Spray Polyurethane Foam Monitoring and Re-Occupancy of High Pressure Open Cell Applications to New Residential Constructions

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Abstract

As part of the SPF Product Stewardship activities, industrial hygiene air monitoring was conducted during the application and trimming of overspray of BASF Corporation ENTERTITE NM® open cell spray polyurethane foam (SPF) in two homes located near Houston, TX, and at the BASF Houston Research/Training Center. The purpose of the study was to determine SPF emissions during application and to evaluate emissions 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 VOC's were evaluated during and after application of spray polyurethane foam in the spray booth and field environments. Industrial hygiene monitoring was completed using NIOSH, OSHA and other validated air sampling methods. The EPA method TVOC-15 was used for collection of volatile organic hydrocarbons.

BACKGROUND
This study focused upon the field spray application of high pressure polyurethane foam liquid compounds formulated and produced by BASF Corporation. The formulations evaluated in this study were half pound density open cell foam, sold under the trade name ENERTITE NM®. Two homes were insulated in the Houston, Texas, USA area during late January and late March of 2014. Each home was under construction and foam was being applied to the building envelope areas.

Inside Spray Rig

Trimming Foam

House Number 1

The first home (above) located in near Houston in Fulshear, Texas was being sprayed on the second floor wall areas and parts of the underside of the plywood roof deck while we tested in late January 2014. The applicator had several parts of this home project already insulated with ENERTITE NM® from previous trips to the jobsite. Part of the sampling for the open cell high pressure SPF components was also conducted at BASF's facility while a worker scarf or trimmed and cut the foam.

Side

Front

House Number 2

The second home was a very large home (Approx. 7,000 square feet) consisting of 2 floors and a loft area. We monitored during application of foam to each floor and during trimming to evaluate the worker's potential exposure to the SPF components. At times the tasks such as trimming were all that was going on, no spraying. Other times, multiple tasks were going on such as trimming in one area, spraying and trimming in another area of the house. At times two rigs were spraying at the same time and also trimming going on. Sampling was conducted in late March

in the Houston (Woodlands area), Texas. There was no attempt to mechanically ventilate emissions with engineering controls; however open doors and windows provided natural ventilation in the house during the days we monitored.

The typical finished open cell half pound density SPF foam is field manufactured when the liquid "A" side and the liquid "B" side are combined though special high pressure heated airless spray application equipment. The "A" side or specific chemical called 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, and surfactants.

The applications were performed by D7 Spray Foam Insulation employees and followed CPI's and OSHA's guidance on personal protective equipment and the CPI/ Spray Foam Coalition SPF Industry best practices... This included nitrile gloves, a full face air supplied respirator, full Tyvek® suit to minimize exposed skin. Individuals not spraying or helping were not allowed in the spray area. PPE was used by those monitoring near the spray area or in or near the house. The collection and work stations were located well away from the active spray or trimming areas.

The top of the stairwell shows both a TO-15 sample collection can as well as impingers which were used to collect air samples

Table 1: SPF Chemicals Selected for Evaluation		
Liquid A – Side Compound		
Chemical	Common Name	Occupational Exposure Limit
Polymeric methylene diphenyl diisocyanate	PMDI	Not Established
Monomeric methylene diphenyl diisocyanate	2, 4 - MDI and 4,4 - MDI	0.005 ppm*
Liquid B – Side Compound		
Tertiary Amine Catalysts Bis-(2-Dimethylaminoethyl)ether N,N,N,- Trimethylaminoethylethanolamine	 BDMAEE TMAEEA	 0.05 ppm* Not Established
Fire Retardant Tris-(1-chloro-2-propyl) phosphate	 TCPP	 Not Established
Total Volatile Organic Chemicals	TVOV	Not Established

The Occupational Safety & Health Administration (OSHA) specifies a ceiling limit for MDI of 20 parts per billion (ppb), equivalent to 0.2 mg/m3. This is the exposure concentration which should never be exceeded without respiratory protection.

*The American Conference of Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) guideline for MDI is 5 ppb as an 8-hour Time-Weighted Average (TWA).

The current occupational exposure limit for MDI applies only to the 2-ring monomeric MDI (Diphenylmethane-4,4'-diisocyanate CAS # 101-68-8). The MDI that is used in the SPF industry is a polymeric version of MDI, which contains monomeric MDI as well as other higher ring isomers of MDI. The combination of the 2-ring and 3-ring MDI isomers typically constitutes approximately 80% of the total MDI isomers contained in polymeric MDI. Some manufacturing processes can generate aerosols that result in a greater potential for exposure to the 3-ring isomer. Therefore, for the purposes of providing a more accurate assessment of MDI exposure and body burden to the active metabolic isocyanate functional group, we report the 2-ring, 3-ring, and total MDI. For regulatory compliance purpose, the occupational exposure limit is applied to only the 2-ring MDI. However, BASF recommends and encourages customers to evaluate and develop a MDI control program based on the combination of the 2-ring and 3-ring isomer.

There is no Occupational Safety & Health Administration (OSHA) permissible exposure limit (PEL) nor American Conference of Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) guideline for the flame retardant, Trichloropropyl phosphate (TCPP).

The amine catalysts were bis(2-Dimethylaminoethyl)ether (BDMAEE) and N,N,N-Trimethylaminoethylethanolamine (TMAEEA). There are no established OSHA PEL's for the amine catalysts monitored during this survey; however, the American Conference of Industrial Hygienists (ACGIH) has set a TLV of 0.05 ppm as an 8-hour TWA and a Short Term Exposure Limit STEL of 0.150 for BDMAEE. There have been no inhalation studies that conclusively establish concentrations which workers can be repeatedly exposed day after day without adverse effect for N,N,N- Trimethylaminoethylethanolamine (TMAEEA).

In addition to common raw materials, the levels for certain VOCs were also monitored. No standards have been set for VOCs in non-industrial settings.

ANALYTICAL TECHNIQUES AND METHODS

MDI

Air sampling pumps were used to collect area samples of MDI aerosol and vapor. The pumps were calibrated to a flow rate of 1.0 L/minute with a flow calibrator before and after sampling. The average flowrate was used to calculate air volumes unless otherwise noted. The MDI samples were collected in 15 mls of 1-(2-pyridyl) piperazine (1,2-PP) in glass impingers with a backup 13 mm glass fiber filter, impregnated with 5 mg of 1-(2-pyridyl) piperazine (1,2-PP). Impingers were changed to keep sample times less than four hours. After samples were collected, the filter was removed from the cassette with tweezers and placed in a vial. Two milliliters of 90% acetonitrile and 10% dimethyl sulfoxide solution (DMSO) with 1,2-PP were rinsed through the front tapered section of the filter cassette to flush dust on the inside of the cassette into the vial containing the filter. The vial was hand agitated to ensure the particulate on the filter was completely wetted by the acetonitrile/DMSO solution.

The vials of acetonitrile/DMSO solution with filters, along with a blank filter in a vial of solution, were shipped to the BASF lab in Wyandotte, Michigan. The samples were analyzed following a modified version of NIOSH 5521 Method at an American Industrial Hygiene Association (AIHA) accredited laboratory. The deritivization solvent used was 1,2 PP instead of 1, 2 MP = 1-(2-methoxyphenyl) piperazine as noted in NIOSH Method 5521 because the lab is much more familiar with this solvent. To ensure there was no breakthrough of MDI, a backup filter was used as described in NIOSH Method 5525. The concentration of MDI reported in parts per billion, includes MDI vapor and MDI associated with foam particles.

To assess the potential health impact of polymeric MDI, the concentration of two plus three ring MDI was also calculated for comparison to the occupational exposure limit.

Triethyl Phosphate (TCPP)

Air sampling pumps were used to collect area samples of TCPP vapor. The pumps were calibrated to a flowrate of around 1.0 L/minute with a flow calibrator before and after sampling. The average flowrate was used to calculate air volumes unless otherwise noted. Samples were collected on a XAD-7 OVS tube (glass fiber filter, 13-mm; XAD-7, 200mg/100mg) per NIOSH Method 5523. The XAD-7 OVS tubes, along with a blank tube, were shipped to the BASF lab in Wyandotte, Michigan. The samples were analyzed following NIOSH 5523 Method at an American Industrial Hygiene Association (AIHA) accredited laboratory. The concentration of TCPP was reported as ppm (and) mg/m3.

Amine Catalyst Monitoring Methods
Two amine air sampling methods were used for portions of the study. Samples collected during the application and trimming tasks conducted during residential SPF application were obtained using standard field monitoring procedures. A second method having greater analytical sensitivity was used in the spray booth to evaluate catalyst emissions during the trimming of aged SPF.

Air samples collected during SPF application in the two homes for amine catalyst evaluation were collected by drawing air through tubes containing XAD-2 sorbent material with calibrated Gillian low flow pumps. Following collection, the samples were submitted to the ESIS Environmental Health Laboratory, an AIHA accredited laboratory, where they were solvent desorbed and analyzed by gas chromatography using an NPD detector.

Air samples collected in the BASF Houston Research and Training Center during the trimming of aged SPF were obtained in accordance with the procedure described in the draft ASTM work item 40292 "Sampling and Determination of Vapor-Phase Organic Compounds Emitted from Spray Polyurethane Foam (SPF) Insulation in Micro-Scale Chambers using Sorbent Tubes Analyzed by Thermal Desorption Gas Chromatography and Mass Spectrometry". Pumps equipped with low flow adapters were used to draw air through glass tubes containing Tenax sorbent material. Following sample collection, both amine catalyst and TCPP were thermally desorbed from the Tenax and analyzed by the GC/MS method described in the draft ASTM standard.

Total Volatile Organic Hydrocarbon (TVOC) EPA Method TO-15
The atmosphere sample is drawn into a specially-prepared stainless steel canister. The canister is an evacuated canister that is cleaned of all residual chemicals and sealed. A field sample of air is drawn through an orifice connected to the can with a gauge to regulate the rate and duration of sampling into the pre-evacuated canister.. Canisters were sealed and shipped back to a third party laboratory for analysis per EPA TO-15 method for the first and second homes.

It should be noted in the laboratory report, parts per billion concentrations of acetone, hexane, ethanol and toluene were detected which are not reported in this paper. These solvents were all expected due to construction of the homes and usage of adhesive and glues containing these products. Toluene was introduced to each home by the toluene impinger method used to capture MDI. Thus, these chemicals were not reported herein.

SAMPLE LOCATIONS
The sampling plan was designed to collect and measure major chemical ingredients contained in the liquid A and B compounds and to determine if any SPF chemical components become airborne during and after application. SPF chemicals monitored include: MDI (2-ring and 3-ring) the A side component; TCPP, a flame retardant, total volatile organic hydrocarbons (TVOC – a scan of solvents and odoriferous compounds that may be present in indoor air per EPA method TO-15) and amine catalysts.

Air sampling for amine catalyst and TVOC-15 were collected on the second floor and the main level in both homes where other trade workers could potentially be exposed during SPF application. The study evaluated area samples for MDI, TCPP and TVOC during SPF application. Personal samples were also gathered for amines during SPF application. As noted earlier, previous data on MDI exposures indicate the sprayer and his helper generally exceed recommended exposure guidelines, therefore personal air monitoring for MDI was not conducted. The applicator and helper wore supplied air respirators and full personal protective equipment during all spray application activities. The personal protection equipment provided worker protection for eyes, respiratory and skin overspray exposure.

Laboratory Evaluations

In an effort to evaluate emissions under controlled conditions, air monitoring was completed at BASF's Research and Technical Training Center in Houston. Panels, approximately 3ft x 4ft were sprayed with Enertite (BASF Trade Name) open cell formulation and placed in a ventilated spray booth. The mechanical ventilation was not in operation throughout the experiments. Air monitoring was then 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 hours 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 NCO on the surface of the foam. With the exception of the amine catalyst, all were within acceptable limits.

Personal samples results for BDMAEE ranged from 0.07 to 0.36 ppm. The results do not represent full shift exposures; however they do indicate the potential for excessive exposure to unprotected workers during trimming operations for both fresh foam and foam sprayed five days prior to trimming.

Note: PPE in the shown pictures.

The samples were sprayed in the spray booth and this is also where the trimming was done and measurements shown as indicated by the red arrow pointing to the TO-15 air sample collection can

Sample collection equipment is indicated by **RED** arrows in the photograph.

Wall stud cavity mock ups were used, so continuous measurements could be taken while several panels were trimmed during several hours

Field Evaluations

In late March, sampling was initiated again in the Houston (Woodlands), Texas during application of open cell foam. The home was being insulated using open cell foam as a building envelope insulation and air barrier application. Ceiling heights of (12-15 feet) and most rooms were sized (20 x 30 feet) were much higher and larger than traditional homes. This was a very large 7,000+ square foot high end home. The walls had not been installed yet. So the sprayer and his helper used air purifying respirators. Area (for MDI and TCPP) samples (north and south ends) were obtained during spraying of SPF about 10 to 15 feet from the applicator on the second floor. Area samples (for MDI, amines, and TCPP) were obtained while trimming foam immediately after spraying. The next day, samples (for MDI and TCPP) were taken during trimming foam sprayed the previous day.

On the first floor, the second day the applicator applied foam on the walls (samples for MDI and TCPP were obtained about 10 – 15 feet from the sprayer).

Personal amine samples were collected the first day as sprayers and helpers sprayed attic areas in the northeast and southeast wings of the house. Air samples were also collected as helpers trimmed excess foam minutes after application. On the second day additional personal samples were collected as SPF was applied to the first floor. A personal sample was also collected as a helper trimmed foam on the second floor. The foam had been sprayed the previous day.

RESULTS AND DISCUSSIONS
First Home (attic and walls)
The first house in Fulshear, Texas

MDI was detected (1st floor stair well 0.072 ppb and 2nd floor top of stairwell 0.12 ppb) in area samples during spray polyurethane foam application on the second floor. TCPP, the flame retardant, level was not measured due to the loss of the samples in transit to the lab. TVOC samples were in the parts per trillion. Common solvent such as acetone, ethanol and isopropanol were noted with the high sample of 19 ppt. An area sample for MDI was also taken in the spray rig on top of the MDI drum; results were below detection. An area sample for MDI was taken during cutting and trimming of foam in the BASF facility. It was also below detection limits.

Personal samples collected on the sprayer and his helper during spraying and trimming on the second floor for BDMAEE catalyst ranged from 0.33 to 0.51 ppm. One area sample collected on the first floor resulted in a concentration of 0.021ppm. TMAEEA was non-detectable. As noted, applicators were in full personal protective equipment.

Second Home, first day (Attic, 1-3 walls and ceiling)
The second house in Woodland, Texas,

It was sprayed in late March of 2014, and was a very large home. Area samples were obtained during SPF application on the north and sound end of the home. There were two teams (a sprayer and his helper) applying foam. Area samples were taken for MDI and TCPP 10-15 feet from the sprayer. On the north end, MDI and TCPP were below detection limits. The south sprayer seemed to be much closer to the area sampler because MDI was measured at 1 ppb for the monomer and below detection for the 3 ring MDI. TCPP was 16 ppb (0.15 mg/m3). Area samples were obtained during trimming of the foam. One operator was next to the applicator during spraying trimming

within minutes after application. His exposure was 2 ppb for 2 ring MDI monomer and 0.55 ppb for 3 ring MDI and TCPP results were 12 ppb (0.11 mg/m3). The other helper, who trimmed 15 plus feet from the sprayer, did not have a detectable concentration of MDI and TCPP was 8 ppb (0.09 mg/m3). TVOC samples were in the parts per trillion. Common solvent such as acetone, ethanol and isopropanol were noted with the high sample of 26 ppt.

BDMAEE catalyst samples during application in the attic areas ranged from 0.52 to 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 confined attic area. All other concentrations were below detection limits.

Second Home; second day (trimming on 2nd floor; SPF on 1st floor)

MDI was non-detectable (one hour sample) during trimming of the foam. TCPP was extremely low also at 1.4 ppb (0.016 mg/m3). Air samples were taken about 10-15 feet from the SPF applicator on the first floor. MDI was 0.22 ppb for 2 ring MDI and ND for the 3 ring; TCPP was measured at 3.7 ppb (0.026 mg/m3). The TVOC's samples were in the parts per trillion. Common solvent such as acetone, ethanol and hexane were noted with the high sample of 29 ppt. BDMAEE catalyst concentrations for personal samples collected during spray application on the first floor were 0.76 ppm and 1.84 ppm. A personal sample collected during the trimming of foam sprayed 24 hours earlier resulted in a BDMAEE concentration of 0.073. An area sample collected in the central area of the second floor during the trim operation also resulted in a concentration of 0.073 ppm. TMAEEA concentrations were all below analytical detection limits.

RECOMMENDATIONS AND CONCLUSIONS

MDI concentrations were measurable if the trimmer moved within about 15 feet of the sprayer. TCPP results were also measured at this distance from the sprayer. Trimming of foam showed if the worker was not close to the SPF applicator, there was no detectable concentration of MDI. Concentrations of the emissive catalyst, BDMAEE exceeded the ACGIH TLV-TWA of 0.05 ppm during application and during the trimming of fresh foam and foam aged for 24 hours. The non-emissive catalyst, TMAEEA was only detected in two personal samples collected during the application in the confined attic space having no mechanical ventilation.

Based on the findings from this study, the authors believe that current PPE and work practice recommendations for spray foam applicators must be followed. It is also recommended that mechanical ventilation be used during and after application as recommended by the Environmental Protection Agency and the Center for the Polyurethanes Industry, to reduce emissions, particularly emissive catalyst concentrations below occupational exposure limits. The authors also recommend additional research is needed to provide data related to long term emissions from open cell formulations.

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