

SSPC: The Society for Protective Coatings

TECHNOLOGY UPDATE No. 8

The Use of Isocyanate-Containing Paints as Industrial Maintenance Coatings

1. Background Information

Isocyanates are chemicals that contain at least one isocyanate (-NCO) group. Depending on the number of isocyanate groups, one can distinguish among monoisocyanates (1 group), diisocyanates (2 groups), or polyisocyanates (3 or more groups).

Monoisocyanates are of no value in coatings because they cannot build the polymeric structure needed for a coating raw material. Nevertheless, diisocyanates, often called monomers, are important building blocks for coating raw materials.

Commonly used diisocyanates are MDI (diphenylmethane diisocyanate), TDI (toluene diisocyanate), IPDI (isophorone diisocyanate), HDI (hexamethylene diisocyanate), HMDI (bis(4-isocyanatocyclohexyl)methane), and TMXDI (tetramethylylene diisocyanate).

Evaporation rates determine how quickly a material is vaporized and dispersed into the atmosphere. High evaporation rates cause faster dispersion and more vapor exposure than lower evaporation rates. Diisocyanates have varying evaporation rates. For example, the evaporation rates of TDI and HDI are considerably higher than that of MDI.

In order to make TDI and HDI safer to use as coatings raw materials, they are further reacted to make slightly larger polyisocyanates that may contain from 3 to 7 units of the starting diisocyanate monomer. These polyisocyanates do not evaporate and can become airborne only during spray application. However, the polyisocyanates do contain a very small amount (0.15% to 1.6%) of residual free HDI and unreacted TDI monomer that can still evaporate.

TDI, MDI and their polyisocyanates are known as aromatic isocyanates. These materials absorb ultraviolet light (UV) from the sun and therefore become dull due to a chalky layer that forms on the paint surface. Therefore, paints based on these materials are not typically used as topcoats in outdoor applications. On the other hand, HDI, IPDI, HMDI and TMXDI are called aliphatic isocyanates. These do not absorb much UV light and therefore can be used in formulating outdoor topcoats.

"Polyurethane" (PU) is the name of the material formed by the chemical reaction of an alcohol and an isocyanate or, more precisely, polyalcohols and polyisocyanates.

Polyurethane coatings can be of several types. In a one-component or moisture-cure polyurethane, the polyisocyanate reacts with water in the atmosphere. In a two-component system, the polyisocyanate reacts with a resin having reactive hydrogen, which can be acrylic, polyester, polyether, vinyl, castor oil, etc.

The paint film resulting from this chemical reaction is the foundation of the performance properties of polyurethanes:

durability, corrosion and chemical resistance, and color and gloss retention. These properties have resulted in the use of polyurethanes in a wide range of industry segments.

In 1998, 13.3 million gallons of PU coatings were used in transportation, 12.7 million gallons in industrial maintenance, 28.8 million gallons in architectural, and 53 million gallons in product finishing applications. Some typical industrial maintenance applications are bridges, chemical plants, tank farms, power plants, and municipal structures (e.g. as anti-graffiti coatings).

High performance paints can contain diisocyanates, polyisocyanates, solvents, pigments, additives, and other resins. All these ingredients can present certain potential health hazards if one is exposed to a sufficiently high dosage. This is why the applicator and any other workers in the application area must be properly protected. All coatings, including those containing isocyanates, can be applied safely when proper personal protective equipment (PPE) is worn and safe work practices are observed.

This technology update focuses on the isocyanates in industrial maintenance coatings. Exposure to polyisocyanates in excess of recommended limits can irritate the eyes, nose, throat, skin, and lungs. An overexposed person may develop skin sensitization and/or respiratory sensitization resulting in asthmatic symptoms that could be permanent. Exposure in excess of recommended limits may also result in a reduction in lung function and possible permanent lung damage. Symptoms of overexposure can include flu-like symptoms such as fever, chills, or an achy feeling. There is no evidence that isocyanate exposure causes human cancer, birth defects, nerve damage, or reproductive effects.

2. Worker Exposure

2.1 RECOGNITION OF HAZARD: In order to determine whether a particular coating contains isocyanates, one should refer to the paint can label and the material safety data sheet (MSDS). 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 isocyanate 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 usually contain unreacted isocyanates at the time of application to the substrate. The two-package types have a "paint" side that needs to be mixed with a hardener, activator or "catalyst", just before application. The hardener is the part that typically contains the unreacted

isocyanate. Because these two parts of the paint system are packaged and shipped separately, the supplier often provides two different MSDSs, one for the "paint" side and one for the "catalyst" side. Both MSDSs must be reviewed in such a case because the "paint" side MSDS will typically not mention that "free" isocyanates may be present.

Another type of polyurethane coating typically used in industrial maintenance is the one-package, moisture-cure system. This type does contain the isocyanate ingredient in the single can. This type of paint cures by reaction of the unreacted isocyanate with atmospheric moisture once the can has been opened to the ambient environment.

Specific words and acronyms to look for on labels and MSDSs are: isocyanate, polyisocyanate, aliphatic isocyanate, aromatic isocyanate, hexamethylene diisocyanate (HDI), diphenyl methane diisocyanate (MDI), isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), dicyclohexylmethane diisocyanate (HMDI), TMXDI (tetramethylxylene diisocyanate), HDI homopolymer, isocyanate prepolymer, isocyanate oligomer, isocyanate monomer, etc.

If the applicator suspects that a particular coating contains isocyanates but cannot find any mention of them on the label or MSDS, a second step would be to call the paint supplier and ask to speak to a product safety specialist. Often the MSDS itself will list the name of the contact.

2.2 EVALUATION: Once it has been established that a particular paint system does contain an isocyanate ingredient, the workplace atmosphere should be characterized to determine the airborne concentration. Most diisocyanate monomers have an OSHA⁽¹⁾ Permissible Exposure Limit (PEL), an ACGIH⁽²⁾ Threshold Limit Value (TLV), a NIOSH⁽³⁾ Recommended Exposure Limit (REL), or a Manufacturer's Guideline Limit (MGL). Most commonly, the 8 hour Time Weighted Average (TWA) airborne concentration guideline or standard for diisocyanates is five parts per billion parts of air (ppb). For HDI monomer, this is equal to 0.034 milligrams/per cubic meter of air (mg/m³). Polyisocyanates are less toxic and therefore can have a higher allowable TWA exposure. The MGL (and Oregon OSHA PEL) for HDI polyisocyanates is usually 0.5 mg/m³ as an 8-hour TWA and 1.0 mg/m³ as a 15 minute Short Term Exposure Limit (STEL). MSDSs often list the applicable airborne concentration guidelines/standards. Another

source for diisocyanate monomer exposure standards is the ACGIH publication entitled "Guide to Occupational Exposure Values."

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.

At present, the recommended method for sampling and analysis of HDI, TDI, and IPDI polyisocyanates in spray applications is Bayer Method 1.4.4.⁽⁴⁾ Samples are collected using impingers containing 2×10^{-4} M N-(4-nitrobenzyl)-propylamine (nitroreagent) in toluene. Analysis is by high performance liquid chromatography (HPLC) and ultraviolet detection at 254 nanometers. Bayer has developed Method 1.4.4 independently and used it successfully for 20 years. In terms of current NIOSH methods, the one which is perhaps most similar is Method 5521 which uses an impinger containing methoxyphenyl piperazine (MOPP) reagent in toluene.⁽⁵⁾ This NIOSH method uses both electrochemical and ultraviolet (UV) detectors. However, if only the UV detector is used and the calibration curves are run using diisocyanate monomer and commercial polyisocyanate, the method would be quite similar to Bayer 1.4.4. In addition, OSHA Method 18⁽⁶⁾ would be similar to Bayer 1.4.4 if an impinger jet inlet were used instead of the fritted glass bubbler inlet specified in OSHA 18.

For situations in which only HDI, TDI, IPDI, HMDI, TMXDI monomer vapors would be present, such as in non-spray handling and use, Bayer Method 1.7.6 is recommended. Samples may be collected using a 1-(2-pyridyl) piperazine impregnated glass fiber filter with analysis by HPLC. Bayer 1.7.6 is OSHA Method 42 modified by coating the filter with 2 mg of derivatizing reagent instead of 0.1 mg and by loading the filter in the cassette with a stainless-steel backup screen in place of the mixed-cellulose ester back-up pad. Both of these modifications are designed to prevent the loss of derivatizing reagent. Such a depletion of reagent can result in under-estimation of airborne isocyanate concentrations.

Air monitoring for MDI can be performed using Bayer Method 1.7.7. This method is similar to Method 1.7.6 above but uses a 13 millimeter (mm) diameter glass fiber filter instead of a 37 mm filter.

⁽¹⁾ US Dept. of Labor, 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, 1330 Kemper Meadow Drive, Suite 600, Cincinnati OH 45240 (<http://www.acgih.org>).

⁽³⁾ National Institute for Occupational Safety and Health, 200 Independence Avenue, SW, Washington, DC 20201. (<http://www.cdc.gov/niosh>).

⁽⁴⁾ Bayer Product Safety Department at Bayer Corporation, 100 Bayer Road, Pittsburgh, PA 15205-9741, Phone: (412) 777-2867. (Contact for information on the Bayer methods mentioned in this report.)

⁽⁵⁾ NIOSH Publications, 4676 Columbia Parkway, Mail Stop C-13, Cincinnati, OH 45226-1998. May be downloaded from NIOSH web page at <http://www.cdc.gov/niosh/nmam/nmammenu.html>

⁽⁶⁾ Method 18 from US Dept. of Labor, OSHA, Office of Public Affairs, Room N3647, 200 Constitution Ave., Washington DC 20210, (<http://www.osha.gov/readingroom/html>)

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Continuous or direct reading monitors for diisocyanate monomer vapors have recently been developed. It must be pointed out, however, that these units may not be suitable for monitoring in spray application environments since the spray paint mist droplets can coat the optics and/or the treated paper tape and give erroneous readings. These instruments may provide information as to 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 in spray application of coatings.^(7,8)

The technology for evaluating skin exposure to isocyanates is not as advanced as that for airborne monitoring. Check for any visual evidence of deposition of paint onto the skin. Usually, this is rather obvious because of the paint pigmentation and/or a feeling of stickiness on the skin. If the user wishes to check a surface to determine if isocyanate residue has been removed, such as after a spill clean-up, he should consider purchase and use of Swype™ Test kits which are manufactured by Colorimetric Laboratories, Inc.⁽⁹⁾

3. Control of Health Hazards

3.1 ENGINEERING CONTROLS: Ideally, hazard control of vapor or spray mist is accomplished through engineering controls. Effective engineering controls should be used whenever possible to reduce and/or eliminate worker exposure to all respiratory hazards.

There are several engineering controls available to reduce exposure to vapors and mists generated by the use of these products. The most common is a properly designed and ventilated enclosure. General dilution ventilation, local exhaust ventilation, or isolation may prove adequate under certain conditions. "Adequate" generally means ventilation sufficient to keep airborne concentrations of contaminants below their respective Threshold Limit Values (TLVs), Permissible Exposure Limits (PELs) and Manufacturer's Guideline Limits (MGLs). Whenever possible, local exhaust ventilation should be provided in accordance with the guidelines provided in Industrial Ventilation, A Manual of Recommended Practice.

Use of alternative application equipment (e.g., airless, HVLP, or electrostatic spray equipment) may help reduce spray mist generation during spray painting. In addition, the use of spray gun extenders may help reduce the amount of spray mist in the breathing zone of the painter.

The likelihood of overexposure in non-spray, non-heated

applications of coatings containing polyisocyanates is reduced due to the low volatility of these materials. Hence, the use of brush, roller, or squeegee for coating application reduces the likelihood of inhalation overexposure.

3.2 RESPIRATORY PROTECTION: One manufacturer of polyisocyanates recommends air-supplied respirators for spray application if the airborne concentrations are unknown or if they exceed ten times the appropriate airborne concentration standards/guidelines.¹ However, the same manufacturer states that air-purifying respirators may be used under the following conditions:

- if airborne concentrations are known to be less than 10 times the standard/guideline concentration;
- if the spraying is not being done in a confined space;
- if pre-filters are changed as needed to prevent excessive breathing resistance; and
- if appropriate change schedules are implemented for the organic vapor cartridges (OVCs) in accordance with 29 CFR 1910.134.

Studies have shown that HDI polyisocyanates are essentially non-volatile and become airborne only as mechanically generated aerosols during spray application.² Furthermore, these aerosols are efficiently collected by the particulate pre-filters of a spray painting air-purifying respirator.^{3,4,5,6} The same studies show that these pre-filters did not fail by allowing breakthrough of the aerosol. Rather, they simply became increasingly clogged until airflow resistance was too great to allow easy breathing. Therefore, when breathing resistance becomes noticeably higher during use, the respirator wearer need only replace the used pre-filters with new ones.

A recent study⁷ has shown that:

- Organic vapor respirator cartridges demonstrated a collection efficiency for HDI vapors greater than 99.6% for 40 hours.
- Neither saturation of the cartridge with solvent vapors nor variation of the relative humidity resulted in breakthrough of HDI vapor.
- There was no evidence of desorption or migration of HDI within the cartridge during storage at room temperature overnight for five nights, after repeated exposures to high concentrations of HDI and solvents day-after-day for five days.

Therefore, for coatings containing HDI polyisocyanates and a small amount of unreacted HDI monomer, there is good evidence that a respirator equipped with organic vapor cartridges and P-95 particulate prefilters will provide good

⁷⁾ Information concerning direct reading diisocyanate vapor monitors can be obtained from: Zellweger Analytics, 405 Barclay Blvd., Lincolnshire, IL 60069, (847) 634-2800 or (800) 323-2000, or Bacharach Inc., 625 Alpha Drive, Pittsburgh, PA 15238, (412) 963-2200 or (800) 736-4666.

⁽⁸⁾ Information on the Bayer methods mentioned above can be obtained by contacting the Bayer Product Safety Department at Bayer Corporation, 100 Bayer Road, Pittsburgh, PA 15205-9741, Phone: (412) 777-2867.

⁽⁹⁾ Colorimetric Laboratories (CLI Labs), 1261A Rand Road, Des Plaines IL 60016 (<http://www.clilabs.com>).