

SSPC: The Society for Protective Coatings

TECHNOLOGY UPDATE No. 8

Safe Use and Handling of Isocyanate-Containing Polyurethane and Polyurea Coatings for Industrial Maintenance Applications

1. Background Information

Polyurethane is the name used for the material formed by the chemical reaction of a hydroxyl or $-OH$ -containing polyol, and a polyisocyanate hardener that contains multiple isocyanate (NCO) groups. Polyisocyanate hardeners are formulated into several different types of coatings systems, including one-component moisture cure urethanes, two component polyurethanes, and two component polyurea coatings. In a one-component or moisture-cure polyurethane, the polyisocyanate reacts with water in the atmosphere to fully cure. In a two-component system, the polyisocyanate reacts with a resin having reactive hydrogen groups, which can include acrylic, polyester, polyether, vinyl, castor oil, amine, etc. The polyurethane or polyurea coating resulting from these chemical reactions is the foundation of performance properties, including durability, corrosion and chemical resistance, and color and gloss retention. Aliphatic polyurethane and polyurea coatings are resistant to the sun's ultraviolet (UV) radiation, increasing their color and gloss stability while maintaining a functional non-chalking surface. Aromatic polyurethane and polyureas provide chemical, abrasion, and corrosion-resistance properties, but are not as UV-resistant as their aliphatic counterparts.

High-performance polyurethane coatings can contain a variety of components including solvents, pigments, additives, and other resins along with the polyisocyanate resins. These ingredients can present certain potential health hazards if one is exposed to a sufficiently high dosage during the coating process. This is why the applicator and any other workers in the application area must be properly protected. All coatings, including those containing polyisocyanates, can be applied safely when safe work practices are followed and proper personal protective equipment (PPE) is worn.

This technology update focuses on U.S. safety and health regulations on the isocyanates in industrial maintenance coatings. Regulations in other countries may vary.

2. Worker Exposure

2.1 RECOGNITION OF HAZARD: In order to determine whether a particular coating contains isocyanates, one should refer to the container label and the safety data sheet (SDS). If a coating is referred to as a polyurethane or a polyurea,

it may contain isocyanates. However, some polyurethane coatings are fully reacted. That is, all of the NCO groups are chemically changed to polyurethane groups prior to packaging for shipment. Examples of such coatings would be most one-package, clear, polyurethane wood varnishes sold at retail home improvement stores. Polyurethane coatings used for industrial maintenance painting typically consist of a "paint" or "resin" component that needs to be mixed with a "hardener" or "catalyst" component prior to application. These coating systems will contain unreacted isocyanate groups at the time of application to the substrate. The hardener is the part that typically contains the unreacted isocyanate. The isocyanate groups begin to react immediately upon contact with the components in the coating system to form the polyurethane film. It is the unreacted isocyanate groups that require workers to wear appropriate PPE. Once the coating system has fully cured, the isocyanate groups are no longer present in the coating film.

Because the two parts of the coating system are packaged separately, the supplier often provides two different SDSs, one for the "paint" side and one for the "catalyst" side. The "catalyst" or "hardener" will contain primarily polyisocyanate and a small percentage (less than 0.5%) of diisocyanate monomer. Section 3 of the SDS (Composition/Information on Ingredients) should identify the specific type of isocyanate (diisocyanate monomer/polyisocyanate) along with its percent composition in the product. When reviewing the SDS, it is important to understand specific words, terms and acronyms common to polyurethane coating systems such as:

- **Isocyanates:** organic compounds consisting of one nitrogen, one carbon and one oxygen atom attached by a double bond and illustrated by the chemical formula NCO . Isocyanates are a family of highly reactive chemicals that are widely used to make polyurethane coatings as well as flexible foam and rigid foam insulation.
- **Diisocyanate (monomers):** these are isocyanates that contain two NCO functional groups and because of their functionality are widely used in the polyurethane industry; common examples of monomeric isocyanates used in coating systems include Aliphatic Diisocyanates such as 1,6-hexamethylene diisocyanate (HDI),

isophorone diisocyanate (IPDI), and methylene bis(4-cyclohexylisocyanate (HMDI); and Aromatic Diisocyanates such as 2,4 and 2,6-toluene diisocyanate (TDI) and 4,4-diphenylmethane diisocyanate (MDI). The monomeric diisocyanates have occupational exposure limits: (Occupational Safety and Health Administration (OSHA)⁽¹⁾ Permissible Exposure Limit [PEL]; American Conference of Governmental Industrial Hygienists (ACGIH)⁽²⁾ Threshold Limit Value [TLV]; U.S. Centers for Disease Control, National Institute for Occupational Safety and Health (NIOSH)⁽³⁾ Recommended Exposure Limit [REL]); and are generally the focus of most exposure-monitoring (air-sampling) studies. Therefore, the percent content of the diisocyanate monomer within the catalyst or hardener and the isocyanate-to-resin ratio are important characteristics associated with the coating system in assessing the potential for worker exposure.

- **Polyisocyanates:** compounds that contain three or more NCO functional groups. To reduce the vapor hazards associated with lower molecular weight diisocyanate monomers (i.e., 1,6-HDI), polyisocyanate forms of these diisocyanates were developed and have significantly reduced the monomer content in many product formulations. Polyisocyanate compounds are derived from diisocyanate monomers either by directly linking the specific diisocyanate monomer within the product to form larger compounds referred to as a homopolymer or by reacting the monomer with a polyol (polyalcohol) or amines to form a prepolymer. Polyisocyanates or prepolymer compounds are characterized by high molecular weight and a low evaporation rate at ambient temperatures. NCO groups associated with a polyisocyanate can only be an inhalation hazard if mechanically aerosolized (e.g., sprayed) or heated in the work environment to temperatures well above 100 °F (38°C). Polyisocyanate compounds are not assigned an occupational exposure limit (OEL) by the ACGIH, federal OSHA or NIOSH. Some manufacturers and state OSHA agencies have published OELs for polyisocyanates that are typically established at a higher value than OELs for the diisocyanate monomers.

If the applicator suspects that a particular coating contains isocyanates but cannot find any mention of them on

the label or SDS, it is advisable to contact a product safety specialist from the coating supplier for additional information. Most SDSs provide a department name and phone number for those individuals seeking additional health and safety information.

2.2 EVALUATION: Once it has been established that a particular coating system contains a diisocyanate or polyisocyanate, the workplace atmosphere should be characterized to determine the airborne concentration. Air sampling is the preferred method of evaluating the airborne concentration in the work environment. Table 1 is a summary of the 2017 OSHA, ACGIH and NIOSH occupational exposure limits (OELs) for commonly used diisocyanate monomers and polyisocyanates.

Federal OSHA permits states to develop and operate their own job safety and health enforcement programs, referred to as an OSHA-approved State Plan. States with approved plans include AK, AZ, CA, CT, HI, IL, IN, IA, KY, MD, MI, MN, NJ, NM, NV, NY, NC, OR, SC, TN, UT, VA, VT, WA, and WY. States must have PELs equal to or lower than Federal OSHA limits. It is important to check the diisocyanate PELs when applying coatings in a region with an OSHA-approved State Plan.

For all diisocyanate monomers except TDI, the 8-hour Time Weighted Average (TWA) airborne concentration exposure limit or guideline is 5 parts per billion parts of air (5 ppb). In February 2016, the 8-hr TLV-TWA for TDI was lowered to 1 ppb and the 15-minute Short Term Exposure Limit (STEL) to 5 ppb.¹ With regard to HDI polyisocyanates, past health studies suggest that they are less potent in causing allergy and asthma than 1,6-HDI monomer.² Therefore, HDI polyisocyanates have a higher exposure limit value. The MGL (and Oregon OSHA PEL) for HDI polyisocyanates is 0.5 milligrams per cubic meter (mg/m³) as an 8-hour TWA and 1.0 mg/m³ as a 15-minute STEL^{3,4}. The units of measurement for HDI polyisocyanates are expressed in a mass-to-volume ratio (mg/m³) and not in a volume-to-volume ratio (ppb) because HDI polyisocyanates typically do not exist as a vapor in the work environment. HDI polyisocyanates can only be measured within an aerosol (i.e., coating mist) during a spray application. SDSs often list the applicable airborne concentration guidelines or standards in Section 8 (Exposure Controls). Another source for diisocyanate monomer exposure standards is the ACGIH *Guide to Occupational Exposure Values*.¹

Monitoring of the workplace air to determine concentrations of isocyanates is a key step in determining the effectiveness of engineering controls as well as in determining the type of respiratory protection and other personal protective equipment which may be required. Specific sampling and analytical techniques have been developed to determine these levels.

⁽¹⁾ U.S. Dept. of Labor, Occupational Safety and Health Administration (OSHA), Office of Public Affairs - Room N3647, 200 Constitution Ave., Washington DC 20210, or contact via internet at <http://www.osha.gov/readingroom/html>

⁽²⁾ American Conference of Governmental Industrial Hygienists (ACGIH), 1330 Kemper Meadow Drive, Suite 600, Cincinnati OH 45240, <<http://www.acgih.org>>

⁽³⁾ U.S. Centers for Disease Control, National Institute for Occupational Safety and Health (NIOSH), 200 Independence Avenue, SW, Washington, DC 20201, <<https://www.cdc.gov/niosh/>>

⁽⁴⁾ Oregon Department of Consumer and Business Services, Oregon Occupational Safety and Health Division, 350 Winter St. NE, Room 430 Salem, OR 97303-0135, phone: 503-326-7448, fax: 503-326-7448, email: info@oregonosha.gov

TABLE 1
SUMMARY OF 2017 OSHA, ACGIH AND NIOSH
OCCUPATIONAL EXPOSURE LIMITS FOR COMMONLY USED DIISOCYANATE
MONOMERS AND POLYISOCYANATES

Chemical	CAS #	ACGIH TLV	OSHA PEL	NIOSH REL
1,6-HDI Diisocyanate	822-06-0	5 ppb (34 $\mu\text{g}/\text{m}^3$) (8-hr TWA)	Not Established	5 ppb (34 $\mu\text{g}/\text{m}^3$) (8-hr TWA) 20 ppb (140 $\mu\text{g}/\text{m}^3$) Ceiling Limit
HDI Polyisocyanate (1,6-HDI homopolymer)	28182-81-2	Not Established	Not Established	Not Established
2,4 and 2,6-TDI Diisocyanate	584-84-9; 91-08-7	1 ppb (7 $\mu\text{g}/\text{m}^3$) (8-hr TWA) 5 ppb (36 $\mu\text{g}/\text{m}^3$) (15-min STEL)	20 ppb (140 $\mu\text{g}/\text{m}^3$) Ceiling Limit	Lowest Feasible Concentration
4,4'-MDI Diisocyanate	101-68-8	5 ppb (50 $\mu\text{g}/\text{m}^3$) (8-hr TWA)	20 ppb (200 $\mu\text{g}/\text{m}^3$) Ceiling Limit	5 ppb (50 $\mu\text{g}/\text{m}^3$) (8-hr TWA) 20 ppb (200 $\mu\text{g}/\text{m}^3$)
2-4'-MDI Diisocyanate	5873-54-1	Not Established	Not Established	Not Established
2-2''-MDI Diisocyanate	2536-05-2	Not Established	Not Established	Not Established
Polymeric MDI	9016-87-9	Not Established	Not Established	Not Established
IPDI Diisocyanate	4098-71-9	5 ppb (45 $\mu\text{g}/\text{m}^3$) (8-hr TWA)	Not Established	5 ppb (45 $\mu\text{g}/\text{m}^3$) (8-hr TWA) 20 ppb (180 $\mu\text{g}/\text{m}^3$) (15-min STEL)
HMDI Diisocyanate	5124-30-1	5 ppb (54 $\mu\text{g}/\text{m}^3$) (8-hr TWA)	Not Established	10 ppb (110 $\mu\text{g}/\text{m}^3$) Ceiling Limit

Note: ppb is read parts per billion; $\mu\text{g}/\text{m}^3$ is read micrograms per cubic meter.

At present, a number of sampling and analytical methods are available for monitoring isocyanates in the work environment. Care must be taken to ensure that the appropriate method is chosen before sampling is performed in the work area. Isocyanates are highly reactive compounds, therefore methods used for monitoring airborne concentrations must be capable of trapping and derivatizing the isocyanate (NCO group) to a stable urea derivative as they are being sampled. The most common isocyanate air-sampling methods are published by OSHA and NIOSH. In addition, an International Standards Organization⁽⁵⁾ isocyanate sampling and analytical method has recently been published. The most common sampling and analytical methods for diisocyanates are listed below:

- [OSHA Method 42](#) (TDI, HDI, IPDI, HMDI)
- [OSHA Method PV2125](#) 1,6-HDI polyisocyanate

- [OSHA Method 47](#) (MDI)
- [NIOSH Method 5521](#) (TDI, MDI, HDI, IPDI, HMDI)
- [ISO 17734](#) Asset (EZ4™-NCO Dry Sampler for TDI, HDI, IPDI, and MDI)

All of the methods listed above are effective when the isocyanate exists as a vapor in the work environment. Isocyanate manufacturers have made minor modifications to OSHA Methods 42 and 47. These modifications were made to improve the collection efficiency of isocyanates during air sampling. Many national laboratories have adopted these modifications; for example, coating the glass-fiber filters used in these methods with 2 milligrams (mg) of 1-(2-pyridyl) piperazine (PP) compared to 0.1 mg PP in OSHA Method 42 and 1.0 mg PP in OSHA Method 47. Isocyanate manufacturers also recommend using a 13-mm glass-fiber filter mounted in a Swinnex® holder versus a standard 37-mm glass-fiber filter when sampling for MDI.

⁽⁵⁾ International Organization for Standardization (ISO), Case Postale 56, Geneva CH-1211, Switzerland. In the United States, ISO standards may be obtained from the American National Standards Institute (ANSI) at <<http://www.ansi.org>>

For spray painting applications, isocyanate manufacturers recommend using modifications to NIOSH Method 5521 and OSHA Method 47 which involve using glass impingers containing a derivatizing solution (PP/toluene). These modifications improve the NIOSH and OSHA sample methods so that they more efficiently collect and analyze isocyanate aerosols (i.e., spray mist particles as well as vapors).

Industrial hygiene consultants or national laboratories that perform isocyanate analysis should be contacted for help in selecting the proper air-sampling method. Various factors affect the isocyanate sampling method chosen. For example, the method of application (e.g., spray, brush, roller) of the coating system, the physical state of the isocyanate likely to be present in the air being sampled (i.e., vapor and/or aerosol), and the specific isocyanate or polyisocyanate to be evaluated. The air-sampling techniques may include the use of impingers, filters, denuders; or some combination of each of these devices.

Direct reading instruments are available for measuring airborne HDI, TDI or MDI vapors in the work environment. The direct reading instruments draw air across a chemically impregnated carrier (i.e., amine treated paper tape). The diisocyanate (NCO group) reacts with the chemical on the tape to produce a color reaction. The color change is read optically by the instrument which is converted to a digital display reading in ppb. It must be pointed out, however, that these direct read instruments are not suitable for monitoring in spray application environments since the spray coating mist droplets can coat the optics and/or the treated paper tape and give erroneous readings. These instruments may be used to evaluate airborne diisocyanate monomer vapor concentrations during non-spray applications such as: mixing, repackaging, batchmaking, coil coating, and brush/roller/squeegee application. To date, no direct reading instrument

has been developed which can be used to accurately determine airborne concentrations of polyisocyanates during spray application of coatings.

Evaluation of worker exposure to diisocyanates has focused primarily on air sampling. However, there is growing interest in assessing for unreacted isocyanates on surfaces due to the need to prevent skin contact with this chemical. This has led to the use of wipe test kits to evaluate for surface contamination. The technology for evaluating for surface contamination of isocyanates is not as advanced as that for airborne monitoring. To check for surface contamination, wipe test kits are available from Colorimetric Laboratories Inc.⁽⁶⁾ (CLI Surface Swype™), and ChemTeq⁽⁷⁾ (ChemWipes™). Both of these wipe test products are qualitative assessment tools and rely on a color change to assess for the presence of the diisocyanate monomer. The degree of color change on the wipe pad provides a visual indication of the degree of surface contamination. A positive response using the wipe pad does not represent employee exposure, only that an unreacted isocyanate group exists on the surface. The information should be used to assess safe work (i.e., employees removing PPE in work areas), personal hygiene and housekeeping practices.

One of several important properties to characterize the potential for a diisocyanate/polyisocyanate to exist in the air during brush and roll applications is the vapor pressure since evaporation will be the predominant method to generate airborne polyisocyanate and isocyanate monomers. All spray applications involving an isocyanate result in potential aerosol (spray mist) exposure. Therefore, vapor pressure is not an important characteristic to consider for spray applications. Generally, a low vapor pressure is associated

⁽⁶⁾ Colorimetric Laboratories, Inc., 1261A Rand Road, Des Plaines, IL 60016-3402 Phone: int+1-847-803-3737, <<http://www.cilabs.com>>

⁽⁷⁾ ChemTeq, 800 West 24th Street, Suite B, Norfolk, VA 23517 Phone: int+1-757-622-2223, <<http://chemteq.net>>

TABLE 2
VAPOR PRESSURE OF COMMONLY USED
DIISOCYANATE MONOMERS AND
POLYISOCYANATES)

Chemical	CAS#	Vapor Pressure (mm Hg 20°C)
HDI Polyisocyanate	28182-81-2	<1 x 10 ⁻⁶
HMDI Monomer	5124-30-1	1.5 x 10 ⁻⁵
MDI Monomer (4,4'-MDI)	101-68-8	<1 x 10 ⁻⁴
Polymeric MDI	9016-87-9	<1 x 10 ⁻⁴
IPDI Monomer	4098-71-9	0.0005
HDI Monomer	822-06-0	0.01
TDI Monomer (2,4 and 2,6 TDI)	584-84-9; 91-07-7	0.02

Note: For comparison, methyl ethyl ketone (MEK) has a vapor pressure of 78 mm Hg at 20°C.

Courtesy of Covestro LLC