Industrial Hygiene Aspects of Polyamines and Polyetheramines (B Component)

R. Everett Langford, Ph.D., CIH, CSP, FAIC
Global EHS Group
Huntsman Corporation
What are Polyamines?

- Polyamines are organic compounds containing two or more -NH₂ groups (primary amines) or -NH- groups (secondary amines).
- The general formula for primary amines:
  \[ \text{H}_2\text{N} - \text{R} - \text{NH}_2 \]
- The general formula for secondary amines:
  \[ \text{R} - \text{HN} - \text{R}' - \text{NH} - \text{R}'' \]
  where R, R', R'' may be aromatic or aliphatic.
What are Polyetheramines?

- Polyetheramines are organic compounds containing amine (-NH₂ or -NH-) groups with internal ether (R – O – R’) linkages.
- The general formula (primary amine) is \( \text{H}_2\text{N} – \text{R} – \text{O} – \text{R’} – \text{NH}_2 \)
  where R and R’ may be aromatic or aliphatic.
JEFFAMINE® Polyetheramines

• JEFFAMINE® D-400 and D-2000:

\[
H_2N - CH - CH_2 - [ - O - CH_2 - CH - ]_x - NH_2
\]

\[
\begin{array}{c}
| \\
CH_3 \\
| \\
CH_3
\end{array}
\]

where \( X = 5 - 6 \) for JEFFAMINE D-400 and 

32 - 34 for JEFFAMINE D-2000
JEFFAMINE® Polyetheramines

- JEFFAMINE® T-5000:

\[
\begin{align*}
\text{CH}_2 & - \left[ - \text{O} - \text{CH}_2 - \text{CH} - (- \text{CH}_3) - \right]_x - \text{NH}_2 \\
\text{HC} & - \left[ - \text{O} - \text{CH}_2 - \text{CH} - (- \text{CH}_3) - \right]_y - \text{NH}_2 \\
\text{CH}_2 & - \left[ - \text{O} - \text{CH}_2 - \text{CH} - (- \text{CH}_3) - \right]_z - \text{NH}_2 \\
\end{align*}
\]

where \( x + y + z = \text{ca. } 81 \)
Health Hazards of Polyamines and Polyetheramines

- Polyamine and polyetheramines can cause eye irritation and chemical burns of the eye.
- They can cause severe irritation of the skin with resulting chemical burns.
- Inhalation can cause irritation, nasal discharge, coughing, and discomfort in nose and throat.
Health Hazards of Polyamines and Polyetheramines

- In case of accidental ingestion, polyamines and polyetheramines can cause burning of the mouth, throat, and stomach with abdominal and chest pain, nausea, vomiting, diarrhea, thirst, weakness, and collapse.
Health Hazards of Polyamines and Polyetheramines

- Swallowing can cause severe ulceration, inflammation, and possible perforation of the upper alimentary tract, with hemorrhage and fluid loss.
- Repeated skin contact can cause persistent irritation or dermatitis.
Health Hazards of Polyamines and Polyetheramines

- Exposure to polyamines and polyetheramines can cause temporary, reversible hazy or blurred vision.
- Vapors or mists, especially from heating polyamines and polyetheramines, can cause nose and throat irritation or difficulty breathing.
What are the Routes of Exposure?

• The principal occupational route is via the skin (dermal) from potential exposures during manufacture, formulation, and use.

• Accidental routes include swallowing (ingestion), and inhalation.
What PPE Should Be Worn?

- Wear protective clothing such as coveralls or lab coats, gloves resistant to chemicals and petroleum distillates, and chemical type goggles with face shield when working with polyamines and polyetheramines.
What PPE Should Be Worn?

- At high exposure levels, wear a full facepiece respirator with organic vapor cartridge (with change-out schedule) and dust/mist prefilter when working with polyamines and polyetheramines.

- When used with isocyanates in polyurea applications, use a supplied air line respirator in positive pressure mode with full faceshield.
What PPE Should Be Worn?

- Coveralls
- Boots
- Gloves
- Airline Respirator
- Full faceshield
Is There a Medical Test to Show If I’ve Been Exposed to Polyamines?

• There are no direct or specific tests for exposure to polyamines and polyetheramines (such as urine or blood), but non-specific medical tests may be used in cases of suspected over-exposure.
Are There Exposure Standards for JEFFAMINE® Polyamines Used in Polyurea Applications?

• OSHA has not established a PEL.
• NIOSH has not recommended an REL.
• NIOSH has not recommended an IDLH.
• The EPA has not established an RQ.
• The ACGIH has not established a TLV.
What Else Should I Know about Polyamines and Polyetheramines?

- Polyamines and polyetheramines have extremely low volatility, so air concentrations are generally very low.

- At end of workshift, wash any areas of your body that may have contacted polyamines or polyetheramines, whether or not known skin contact has occurred.
What Else Should I Know about Polyamines and Polyetheramines?

• Wash hands carefully before eating or smoking.
• Most polyamines and polyetheramines have faint ammonia-like odors.
• Do not allow exposure in poorly ventilated areas or confined spaces, especially at elevated temperatures.
What Else Should I Know about Polyamines and Polyetheramines?

- Most polyamines and polyetheramines are not thought to be carcinogens, mutagens, or other long-term health risks.
- JEFFAMINE® polyetheramines used in polyurea applications are not believed to be sensitizers.
Additional Information

• The greater risks are during application rather than potential exposures to the chemicals involved.
• These risks include the high pressure spray, high pressure spray equipment, aerosolization of unreacted components, and overspray.
Additional Information

- ETHACURE® 100 (diethyltoluenediamine, DETDA) and ETHACURE® 300 (dimethylthiotoluenediamine, DMTDA) made by Albemarle Corporation, and UNILINK® 4200 (N,N’-dialkylaminodiphenylmethane) made by UOP LLC, are common aromatic chain extenders.
Additional Information

- CLEARLINK® 1000 (a mixture of aliphatic diamines) made by UOP LLC, and isophoronediamine (IPDA) from a number of manufacturers are common aliphatic chain extenders.
Additional Information

- Aromatic chain extenders are used to modify processing time and ultimate properties of the coating.
- Aliphatic chain extenders are used where light stability is important, but may be expensive.
- For industrial hygiene information, review the manufacturer’s MSDS or contact your distributor.
Additional Information

• In general, for polyurea applications, the isocyanate (A Component) is more hazardous than the polyamine or polyetheramine (B Component).

• The isocyanates are potential sensitizers as well as occupational asthmagens.
Additional Information

- For the A Components: methylene bisphenyl isocyanate (MDI) has an 8-hour Time-Weighed Average (TWA) Threshold Limit Value (TLV) of 0.005 parts per million (ppm).

- Toluene-2,4-diisocyanate and toluene-2,6-diisocyanate (TDI) have a TWA-TLV of 0.005 ppm with a Short-Term Exposure Limit (STEL) of 0.02 ppm.
Additional Information

• For the A Components: OSHA has set the Permissible Exposure Limit (PEL) for methylene bisphenyl isocyanate (MDI) at 0.02 parts per million (ppm), and for toluene-2,4-diisocyanate (TDI) a PEL at 0.02 ppm.
Summary

- Polyamines are usually a colorless to light yellow liquid.
- Polyamines generally have an faint ammonia-like odor, and have extremely low volatility.
Summary

• Wear protective clothing, gloves, and eye protection.
• Wear a respirator at high exposure levels, especially if aerosolization is possible.
• For polyurea spray applications, use a supplied-air respirator with full faceshield.
Summary

• Polyamines can cause serious skin and eye burns.
• Wash at end of shift, and before eating or smoking.
• Read and understand the MSDS.
Summary

• For polyurea spray applications, there are additional risks from the high pressure spray, the spray equipment (including hoses), overspray, and the isocyanate component.

• The Huntsman EHS Group is available to assist you with questions or concerns.
Questions or Comments?
Everett Langford
Manager of Industrial Hygiene
Global EHS Group
Huntsman Corporation
3040 Post Oak Boulevard
Houston, TX 77056-6500
1-713-235-6623
Everett_Langford@huntsman.com