
# Amine Emission Management in Spray Foam – Moving the Industry Forward

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***Air Products and Chemicals, Inc.***

# ANTITRUST POLICY STATEMENT FOR SPRAY POLYURETHANE FOAM ALLIANCE MEETINGS

- It is and shall remain the policy of the Spray Polyurethane Foam Alliance ("SPFA"), and it is the continuing responsibility of every SPFA member company, SPFA meeting or event participant, as well as SPFA staff and leadership to comply in all respects with federal and state antitrust laws. No activity or discussion at any SPFA meeting or other function may be engaged in for the purpose of bringing about any understanding or agreement among members to (1) raise, lower or stabilize prices; (2) regulate production; (3) allocate markets; (4) encourage boycotts; (5) foster unfair or deceptive trade practices; (6) assist in monopolization; or (7) in any way violate or give the appearance of violating federal or state antitrust laws.

- Any concerns or questions regarding the meaning or applicability of this policy, as well as any concerns regarding activities or discussions at SPFA meetings should be promptly brought to the attention of SPFA's Executive Director and/or its legal counsel.

# Topics

- Spray foam emissions
- Airborne emissions testing
- Amine emissions
  - EHS aspects
- Comparative Emissions studies
  - Emissive vs Reactive amine catalysts
- Conclusions

# Polyurethane Additives

- Global leading additives supplier to the polyurethanes industry
- Strong brand recognition globally
  - DABCO® and Polycat®
  - Product line consists of **amine catalysts, metal catalysts,** and **silicone surfactants**
- Focused on new product innovation to help spray foam industry grow, including:
  - **Emissions management** and other environmental drivers
  - HFO blowing agent enabling technology
  - Productivity (expanding seasonal application window, cost-in-use, etc)

# Spray Polyurethane Foam Emissions

**Chemical Emission reduction has become a central issue in the PU Industry!**

Low emission products are becoming a ***requirement of sale*** in many markets

## During Spray/Application

## From Cured Foam

Glaucopsia (Blue Haze)
Fishy odor
Respiratory irritants

Applicator
Contractors
Occupants

# Emission Management Timeline

Air Product's focused on delivering solutions to address PU foam emissions

- **1990s** :
  - VOC reduction emerges in European Auto Market to improve passenger environment
  - Introduction of new reactive amine catalysts for Flex molded foam
    - DABCO NE1060, DABCO NE200, Polycat 15
- **2000s** :
  - Odor reduction / Elimination becomes focal point of Comfort and bedding sector
  - DABCO NE500, DABCO NE300

- **Mid / Late 2000s**
  - Rigid spray foam industry growth
  - Emission management begins to gain broader attention in SPF
    - Odor, Applicator exposure, re-entry/ re-occupancy
  - New amine catalysts for reduced emission SPF developed : Polycat 31

- **2011-2015**
  - SPF emission testing/measurement methods developed for open and closed cell SPF
  - New low emission catalyst technologies developed to meet emerging requirements : Polycat 140, Polycat 141 & Polycat 142,

# Sources of Emissions in Open Cell SPF

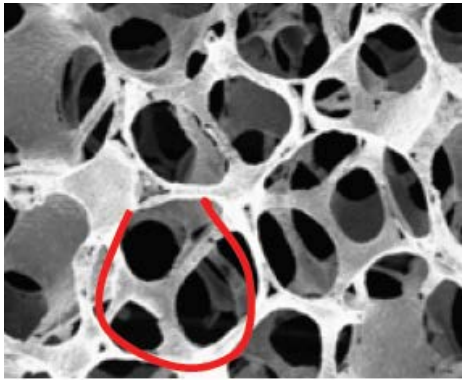
***Open Cell SPF Generic Formulation***

| *Polyol Resin (B-side)* | |
|---|---|
| **Component** | **approx. wt%** |
| **Polyol** | **35** |
| **Flame Retardant** | **25** |
| **Emulsifier** | **12** |
| **Amine Catalyst** | **8** |
| **Surfactant** | **1.0** |
| **Water** | **20** |
| + | |
| *Isocyanate (A-side)* | |
| **Polymeric MDI** **M**ethylene **D**iphenyl **D**iisocyanate | **100** |

Potential "fugitive" components within SPF formulation

- Fugitive, non-reactive components can become sources of airborne emissions during application and curing of the Spray foam within the jobsite

# Airborne Release of Fugitive Components



**Driving forces for Airborne Emissions:**

- Aerosolization of heated components during spray application
- Offgassing of rising foam during cure
  - Exotherm : release of volatile fugitive components
  - Blowing agent and $CO_2$ release during foam reaction

# AP Airborne Emission Testing

Proposed ASTM Method: WK46527

SPF application in ventilated spray room

- Temp, humidity and ventilation control

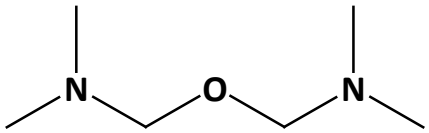
Sampling and capture of airborne emissions after spray application

Identification and quantification of airborne emissions through TD-GCMS

- Emission testing protocols relevant for all chemical emissions
- Focus of presentation is comparing amine emissions from open cell foam using different amine catalysts (both reactive and non-reactive)

# Amine Catalysts

- Typically tertiary amines
- Combinations of catalysts used in SPF
- Facilitate foaming reaction and gelation reaction
- Many different amine catalyst chemistries
  - Reactive vs emissive




BDMAEE

*Industry Standard*

*Non-reactive amine catalyst*


*Reactive amine catalyst*

- All Amines are derivatives of ammonia, and therefore have similar health effects and toxicology

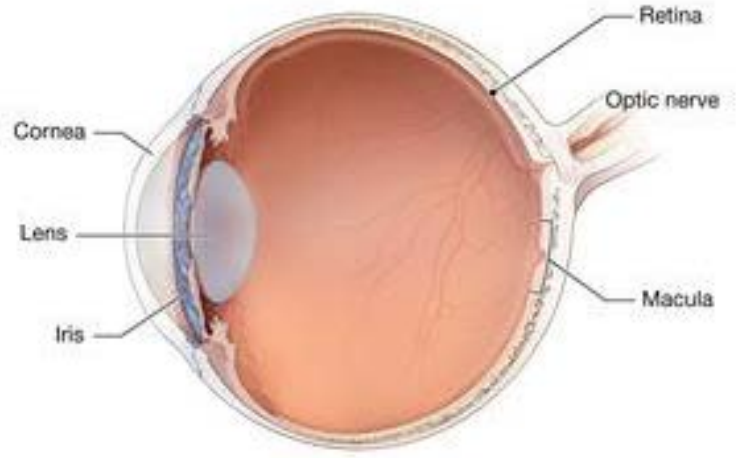
# Tertiary Amines -Heath Hazards

- Tertiary amines emitted from spray foam during and shortly after application may harm unprotected workers
- Potential health effects include:
  - irritation of the eyes
  - skin irritation and rash
  - Respiratory tract irritation
- Very low catalyst concentrations may irritate the cornea of the eye causing halovision

American Chemistry Council (ACC). (2011) **Polyurethane Amine Catalysts: Safe Handling Guidelines. American Chemistry Council**. Center for the Polyurethanes Industry. Issue AX173.

# Halovision / Blue Haze

- Medical term for halovision (“Blue Haze”) is Glaucopsia.
- Glaucopsia is caused by the swelling of the outer layer of the cornea resulting in temporary visual disturbances
- Glaucopsia may be experienced by workers exposed to tertiary amines.
- The effect is temporary, as vision returns to normal within 2 to 4 hours
- Glaucopsia thresholds may be higher than published exposure limits

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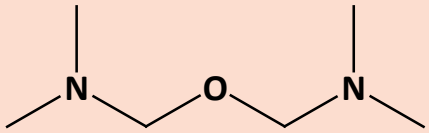
# Glaucopsia (Blue Haze) Thresholds

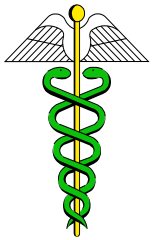
**Blue Haze threshold Levels are often significantly higher than airborne Occupational Exposure Limits!**

| Substances | Glaucopsia (ppm) | Occupational Exposure Limit (ppm) |
|---|---|---|
| Bis(dimethylaminoethyl)ether<br>BDMAEE<br>  <br> | 4.6 | 0.05 (8hr –TWA)<br>0.15 (15 min – TWA)<br><br>*TWA : Time-weighted average* |

Ballantyne, B., 2004, "Glaucopsia: An Occupational Ophthalmic Hazard," *Toxicol. Rev.* 23 (2).

# Aggravate pre-existing Medical Conditions

- Medical conditions aggravated by exposure:
  - Asthma
  - Skin disorders and allergies
  - Chronic respiratory disease
  - Eye disease

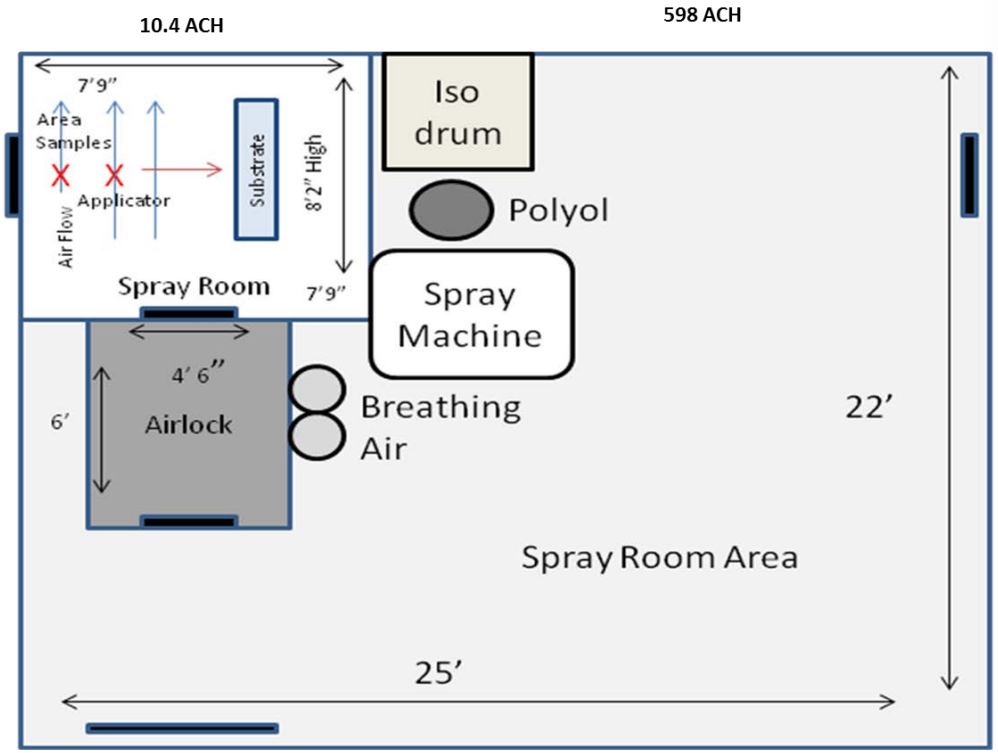


# Comparative Study: Evaluation of Airborne Amine Emissions after SPF Application

- Two open cell (0.5lb) formulations were evaluated:
  - A control formulation containing the emissive catalyst, Bis(dimethylaminoethyl)ether (BDMAEE)
  - A comparative formulation based on reactive amine catalysts: Polycat® 140, Polycat® 31, Polycat® 142
- The SPF formulations were sprayed separately under controlled laboratory conditions in a ventilated spray room

# Ventilated Spray Room

- Approximately 7ft x 7ft x 8ft
- Adjustable air flow rates range between 1 ACH and 13 ACH
- Temperature and humidity controlled




Courtesy of Air Products and Chemicals, Inc.

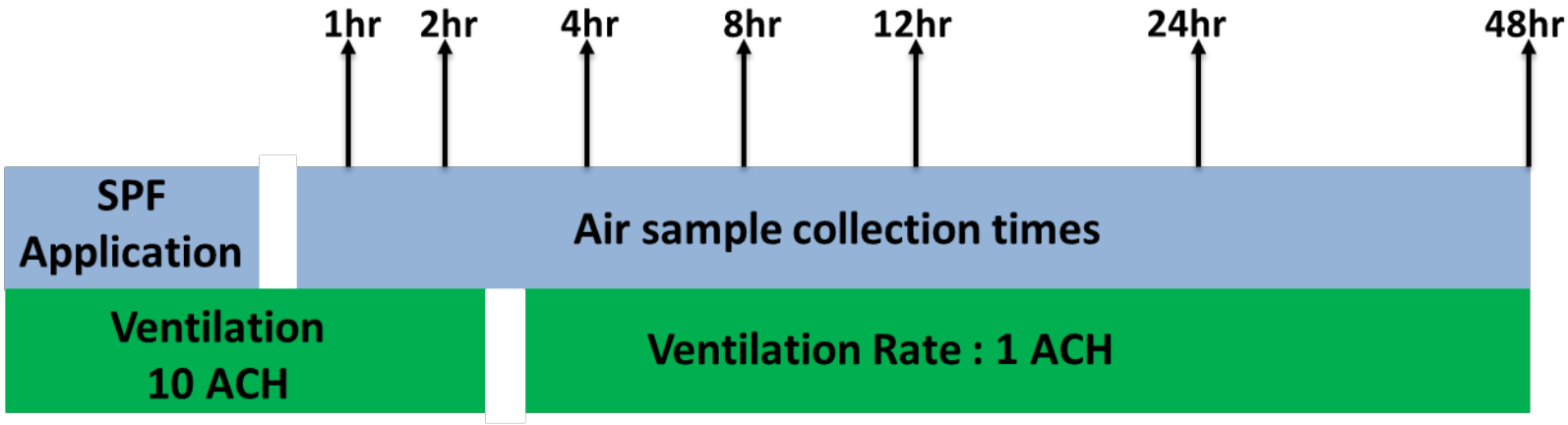
# Test Conditions

- Air sampling conducted 1 hour after SPF application.
- Two air exchange rates were selected for the study.
- Worst case conditions field conditions such as in an attic or crawl space after spray.
- 10 ACH selected for the first segment of the study representing minimal mechanical ventilation and open windows.
- 1 ACH rate considered to be passive ventilation / no mechanical ventilation.

# Work Process

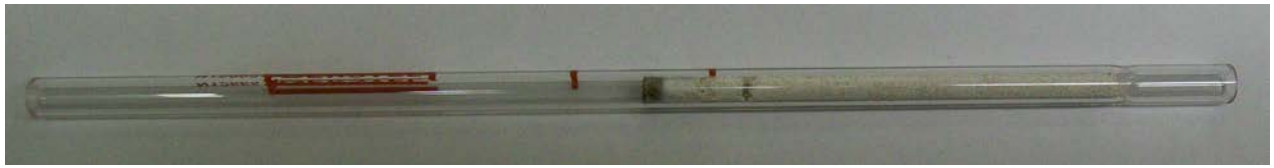
- Twelve (12) inserts sprayed as ventilation operated at 10 ACH.
- No air sampling conducted during SPF application.
- Sprayed inserts remained in the ventilated room.
- Ventilation operated at 10 ACH for 2 hours post application then reduced to 1 ACH for the remainder of the study

# Air Sampling Timeline

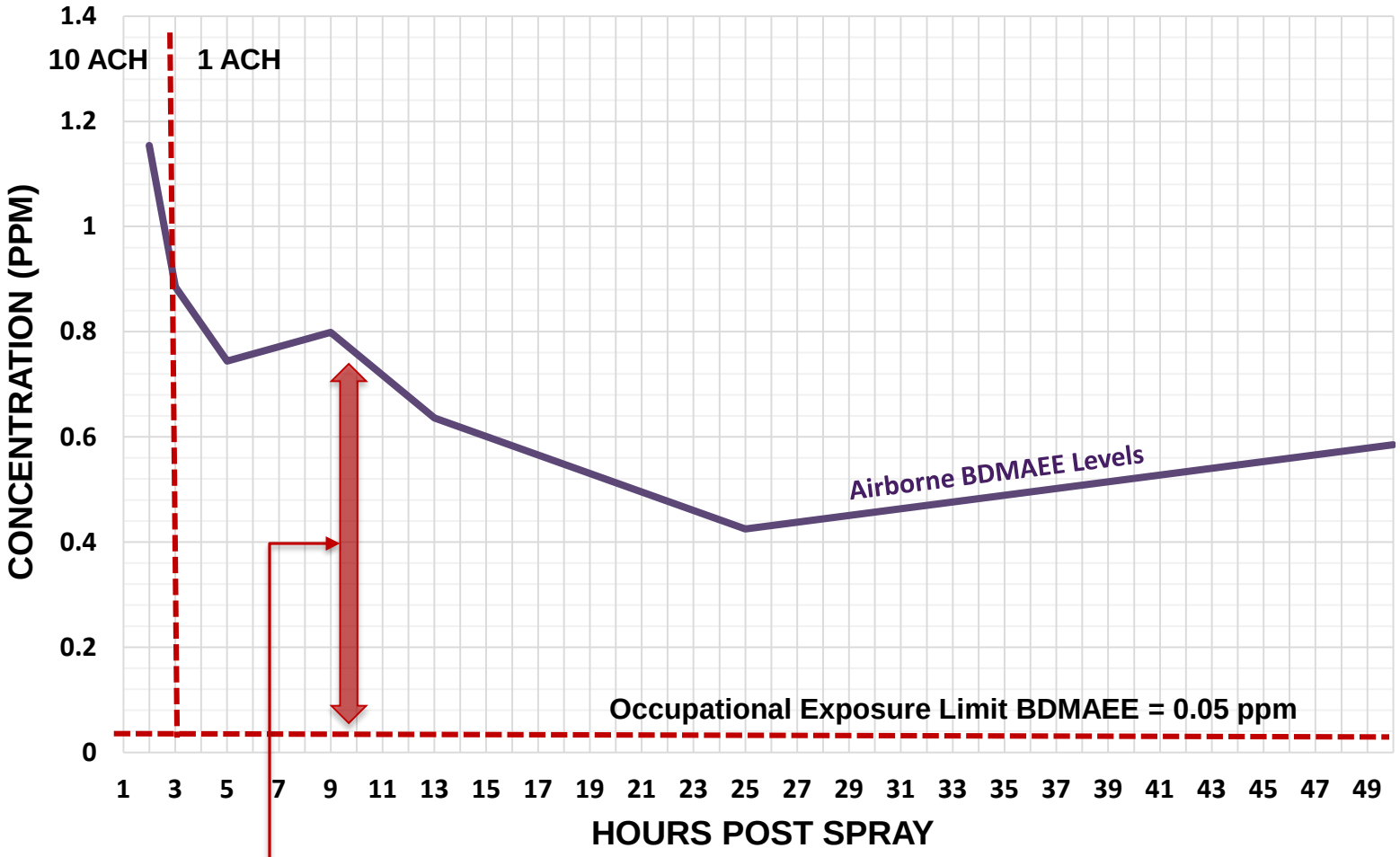


# Air Sampling Methodology

- Airborne chemical emissions collected on Tenax Sorbent Tubes
- Emissions thermally extracted from Sorbent Tubes analyzed and quantified by Thermal Desorption Gas Chromatography and Mass Spectrometry.
- Proposed ASTM Method: WK40292



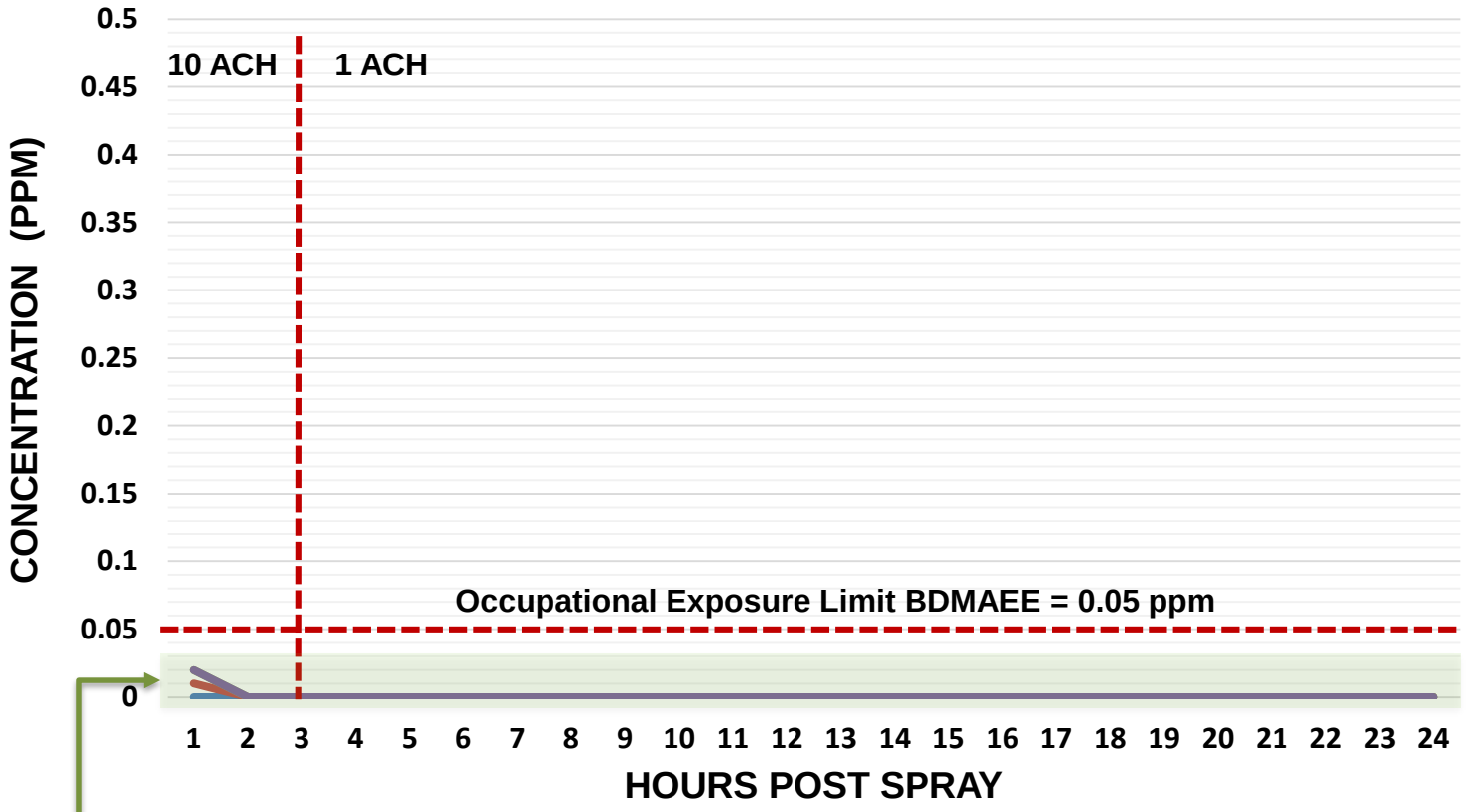
# Amine Catalyst Emissions:
## Control Formulation Containing
## Non-reactive amine catalyst (BDMAEE)




**BDMAEE Airborne Amine emission levels above OEL limits throughout the 48hr study**

# Amine Catalyst Emissions

## Reactive catalyst formulation containing:
## Polycat 31+ Polycat 140+ Polycat 142




**Reactive amine catalyst emissions well below exposure limit or non-detectable throughout air sampling study**

# Discussion/Conclusions

- Capabilities for testing, measuring and quantifying airborne emissions from SPF in controlled environments have been established by Air Products
  - Proposed ASTM method WK4267
- Non-reactive amine catalysts such as BDMAEE can be detected as amine emissions above published exposure limits during and after SPF application (through 48 hours)
- Use of reactive amine catalysts can significantly reduce amine emissions during and after SPF application to below published exposure limits.
- Airborne chemical emissions can be a significant factor impacting overall air quality, and affecting worker re-entry times and building occupant re-occupancy times.
- Additional studies are recommended to characterize emissive catalyst emissions for a period greater than 48 hours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