The Development of Testing Methods for Characterizing Emissions ~~&~~and Sources of Exposures from Polyurethane Products

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Background

The relationship between on~~-~~site manufacture of spray polyurethane foam insulation (SPFI) and potential exposures is not well understood. ~~There are c~~Currently, no comprehensive standard test methods exist ~~to~~for characteriz~~e~~ing and quantifying product emissions. Exposures to diisocyanate compounds, amine catalysts, flame retardants, and blowing agents, as well as aldehydes and other volatile or semivolatile organic compounds that may be emitted as the product cures and afterward, are of interest. ~~-~~EPA, along with federal and other partners, is investigating protocols for characterizing chemical emission rates from SPF products. This supports the ASTM Committee D 22.05 SPFI emissions test method development task, a critical component of a broader strategy to develop chamber emissions test methods specific to SPF~~ insulation~~I, and ~~to develop~~ assessment tools and models to relate product emissions to potential exposures.

In 2009, representatives from EPA, other federal agencies, and the SPF industry met to discuss concern~~s~~ for worker and consumer exposure~~s~~ to these products. In 2010, EPA and other federal agencies convened to discuss exposure assessment research needs and priorities. In 2011, using its authority under the Toxic Substances Control Act (TSCA), EPA released chemical action plans requesting information and studies regarding potential exposures during the use of SPF products~~ using its authority under the Toxic Substances Control Act (TSCA)~~.

What is needed?

- Test ~~M~~methods and ~~P~~protocols are needed to generate reliable data to fill critical knowledge gaps:
  - What compounds are emitted from SPFI and for how long?
  - How do environmental variables during application and curing, such as temperature, relative humidity, substrate temperature, and moisture level, impact emissions?
  - How do application variables such as A and B side formulations and ratios, lift number and height, applicator technique, and equipment affect emissions characteristics and cure times?
  - How do purity of feedstocks, shipping, handling, and storage conditions impact emissions?
- Strategies are needed to integrate emissions data within the SPFI production pathway to reduce or eliminate exposures of concern.
- Exposure d~~D~~ata and m~~M~~odels are needed to support risk management considerations and refine protective workplace and residential consumer practices.

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- What role do application-phase and post-application-phase emissions play in exposure, and how can they best be managed?
- What routes of exposure (e.g., dermal, inhalation, ingestion) are of concern ~~(dermal, inhalation, ingestion)~~?
- Are there other relevant life-cycle issues?
  - Exposure during maintenance, remodeling, or deconstructing at end-of-life?
  - Exposure~~s~~ related to product decomposition over lifetime of use?

Approach

Wirts et. al., 2002, 2003 demonstrated a method to characterize Methylene diphenyl diisocyanate (MDI) emitted from polyurethane (PU) adhesives in small test chambers (2.2 L). Efforts to scale from small to larger test systems were not successful, in part due to sorption of MDI by chamber walls. Also, Wirts' research did not attempt to address the full range of emissions associated with PU adhesives. Current research into develop~~ment~~ing and demonstrat~~ion of~~ing ~~a~~ comprehensive emissions test methods specific to SPFI (Sebroski, CPI/Bayer Material Sciences) has identified many technical challenges. Preliminary results indicate that factors such as chamber surface material and relative humidity of chamber supply gas may be expected to impact recovery of isocyanates, amines, and flame retardants. The results also suggest that as presently configured, commercially available micro chambers are not suitable for characterization of MDI emissions from SPFI. However, preliminary results of this work suggest that ~~there are~~ many volatile organic compound (VOC) emissions ~~that~~ can likely be characterized using conventional emissions test chambers typically used for product emissions characterization. The work of Wirts and Sebroski suggests the need for:

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(1) Development of a test system (or systems) using the approach of Wirts, specific to SPFI, to characterize isocyanate , amine, and flame-retardant emissions.
(2) Development of knowledge and test protocols to relate emissions determined in very small systems to full-scale environments.
(3) Development and demonstration of test protocols specific to SPFI VOC emissions using conventional emissions test chambers.

Pending developments in industry efforts by the International Isocyanates Institute (III) to adapt the micro chambers for characterization of isocyanate emissions, EPA plans to:

- Conduct pilot studies in test chamber systems:
  - Investigate "near source" versus "bulk air" concentrations of reactive emissions in small-scale and full-scale chambers to provide insight into:
    - Time-course of primary emissions of isocyanates and amines
    - Impact of sorption on chamber surfaces
    - Significance of heterogeneous reactions in chamber air on emissions characterization
    - Range of emissions that can be characterized in small test chambers (e.g., low molecular weight aldehydes, nonpolar volatile organics)
- Evaluate pilot study results and select approaches that provide emissions data for key classes of emissions, and investigate:

    - Reliability and repeatability of test methods
    - Qualitative and quantitative emissions over time
    - Impact of key variables on emissions
- Where appropriate, EPA will partner with other stakeholders to overcome technical challenges.

Issues and Challenges

Source characterization can be a powerful tool for assessing relationships between chemical exposures and the chemicals, materials, and processes associated with production and use of products. ~~It~~Source characterization is most effective when emissions can be related to the chemical makeup of the product. SPFI presents challenges because of the sheer number of variables that may impact emissions, and because methods for characterizing the source composition and emissions are not ~~as~~ yet well developed.

Key issues include:

- There are many basic formulation types and manufacturers for different kinds of SPFI products.
- There are many poorly controlled and/or inadequately characterized variables including:
    - Time and conditions between manufacture, transport, storage, and use.
    - Training and experience of the crew performing the application.
    - Equipment and crew performance during application.
- Comparability of isocyanate measurements: There are many approaches (e.g., quantify individual isocyanate compounds or total reactive isocyanates [DAN method]) and many sampling and analysis techniques with varying specificity and sensitivity. It will be important to establish comparability between isocyanate and amine sampling and analysis methodologies.

Key challenges include:

- Multiple sampling and analysis strategies are needed for characterizing the spectrum of emissions.
- Many of the potential emissions are very challenging to identify and quantify, and standards are not yet available for some.
- Reactive and semivolatile compounds interact with test chamber surfaces, sample transfer lines, and particles in the air.
- Sampling times and method detection limits must permit quantification in timescales that capture important emissions processes.

Conclusion

A sustained and coordinated effort will be required to solve the technical challenges that preclude development of a comprehensive emissions test method for SPFI products and demonstrate ~~and~~ how product emissions relate to potential exposure. However, once demonstrated, these methods will provide key tools for risk management and product stewardship.

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References

1. Wirts, M. and T. Salthammer. 2002. *Environ. Sci. Technol*. 36, 1827-1832.
2. Wirts, M., D. Grunwald, D. Schulze, E. Uhde, and T. Salthammer. 2003. *Atmospheric Environment*. 37, 5467-5475.

3. Sebroski, John, R. 2012. Research Report on Developing Methods to Measure Potential Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation, presented at Polyurethanes 2012 Technical Conference, Atlanta, GA. Sept. 24.