The Symposium on Developing Consensus Standards for Measuring Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation was held on April 30th and May 1, 2015. Sponsored by ASTM Committee D22 on Air Quality, the symposium was held in Anaheim, CA, in conjunction with the standards development meetings of the Committee. ASTM D22.05 is developing tools to assist decision-makers in answering fundamental questions such as: what is emitted from SPF, how long do the emissions persist, how does ventilation impact concentrations and potential exposures? How can we model these processes to address the multiplicity of products, applications, and environmental conditions that may impact exposure to emissions over the life cycle of the material? These are complex and interrelated questions that have challenged the indoor environments research community.

Objectives of Symposium

SPF insulation is manufactured on-site by mixing and spraying chemicals that react to form an effective insulating material. Emissions and potential exposures are poorly understood. Standardized methods are needed to assess the potential impacts of SPF insulation products on indoor air quality, establish re-entry times for trade workers or re-occupancy times for building occupants after product installation and to evaluate post-occupancy ventilation. The objective of the symposium was to provide a forum for SPF manufacturers, regulatory agencies, indoor air quality professionals, testing labs, air quality consultants, instrument vendors and other stakeholder to exchange information. After a series of presentations on the current status of measuring emissions from SPF insulation, participants discussed paths forward for research, method development and development of standards.

The chairs of the symposium cast a broad call for papers on the following topics designed to represent the scope of complex challenges industry and government must address regarding the application and use of SPF insulation products:

- Research and method development for measuring potential SPF emissions of semi-volatile and volatile organic compounds used in the formulation (e.g., isocyanates, blowing agents, amine catalysts and flame retardants) and from potential reaction or byproducts;
- Federal and other governmental agencies' regulatory approaches and supporting investigation, assessment and research needs;
- Modeling, scaling up from lab to large scale chambers or buildings;
- International perspective on regulation and testing of SPF insulation emissions;
- Industry perspective/needs and product stewardship activities;
- Field investigations or large-scale chamber/spray booth studies to evaluate emissions or ventilation rates; and
- Applying the knowledge from product emissions data/research to practice (e.g., stewardship commitment, green building practices, codes for residential ventilation and global leadership).

The collaboration and exchange of information during the symposium and their corresponding research papers will support the development of standards by ASTM D22.05 on Indoor Air for measuring emissions from SPF. New standards are being developed to estimate the emissions of volatile and semi-volatile organic compounds (e.g. blowing agents, catalysts, flame retardants, byproducts) with micro- and large-scale chambers. Analytical methods must be developed to measure emissions from the chambers. Specialized chambers must be evaluated for measuring isocyanate emissions such as methylene diphenyl diisocyanate (MDI) to avoid adhesion to the chamber's surfaces. The data generated from the new ASTM standards may be useful as input parameters in computer simulation modelling software to help manufacturers and distributors, researchers, and government agencies assess exposure potential and control mechanisms for SPF products. In the following paragraphs, the symposium co-chairs summarize key presentations, findings, and knowledge gaps and identify new standard development activities that have been introduced in ASTM Subcommittee D22.05 as outcomes of the symposium.

Selected Technical Papers with Excerpts from Abstracts

Several topics are covered in the selected technical papers (STP) resulting from the symposium including: field investigation studies, emissions measured in various-sized test chambers, emissions from misapplied material, computer simulation modelling of emissions and peak SPF temperatures in residential homes. According to the paper, *Investigating Sampling and Analytical Techniques to Understand Emission Characteristics from Spray Polyurethane Foam (SPF) Insulation and Data Needs,* reliable and validated emission test methods, and sampling and analytical protocols are needed to understand the variables that affect emissions and curing in order to develop and assess residential exposure scenarios.

The paper, *Evaluation of Micro-Scale Chambers for Measuring Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation*, evaluated the use of micro-scale chambers for measuring emissions and compared the results with conventional small-scale chambers. The authors also investigated the effect of the chamber's temperature and trimming samples prior to testing. Automating the micro-scale chamber testing was demonstrated in the paper, *Measurement of Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Using an Automated Micro-Scale Chamber System*. An automated dynamic headspace system was used for on-line, fully automated micro-scale chamber measurements of SPF to evaluate sampling time, volume and temperature. The paper, *Prioritizing Chemical Emissions from Closed-Cell Spray Polyurethane Foam: Utilizing Micro-Scale Chamber Emission Factors and Field Measurement Data,* compared emission factors from the micro-scale chambers in conjunction with a screening model to emissions measured in a residential home after application of SPF insulation.

The paper, *Flame Retardant Emissions from Spray Polyurethane Foam Insulation*, evaluated emissions of a commonly used flame retardant in SPF, tris (1-chloro-2-propyl) phosphate (TCPP), with micro-scale chambers and a full scale Net Zero Energy Residential Test Facility. The authors measured emissions in the test house without the installation of furniture, carpeting, or other household goods to determine if SPF in the facility was the primary source of the airborne concentrations of TCPP. This flame retardant was also investigated in the paper, *Glass Chamber Method for Screening of MDI and TCPP Emissions from Foam Joint Sealant*. The goal of this study was to develop a glass chamber method to examine the emissions of MDI and TCPP, which were measured during a 24-hour chamber test in a 3-L chamber.

There is a great need to determine when it is safe for trade workers to re-enter a work area where SPF was recently applied during retrofit or new construction. Emissions from three generic SPF formulations were evaluated in a room-size chamber at ventilation rates ranging from 1 to 10 air changes per hour in the paper *Estimating Re-Entry Times for Trade Workers Following Application of Three Generic Spray Polyurethane Foam Formulations*. Chemicals selected for evaluation were MDI, amine catalysts, blowing agent and flame retardant that were used in the formulations. The room-size chamber test was also utilized to evaluate commercial products in the paper *VOC Analysis of Commercially Available Spray Foam Products*. The study was aimed at determining if worker re-entry times could be reduced from the industry practice of 24-hours if specific rates of workplace ventilation were employed.

According to the paper, *Assessment and Remediation of Misapplied Spray Polyurethane Foam*, the misapplication of SPF may result in occupant complaints associated with persistent odor, and that SPF installed in homes may fail to cure and perform as anticipated when the contractor does not follow the distributors specified pre-application and installation procedures. This paper discusses strategies for resolving odor complaints and suggests an assessment and mitigation protocol for field use. Emissions from misapplied SPF are also investigated in *VOC Emissions from Spray Foam Insulation under Different Application Conditions*. The researchers compare chemical emissions from SPF insulation applied in four different ways in an attempt to simulate normal and abnormal applications. Application temperature and A to B-side ratios are investigated to determine the effect of emissions.

To begin to understand exposure to emissions from SPF and to identify and characterize uncertainty in assessing chemical exposures, a proof-of-concept multi-zone indoor model to estimate indoor air concentrations of chemicals is described in the paper *A Modelling Approach for Quantifying Exposures from Emissions of Spray Polyurethane Foam Insulation in Indoor Environments*. A recently developed model, i-SVOC, was applied to estimate TCPP emitted from SPF and its fate and transport in a modeled indoor environment in the paper *Predicting TCPP Emissions and Airborne Concentrations from Spray Polyurethane Foam Using US EPA i-SVOC software: Parameter Estimation and Result Interpretation.* In order to evaluate the temperature gradient of SPF in buildings, a one-dimensional transient dynamic numerical simulation was evaluated in the paper, *Computer Simulation of Peak Temperatures in Spray Polyurethane Foam Used in Residential Insulation Applications.*

What We Have Learned and What We Need to Learn

The research methods and results reported in this STP provide a reference point from which to evaluate progress towards development of reliable methods, data, and models that inform our understanding of the relationships between use of on-site applied spray polyurethane foam insulation materials and potential exposures to chemicals emitted from the insulation material. The following paragraphs attempt to capture some of the key observations and identify the research needs that will better inform development of tools and knowledge for managing emissions. The summary is intended to stimulate the reader to probe the manuscripts and to contribute to the discussion of progress and research needs.

Key observations and findings

What is emitted and how long do emissions persist? The chemicals identified in emissions include those used to produce the insulation material, i.e., MDI and polymeric MDI, additives to the polyols such as amine catalysts, blowing agents, flame retardants, as well as chemicals that may be related to production of the primary ingredients, reaction products, or minor constituents. Nie, Poppendieck, and

Won provide insight into the range of compounds identified in emissions reported in the course of methods development experiments reported herein. Most of the studies reported in the STP are of relatively short duration and focus on post application emissions over periods of 2 to 336 hours. Ecoff quantified emissions of blowing agents in the attic and occupied areas of a residence for 16 months. Poppendieck observed airborne concentrations of TCPP attributable to SPF that was applied in the crawl space of a research house two years prior to testing. Ecoff quantified MDI emissions during application in an attic, and did not detect post application emissions. Won observed that MDI emissions in a small glass chamber peaked within about 11 minutes and fell below quantification levels within about an hour. These observations are consistent with post application spray room results reported by Wood and with reports in the literature as summarized by Sleasman.

What factors impact emissions?

Sebroski, Poppendieck, Nie, and Won demonstrated that temperature strongly impacts emission rates for volatile and semivolatile emissions. Won demonstrated that environmental conditions (temperature and relative humidity) impact the amount and duration of post application MDI emissions. Poppendieck demonstrated that TCPP emission rates are impacted by external mass transfer factors (gas phase concentration in the boundary layer, air speed and turbulence) whereas more volatile emissions may be controlled by diffusion rates within the material. Duffy and others demonstrated that amine catalyst emissions vary across product types and formulations, and Won demonstrated that application outside of recommended conditions results in increased emissions. Sebroski demonstrated that trimming the skin affects emissions from open cell foam and that aldehyde emissions correlate better with mass than sample surface area.

How mature are the test methods?

Sleasman provides an overview of the sampling and analysis methods that may be employed to characterize SPF emissions. Although there are many methods that have been validated for specific compounds or classes of compounds for specific uses, e.g., occupational exposure assessment, the adaptability and reliability of these methods for characterization of SPF insulation emissions during and following application have not been well-demonstrated. Two of the approximately eight to ten isocyanate derivatization methods were employed in studies that determined MDI emissions (see Won, Wood, and Ecoff). Won demonstrated an emissions characterization approach that generated model inputs for post application MDI and TCPP emissions, however this approach has not been demonstrated for application phase MDI emissions. VOC collection on single or multi-sorbent traps followed by thermal desorption with GC/MS quantification was employed by several researchers. The methodology provides adequate detection limits for many SPF VOC emissions where sample sizes are appropriate to the concentrations. However, the TD-GC/MS approach does not provide adequate quantification levels for some of the amine catalysts, and sampling media and sample volumes may need to be carefully selected.

Micro chambers, small glass and stainless steel chambers, room-sized spray booth – spray room chambers, and residential structures were employed in emissions tests. Uncertainty regarding interactions between reactive and semivolatile emissions, MDI and TCPP, with chamber surfaces provide challenges to data interpretation in all test systems. Attempts to compare emissions across scales of test systems were characterized by uncertainty due to many factors, including sorption of semivolatile compounds by surfaces, uncertainty of concentration measurements and mixing in full-scale chambers, lack of data to characterize interzonal flows and air exchange rates in buildings.

Interpretation of results

Two general approaches were employed to interpret test results. Duffy and Woods compared concentrations of specific emissions in a defined test environment to occupational exposure values. Won employed the more typical indoor environment approach where chamber emissions data are used to construct a source model that is used in a room or building simulation model to predict potential indoor exposure.

Model system development

Bevington presented a new modeling approach based upon two models developed by EPA, iSVOC and IAQx, to quantify exposures due to application of SPF. Based upon results of a sensitivity analysis, the authors concluded that experimental data is needed to calibrate the model, particularly in the first 24 hours following application, characterize longer term mass transfer, and characterize flow paths and air exchange rates. Tian used literature-based parameters in the indoor simulation system, iSVOC, to calculate TCPP concentrations in a model room due to application of SPF insulation. Tian compared model predictions with predictions based upon micro chamber results and concluded that the micro chamber results were close to the upper end of the iSVOC predictions. Sensitivity analysis suggested that the material – air partition coefficent was the most important parameter for explaining differences between Tian's iSVOC predictions and micro chamber based predictions.

Summary of Research Needs

Research is needed to

- Better characterize emission factors during the first 24 hours following application of SPF to provide data to calibrate models and to improve ventilation guidance for a range of scenarios.
- Characterize interactions of flame retardants with surfaces, characterize interzonal flows and air exchange rates in SPF insulated buildings.
- Improve sampling and analysis of reactive amines compounds that behave poorly in thermal desorption systems.
- Improve parameter estimation techniques and conduct experiments to validate parameters and modeling results.
- Develop a better understanding of how micro chamber derived emission factors can be used to predict concentrations and potential exposures in buildings.
- Develop a better understanding of how off-ratio or application or application outside of specified conditions impacts emissions.

- Better understand how automated and integrated chamber/sampling and analysis systems might improve sensitivity and reliability of test methods.
- Develop an improved understanding of the impact of environmental factors on MDI emissions, reactions and products to improve confidence in modeling potential exposures.
- Better understand how well thermal energy models predict temperatures in applied foam and in attics and crawl spaces.
- Develop full-scale test methods that provide emission factor inputs to models.
- Improve quality assurance procedures to ensure characterization of uncertainty of test systems and test protocols.

ASTM Activities Related to Symposium

Knowledge learned from the symposium has been applied towards the development of standards by ASTM Subcommittee D22.05 on Indoor Air. The subcommittee has continued to develop work item, WK40293, *Test Method for Estimating Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Using Micro-Scale Environmental Test Chambers*. Several of the papers included micro-scale chamber evaluations that examined method parameters (e.g. temperature, area specific flow rate, etc.) and compared the emissions data to small-scale chambers or residential buildings. Isocyanate emissions will require the use of specialized chambers to avoid significant bias from adhesion to the chamber walls; therefore, work item WK51589 "*Test Method for Estimating Emissions of Methylene diphenyl diisocyanate (MDI) from Spray Polyurethane Foam (SPF) Insulation using Emission Cells or Micro-Scale Environmental Test Chambers" was created.*

Two of the symposium papers discussed the use of a large-scale spray room at various ventilation rates as an approach to evaluate potential impacts on the use of protective equipment and controls and re-entry times for trade workers without the use of protective equipment after application of the material. This approach may be useful to provide a better understanding of the emissions that occur during and post application under controlled conditions. As a result, a new work item has been created, WK51588, *Test Method for Measuring Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Samples in a Large-Scale Spray Room*. The emissions data from the large-scale spray room may also be used in conjunction with computer simulation models as a means of calibration or verification. Two of the papers from the symposium discussed estimating emissions in buildings using such models. The input parameters and the use of models to estimate SPF emissions are being addressed in a new work item, WK52052, *Practice for Application of Indoor Emission and Fate Modeling for Spray Polyurethane Foam (SPF) Insulation.* In the future, additional standards may be necessary to measure key input parameters for the simulation models.