

Polyurethanes and Thermal Degradation Guidance

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Purpose

Polyurethane is a material that can be found in many products that we use in our daily lives. Heating of polyurethanes or polyurethane containing-articles may be necessary during processing and/or product applications. Under normal processing conditions, this may not result in thermal decomposition. However, when heated above normal processing temperatures such as during hot work activities, polyurethanes and other polymers may break down and produce airborne particulates, gases, and/or vapors (i.e., smoke). This breakdown is often referred to as thermal degradation.

Thermal degradation can take place when the material is burning (i.e., flaming) or when it is exposed to elevated temperatures without burning (i.e., non-flaming). All combustible materials, whether natural or synthetic, produce smoke when burned and smoke does contain toxic chemicals. This document highlights potentially hazardous chemicals that may be of concern when polyurethanes undergo thermal degradation, and it provides guidance for worker safety and health as it relates to this topic.

Hot work can represent a significant fire risk if not done properly. The conduction of heat from hot work can easily ignite adjacent materials. Hot work may also lead to non-flaming thermal degradation. The operation of hot work may include, but is not limited to the following:

- Welding
- Brazing
- Heating of polyurethane foam while working on pipes
- Heating MDI-based glues
- Soldering
- Treatment with a heat gun
- Cutting with torches or hot wire
- Hot scissors
- Grinding
- Sawing

Definition of Thermal Degradation

The chemical breakdown of materials into airborne particulates, gases, and/or vapors when heat is applied.

It has been estimated that non-flaming thermal degradation of some polyurethane products may begin as low as about 150°C (300°F) to 180°C¹. However, it is important to note that the temperature at which thermal degradation starts can vary due to the many different heating processes and with the various types of polyurethanes used. For example, non-flaming thermal degradation in some urethane modified polyisocyanurate foam, those usually used as industrial insulation, starts above 250°C (482°F)^{2,3}. When polyurethanes undergo thermal degradation, some potentially hazardous chemicals may be emitted. This may or may not be seen as smoke. It is important to be aware of this type of degradation, in part, because of the lack of visible warning signs of the chemicals that may be released during these processes. The use of appropriate control measures (e.g., local exhaust ventilation and proper personal protective equipment (PPE)) reduces the risk of exposure to smoke or vapors from thermal degradation of polyurethanes. Additional information regarding ventilation and PPE is available through the Center for the Polyurethanes Industry's website at www.polyurethane.org and/or possibly through material suppliers.

¹ Wang H, Wang QS, He JJ, Mao ZL; Study on the Pyrolytic Behaviors and Kinetics of Rigid Polyurethane Foams, 2013, 52:377-385.

² C. Dick, E. Dominguez-Rosado, B. Eling, J.J.Liggat, C.I. Lindsay, S.C. Martin, M.H. Mohammed, G. Seeley, C.E. Snape; Flammability of Urethane-modified Polyisocyanurates and its Relationship to Thermal Degradation Chemistry. *Polymer* 42 (2001) 913-923.

³ E. Dominguez-Rosado, J.J.Liggat, C.E. Snape B. Eling, J. Pochtel. Thermal Degradation of Urethane Modified Polyisocyanurates Foams Based on Aliphatic and Aromatic Polyester Polyol. *Polymer Degradation and Stability* 78 (2002) 1-5.

Potential Health Effects

A range of airborne thermal degradation chemicals may be emitted during combustion of polyurethane products. These chemicals may include carbon dioxide, carbon monoxide, nitrogen oxides, hydrogen cyanide, isocyanates, isocyanic acid, amines, hydrocarbons, and other potentially hazardous decomposition products. The composition of these chemicals, when emitted, may vary. Exposure to such chemicals may cause irritation of the eyes and respiratory tract with symptoms of running nose, watering eyes, coughing, headaches, dizziness, nausea and breathlessness. Isocyanates and amines can also cause allergic reactions (sensitization) of the skin and lungs. Workers exposed to thermal degradation chemicals may experience immediate or delayed effects. Obtain medical attention if any symptoms occur.

Prevention & Precautions

To help minimize the potential risks of exposure to thermal degradation chemicals, when performing hot work on or around polyurethanes, keep these safety precautions in mind. The following includes some precautions, but it may not include every precaution:

- PPE and ventilation are in good working order and used correctly.
- Carefully read and follow safety precautions listed on the product label and Safety Data Sheets (SDS).
- As applicable, comply with training and OSHA Hazardous Communication Standard requirements (29 CFR 1910.1200).
- If you experience any symptoms of exposure, stop work immediately and seek medical help.
- Be aware that there may be other federal, state and local regulations that apply to the operations at your worksite beyond those mentioned in this document.
- When possible, do not perform hot work on articles that contain polyurethane (e.g., remove and isolate pipe insulation when welding is carried out).
- No open flames, cutting /welding torches, high intensity heat sources, or smoking materials in storage and application areas.
- Torch cutting, welding, or any other type of hot work may not be permitted on or near installed foam insulation.
- If hot work must be performed within the vicinity of combustible materials, including exposed polyurethane/polyisocyanurate foams, shield from heat and sparks by a fire-resistant barrier, and consider a fire watch.
- Observe good housekeeping procedures.
- Where applicable and safe, consider replacement of torch and hot wire cutting with other cutting devices such as band saws, oscillating saws and high pressure water jets, from which levels of emission breakdown is usually extremely low.

Conclusion

Performing hot work, on or around polyurethanes, may be done safely if workers understand the potential risks associated with this type of job and implement appropriate safety precautions. Inquire about their company's internal product stewardship program for more safety information about working with polyurethanes. You can also visit www.polyurethane.org for more information on polyurethanes.

Legal Notice

This guidance document was prepared by the American Chemistry Council's Center for the Polyurethanes Industry.

It is intended to provide general information to professional persons working in close proximity to polyurethane and doing hot work. It is not intended to serve as a substitute for in-depth training or specific handling or storage requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons working in close proximity to polyurethane have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. The guidance is necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions and economic and technological feasibility. Neither the American Chemistry Council, nor the individual member companies of the Center for the Polyurethanes Industry of the American Chemistry Council, nor any of their respective directors, officers, employees, subcontractors, consultants, or other assigns, makes any warranty or representation, either express or implied, with respect to the accuracy or completeness of the information contained in this guidance document; nor do the American Chemistry Council or any member companies assume any liability or responsibility for any use or misuse, or the results of such use or misuse, of any information, procedure, conclusion, opinion, product, or process disclosed in this guidance document. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.