressure Formulation



Concentrations of the blowing agent, HFC 245fa followed the same pattern as the other B-side components (Appendix 1 / Figure 4). Concentrations dropped significantly from the first to second hour, rose again in the fourth hour after the air exchange rate was reduced. The OEL of 300 ppm was established as a Workplace Environmental Exposure Level (WEEL) by the American Industrial Hygiene Association (AIHA). The WEEL is an 8 hr. TWA concentration. The WEEL has been added to Figure 4 as a point of reference indicating acceptable emissions of blowing agent in terms of worker exposure. Although detectable, HFC 245fa concentrations were more than 3 times lower for the 12 hour period following application, even at the reduced ventilation rate of 1.7 ACH.

Conclusions - Generic Medium Density High Pressure Formulation

Concentrations of MDI, BDMAEE, and HFC245fa were well within occupational exposure limits beginning one to twelve hours after application. Although the measurements do not represent actual worker exposure assessments, the chemicals emitted would not present a significant airborne risk to healthy adult trade workers entering the area following application. All measured chemicals decreased from the first hour following application, rose again as the air exchange rate was decreased from 9.2 to 1.7 ACH four hours application, and then either remained steady or decreased until the completion of the monitoring 12 hours after application. Using established OELs as safe 8 hour exposure concentrations for healthy adult trade workers as a benchmark, and considering 9.2 ACH may have partially controlled emissions during Hour 1 through Hour 3; trade workers could safely re-enter the work area sprayed with the generic formulation after four hours without the use of respiratory protection. This re-entry time is also based on the assumption that the passive ventilation rate of 1.7 ACH would provide limited control of SPF emissions.

Results of Air Sampling – Generic Low Density High Pressure Formulation

The study protocol previously described was followed for the generic high pressure low density formulation. Chemicals monitored included: MDI, three amine catalysts, and the fire retardant, TCPP. Blowing agent samples

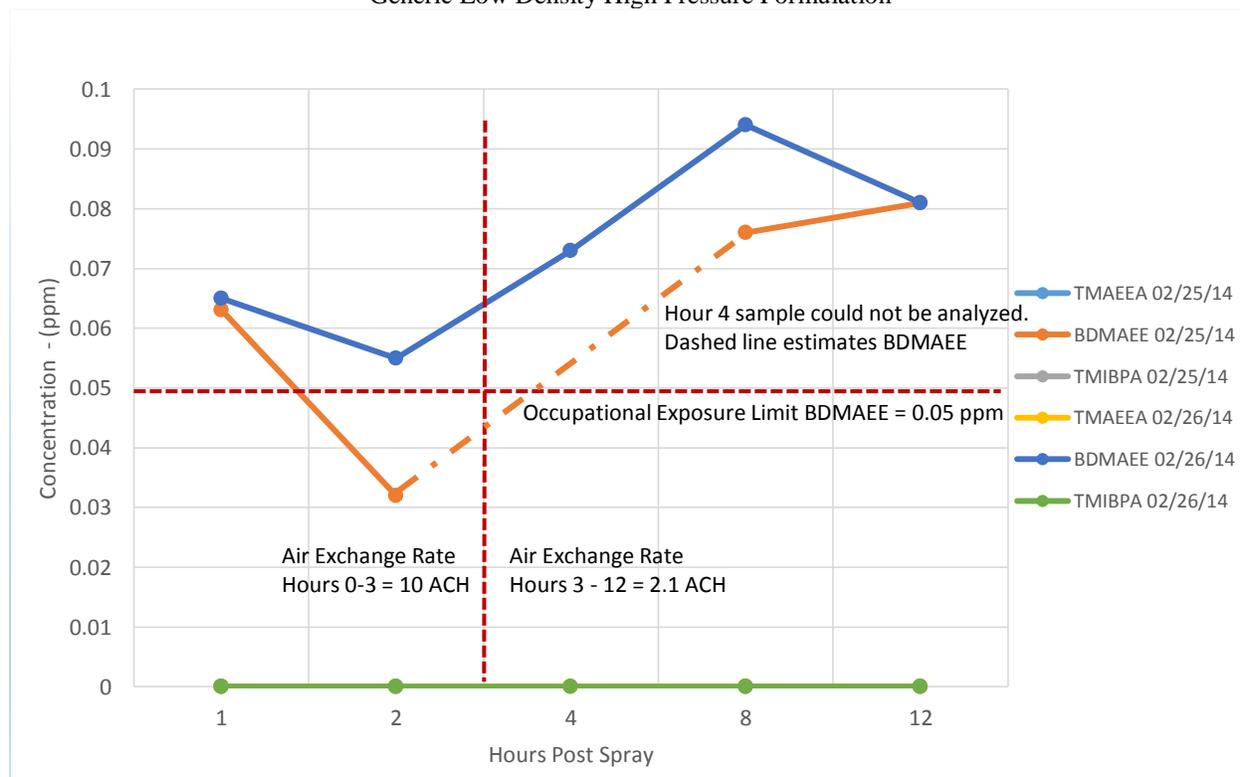
were not collected since water is used in the low density formulation. Similar to the medium density formulation, samples were collected at a measured ventilation rate of 10 ACH at one and two hours after SPF application. Beginning 3 hours after application, the ventilation rate was reduced to a measured ventilation rate of 2.1 ACH. Air samples were again collected at 4, 8, and 12 hours after application at 2.1 ACH. "A-Side" MDI vapor was monitored during hours 1, 2, and 4. "B-Side" components were monitored at each target hour. All samples were collected for 20 minutes with the exception of MDI which were collected for 60 min. Sample times bracketed each target hour.

Air samples were collected prior to spraying the generic formulation to measure potential background concentrations of the SPF components. Field blanks were also submitted following each round of testing. Analysis of background and field blank samples indicated a trace quantity of BDMAEE in one sample; however, the concentration was not significant.

The results of analysis are listed in Appendix 1 and displayed in graphical form in Figures 5 and 6. There were no measureable airborne concentrations of either 2,4-MDI or 4,4-MDI in samples collected 1, 2 and 4 hours after application. The MDI detection limits ranged from 0.00014 to 0.00016 ppm which is significantly below the Occupational Exposure Limit of 0.005 ppm for 4,4-MDI.

One thermal desorption tube sample collected at hour four on the first day of the study could not be analyzed. Therefore BDMAEE and TCPP Hour 4 concentrations have been estimated and displayed as a dashed line connecting the Hour 2 results to the Hour 8 results on Figure 5 and 6. The sample is listed as "Void" in Appendix 1.

Figure 5
Amine Catalyst
Generic Low Density High Pressure Formulation

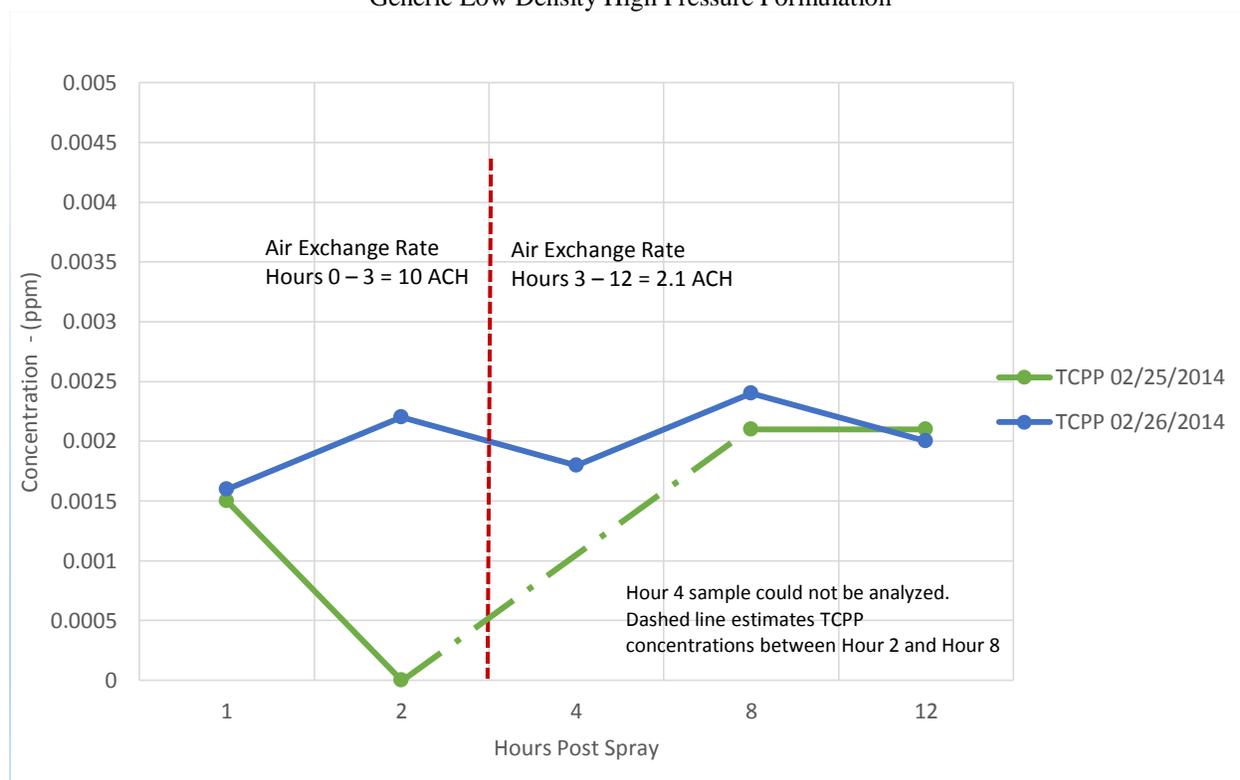


BDMAEE was detected in all thermal desorption tube samples, while TMIBPA and TMAEEA were not detected in any air sample. As demonstrated in Appendix 1 and Figure 5, BDMAEE concentrations were generally above the ACGIH TLV-TWA of 0.05 ppm. Only one sample collected during the second hour after application resulted in a

BDMAEE concentration less than the TLV-TWA. BDMAEE concentrations decreased from Hour 1 to Hour 2 following application, however rose again at Hour 4, after the ventilation rate was reduced to 2.1 ACH. Concentrations continued to rise at Hour 8 and 12 following application on the first day of sampling, decreasing slightly at Hour 12 on the second day.

The quantity of BDMAEE in the high pressure medium density formulation and the low density formulation are similar (0.7% medium density/0.9% low density), therefore the difference in BDMAEE emissions between the two formulations is likely due to the open cell nature of the low density foam. BDMAEE is an emissive catalyst that is not bound in the cured formulation and will readily emit from an open cell foam over time, while the closed cell formulation will encapsulate the catalyst resulting in reduced emissions over time.

Figure 6
TCPP
Generic Low Density High Pressure Formulation



TCPP emissions varied between day 1 and day 2 of the study; however concentrations were very low, close to the analytical detection limit. On the second day, TCPP concentrations rose slightly from the first to second hour, and remained at approximately 2 ppb for Hours 4 through 12. Hours 8 through 12 on the first day of testing resulted in the same 2 ppb TCPP concentration.

Conclusions - Generic Low Density High Pressure Formulation

Concentrations of 2,2 and 2,4 MDI and the amine catalysts TMEEA and TMIBPA were below detection limits. TCPP was present at very low part per billion concentrations, slightly above analytical detection limits. BDMAEE concentrations, however, generally exceeded the ACGIH TLV-TWA during the twelve hour study period. Although the catalyst measurements do not represent actual worker exposure, trade workers entering the area where the generic high pressure open cell formulation had been sprayed, would require respiratory protection in addition to other required PPE.

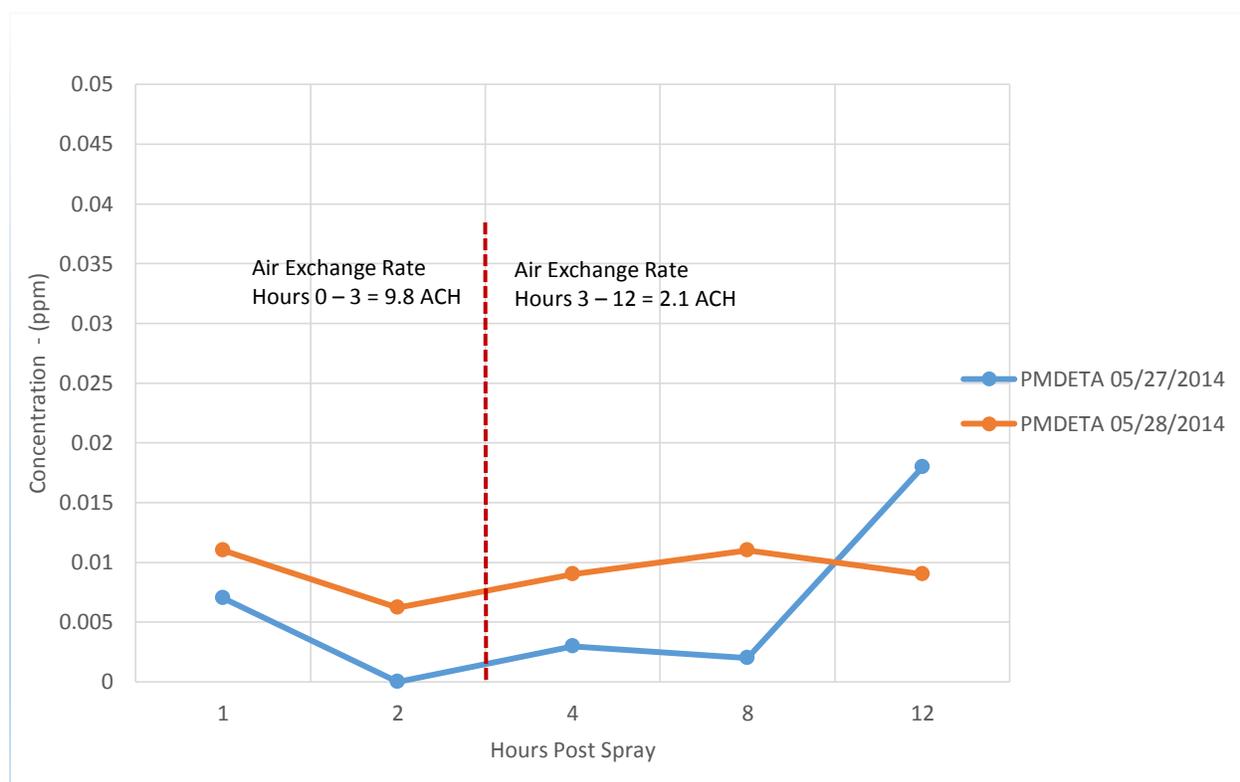
Results of Air Sampling – Generic Low Pressure 2 Component Kit Formulation

The study protocol used for the generic high pressure medium density and low density formulations was again followed for the low pressure kit formulation. Chemicals measured included; MDI, one amine catalyst, PMDETA, the fire retardant, TCPP, and the blowing agent, HFC 134a. Air samples were collected at a measured ventilation rate of 9.2 ACH at 1 and 2 hours after SPF application. Beginning 3 hours after application, the ventilation rate was reduced to a measured air exchange rate of 2.1 ACH and air samples were again collected at 4, 8, and 12 hours after application. “A- Side” MDI vapor was monitored during hours 1, 2, and 4. “B-Side” components were monitored at each target hour. Catalyst and fire retardant samples were collected for 20 minutes while MDI and HF 134a were collected for 60 min. Sample times again bracketed each target hour.

Air samples were collected prior to spraying the generic kit formulation to measure potential background concentrations of the SPF components. Field blanks were also submitted following each round of testing. No test components were detected in background samples or field blanks.

The results of analysis are listed in Appendix 1 and displayed in graphical form in Figures 7 and 8. There were no measureable airborne concentrations of either 2,4-MDI or 4,4-MDI in samples collected 1, 2 and 4 hours after application. The MDI detection limits ranged from 0.00014 to 0.00016 ppm. The blowing agent HFC 134a was also not detected in any sample collected during the 12 hour study period. The detection limits for the blowing agent were 3.91 ppm to 5.91 ppm which is far below the AIHA WEEL of 1,000 ppm.

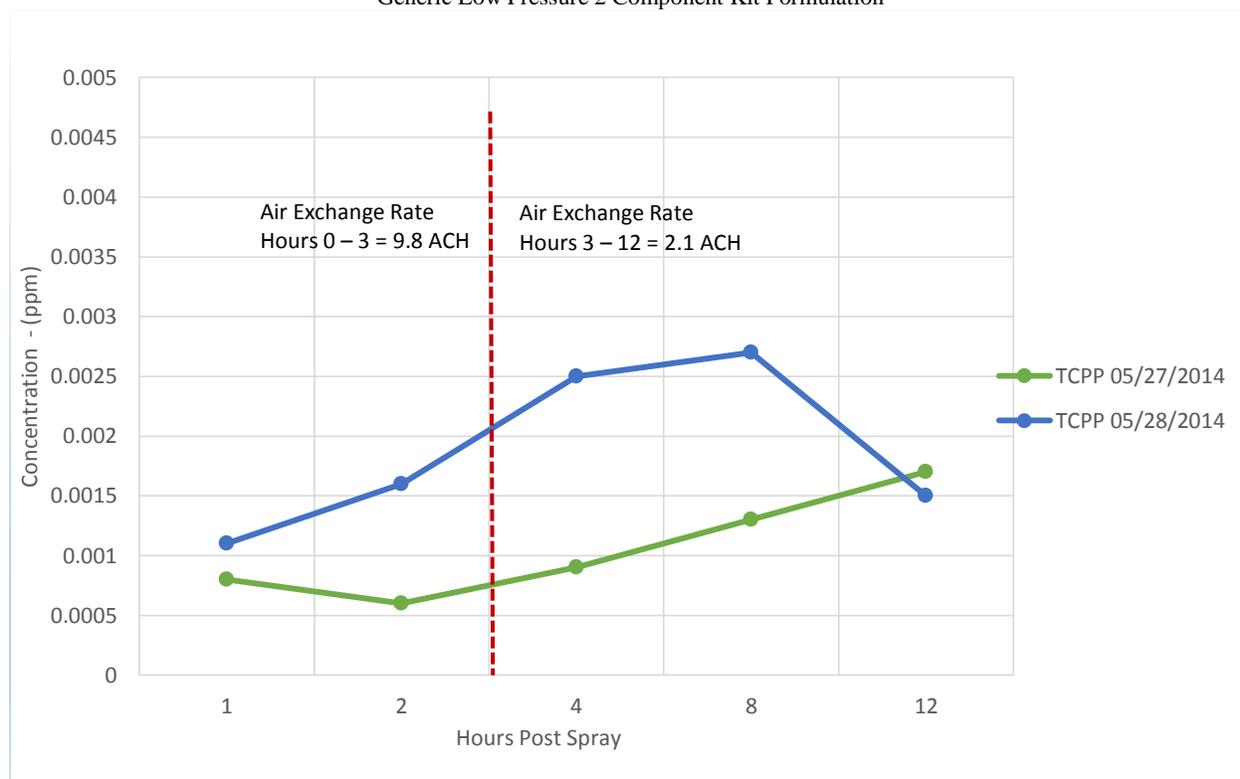
Figure 7
Amine Catalyst
Generic Low Pressure 2 Component Kit Formulation



Pentamethyldiethylene triamine (PMDETA) concentrations listed in Appendix 1 and Figure 7 indicate the amine catalyst was detected in all samples with the exception of the sample collected at Hour 2, day 1. Catalyst concentrations were low on each day of the study, ranging from non-detect to 0.018 ppm. PMDETA concentrations either decreased slightly or remained the same between Hour 1 and 2 and then remained the same or increased

slightly as the ventilation was decreased at hour 4. On day 1, Hour 12 the PMDETA concentration rose from 0.002 ppm to 0.018 ppm. Although there is no clear reason for the increase, the variation is likely due to the fact emissions were near the analytical detection limit where a slight increase in amine concentration would appear significant. Concentrations would likely return to the observed low concentrations if air sampling continued beyond the 12 hour period.

Figure 8
TCPP
Generic Low Pressure 2 Component Kit Formulation



The fire retardant, TCPP varied by several parts per billion (ppb) between the between the first and second day of air sampling. During the first day of the study, TCPP concentrations followed the previously observed pattern of a decrease from Hour 1 to Hour 2 and then a gradual increase after Hour 4. TCPP concentrations on the second day remained steady at approximately 45 ppb and dropped to 15 ppb a Hour 12. Like the amine catalyst, concentrations were very low, with the variation attributable to slight changes in environmental conditions or analytical sensitivity.

Conclusions - Generic Low Pressure 2 Component Kit Formulation

Concentrations of 2,2 and 2,4 MDI and the blowing agent HFC134a were below detection limits. TCPP and the amine catalyst PMDETA were present at very low part per billion concentrations, slightly above analytical detection limits. Based on the reported results of this study, long term emissions from the generic kit formulation were low and would not pose a significant risk to the health of trade workers entering the sprayed area four hours after application.

CONCLUSIONS

2,4-MDI or 4,4-MDI

There were no measureable airborne concentrations of either 2,4-MDI or 4,4-MDI in the samples collected 1, 2 and 4 hours after application. MDI has been shown to present during spray application, however, MDI vapor could not be detected in any sample after 1 hour following application. The detection limits ranged from 0.00014 to 0.00016 ppm which is significantly below the occupational exposure limit of 0.005 ppm for 4,4-MDI.

Amine Catalysts

Measurable quantities of amine catalyst were detected in each generic formulation; however, only one of the five catalysts present in the 3 formulations, bis (2-Dimethylaminoethyl) ether (BDMAEE), has been assigned an occupational exposure limit. The American Conference of Governmental Industrial Hygienists has assigned BDMAEE a Threshold Limit Value (TLV-TWA) of 0.05 ppm. In a status report regarding the five amine catalysts in the CPI generic formulations, the Consumer Product Safety Commission (CPSC) reported "Four of the five amine catalysts had very limited toxicological or exposure data to review; therefore, data relevant to amine catalyst toxicity is based on the chemical with the most information, bis (2-Dimethylaminoethyl) ether." Using CPSC's approach as a guide for interpretation; with the exception of BDMAEE, catalyst emissions from the high pressure medium density formulation and the low pressure kit formulation would be considered acceptable beginning 1 hour after application given the ventilation rates used for this study. BDMAEE emissions measured during the post application of the low density high pressure open cell formulation at the ventilation rates used for this study, were in excess of the 0.05 ppm TLV-TWA and would not be considered acceptable for unprotected trade workers following application.

Tris-(1-chloro-2-propyl) phosphate (TCPP)

The generic formulations contain significant quantities of TCPP ranging from 16 to 30 percent of the total B-side formulation. Although the quantity is significant, most fire retardant remains in the SPF once the material is applied. Following application, as the foam temperature decreases, low ppb concentrations of TCPP were emitted. Although there are no established exposure limits for TCPP, the measured concentrations 1 to 12 hours after application were near analytical detection limits and likely would not pose a risk to the health of unprotected trade workers at the ventilation rates used for this study.

Blowing Agents HFC-145fa and HFC-134a

Measurable quantities of HFC-145fa were detected 1 to 12 hours after application of the high pressure medium density formulation. All concentrations were less than 1 ppm which is well within the occupational exposure limit of 300 ppm set by the AIHA WEEL committee. Concentrations of HFC-134a used in the low pressure kit formulation were below analytical detection limits. The WEEL committee has set an occupational exposure limit of 1,000 ppm for HFC-134a. Based on the findings, blowing agent concentrations emitted from the generic high pressure medium density formulation and the low pressure kit formulation would likely not pose a risk to the health of unprotected trade workers at the ventilation rates used for this study.

Re-Entry Study Conclusions

There are several conclusions that can be drawn from the data generated. In the absence of properly designed ventilation, SPF emissions can be expected to vary between formulations. It is also evident that if the CPI generic formulations represent typical SPF formulations in commercial use today, MDI vapor does not present a significant airborne health risk to unprotected trade workers beginning 1 hour after application even when using minimal exhaust ventilation. Certain emissive catalysts, such as BDMAEE, that are not bound within the sprayed open cell formulation, will continue to be released at concentrations above the occupational exposure limit 12 hours after application if ventilation is not sufficient to control emissions. BDMAEE in the closed cell formulation did not exceed the occupational exposure limit at any time during the 12 hour period. Non-emissive catalysts, such as TMAEEA and TMIBPA present in the same open cell formulation, were bound to the spray foam and were below the detection limits throughout the test period. Given the environmental conditions and the protocol used in this study, other components such as TCPP and the blowing agents HFC-245fa and HFC-134a would not pose a significant health risk for unprotected workers at the ventilation rates used for this study.

Based on the results of this study it is apparent that that emissions of SPF chemicals will vary depending on the type of foam (open cell vs. closed cell) and the specific chemicals comprising the B-side of the formulation. It is therefore essential that emissions from commercial SPF formulations, in particular open cell formulations, be

controlled through the use of mechanical ventilation during application and for 12 hours or more following application. Control effectiveness should be evaluated through industrial hygiene air monitoring. The use of respiratory protection must then be used to supplement ventilation where worker exposure to SPF chemicals cannot be controlled. In those instances where SPF Producers desire reduced re-entry times for commercial products, those formulations should be evaluated in the laboratory using similar ventilation rates used in this study. Laboratory studies should then be validated in the field with contractor-provided mechanical ventilation.

**APPENDIX 1
Generic High Pressure Medium Density Formulation**

Date	Analyte	Concentration (ppm)					Exposure Limit
		Hour 1	Hour 2	Hour 4	Hour 8	Hour 12	
11/19/2013	HFC-245fa	1.3	0.38	0.80	0.54	0.28	300
11/20/2013		1.0	0.26	0.86	0.63	0.38	
11/19/2013	TMAEEA	<0.27	<0.26	<0.26	<0.26	<0.27	N/A
11/20/2013		<0.26	<0.27	<0.25	<0.26	<0.25	
11/19/2013	BDMAEE	0.023	0.0038	0.0043	0.0029	0.0027	0.05
11/20/2013		0.021	0.0065	0.0073	0.0043	0.044	
11/19/2013	DAPA	0.019	0.0053	0.010	0.0064	0.0049	N/A
11/20/2013		0.019	0.0089	0.012	0.0100	0.0096	
11/19/2013	TCPP	0.0028	0.0011	0.00085	0.0010	0.00087	N/A
11/20/2013		0.0029	0.0015	0.0013	0.0013	0.0011	
11/19/2013	2,4-MDI	<0.00016	<0.00015	<0.00015	n/a	n/a	N/A
11/20/2013		<0.00014	<0.00015	<0.00015	n/a	n/a	
11/19/2013	4,4-MDI	<0.00014	<0.00015	<0.00015	n/a	n/a	0.005
11/20/2013		<0.00014	<0.00015	<0.00015	n/a	n/a	

Generic High Pressure Low Density Formulation

Date	Analyte	Concentration (ppm)					Exposure Limit
		Hour 1	Hour 2	Hour 4	Hour 8	Hour 12	
02/25/2014	TMAEEA	<0.015	<0.016	VOID	<0.015	<0.016	N/A
02/26/2014		<0.016	<0.016	<0.015	<0.016	<0.016	
02/25/2014	BDMAEE	0.063	0.032	VOID	0.076	0.081	0.05
02/26/2014		0.065	0.055	0.073	0.094	0.081	
02/25/2014	TMIBPA	<0.016	<0.016	VOID	<0.015	<0.017	
02/26/2014		<0.17	<0.017	<0.016	<0.017	0.017	
02/25/2014	TCPP	0.0015	<0.0011	VOID	0.0021	0.0021	
02/26/2014		0.0016	0.0022	0.0018	0.0024	0.0020	
02/25/2014	2,4-MDI	<0.00016	<0.00015	VOID	n/a	n/a	N/A
02/26/2014		<0.00015	<0.00014	<0.00014	n/a	n/a	
02/25/2014	4,4-MDI	<0.00016	<0.00015	VOID	n/a	n/a	0.005
02/26/2014		<0.00015	<0.00014	<0.00014	n/a	n/a	

Generic Low Pressure (2 Component) Kit Formulation

Date	Analyte	Concentration (ppm)					Exposure Limit
		Hour 1	Hour 2	Hour 4	Hour 8	Hour 12	
05/27/2014	HFC-134a	<5.87	<5.87	<3.91	<3.91	<3.91	1,000
05/28/2014		<5.87	<5.87	<3.91	<3.91	<3.91	
05/27/2014	PMDETA	0.007	<0.002	0.003	0.002	0.018	N/A
05/28/2014		0.011	0.006	0.009	0.011	0.009	
05/27/2014	TCPP	0.0008	0.0006	0.0009	0.0013	0.0017	N/A
05/28/2014		0.0011	0.0016	0.0025	0.0027	0.0015	
05/27/2014	2,4-MDI	<0.00012	<0.00015	<0.00015	n/a	n/a	N/A
05/28/2014		<0.00015	<0.00015	<0.00015	n/a	n/a	

05/27/2014	4,4-MDI	<0.00012	<0.00015	<0.00015	n/a	n/a	0.005
05/28/2014		<0.00015	<0.00015	<0.00015	n/a	n/a	

References

Consumer Product Safety Commission (CPSC). 2012. Status Report: Staff Review of Five Amine Catalysts in Spray Polyurethane Foam. (CPSC-D-07-006).

Wood, R. 2013. CPI Ventilation Research Project Update. Polyurethanes Technical Conference. American Chemistry Council.

“Ventilation Guidance for Spray Polyurethane Foam Application,” published by the U.S. Environmental Protection Agency (EPA), online at www.epa.gov/dfepubs/projects/spf/ventilation-guidance.html

Acknowledgements

The author would like to thank Dr. Brent Altemose, and Stephen Nowakowski, Sabre Health and Safety, Bulent Ozbas and Joel Rogers, Air Products and Chemicals, and Scott Ecoff, Bayer MaterialScience. The author would also like to thank the members of the CPI staff and Ventilation Research Task Force for their time, energy, and commitment to this project.

Richard Wood

Richard Wood is a Certified Industrial Hygienist (CIH). He earned a BA in Biology and Chemistry from Eastern Michigan University and a Master of Public Health degree specializing in Industrial and Environmental Health from the University of Michigan. Rick worked for Air Product and Chemicals, Inc. for over 30 years as the Manager, Global Industrial Hygiene Services. He was responsible for managing industrial hygiene teams and activities for Air Products global operations as well as providing product stewardship support to the epoxy and polyurethane additives business areas.