

Guidance for Working with Aliphatic Diisocyanates

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Purpose

The American Chemistry Council's Aliphatic Diisocyanates Panel prepared this guidance to provide information about important health and safety considerations when working with aliphatic diisocyanates (ADIs). This paper provides additional information to what is contained in your supplier's Safety Data Sheets (SDS), which are a main source of information for handling ADIs. Throughout this document, the term ADI refers to aliphatic diisocyanates, specifically hexamethylene diisocyanate (HDI), methylene dicyclohexyl diisocyanate or hydrogenated MDI (HMDI) and isophorone diisocyanate (IPDI), and their polyisocyanates. The term ADI polyisocyanates is used to address partially polymerized products from ADI monomers.

As warranted, key differences in safe use and handling considerations between these ADI types will be highlighted.

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Introduction

Aliphatic diisocyanates (ADIs) are specialty intermediate chemicals used primarily to make durable coatings, adhesives, sealants and elastomers. ADIs are typically not sold directly for consumer use. Rather, they are sold primarily to industrial customers who use them to make resins used in paint, binders or hardeners during manufacturing processes. They are part of the diisocyanates (DII) family of chemicals, which have been used since the late 1940s. As mentioned, this document focuses on three of the most common ADIs used in polyurethane production and their polyisocyanates:

- hexamethylene diisocyanate (HDI) CAS# 822-06-0
- methylene dicyclohexyl diisocyanate (HMDI) or hydrogenated MDI (HMDI) CAS# 5124-30-1
- isophorone diisocyanate (IPDI) CAS# 4098-71-9

These raw materials come in three main forms:

- Monomeric Diisocyanates – HDI (the most widely used), HMDI, IPDI and several others. These are the main building blocks of the polyisocyanates listed below.
- Blocked Polyisocyanates – Blocked Polyisocyanates are supplied as 100% solids and/or dissolved in a variety of solvents.
- Polyisocyanates – Can be based on HDI, or IPDI. Common products include:
 - o HDI trimer
 - o HDI biuret
 - o HDI uretdione
 - o IPDI trimer
 - o They may also be mixtures of the above and are typically available as 100% solids or dissolved in a variety of solvents.

Identifying Aliphatic Diisocyanates

Typically, aliphatic diisocyanates are clear, colorless to slightly yellow, liquids at room temperature. HDI and IPDI may have a sharp, pungent odor. Some typical values for other physical properties are shown in Table 1:

Table 1. Aliphatic Diisocyanates: Typical Physical Properties

	HDI	IPDI	HMDI
Physical State	Clear Liquid	Clear Liquid	Clear Liquid
Molecular Weight	168	222.32	262
Boiling Point	225°C (491°F)	310°C (590°F)	155 - 160°C (311 - 320°F)
Freezing Point	-67°C (-88.6°F)	-60°C (-76°F)	20°C (68°F)
Specific Gravity	~1.05 @ 25°C	~1.06 @ 20°C	~1.07 @ 20°C
Density (g/cm ³)	~1.05 @ 20°C	~1.06 @ 20°C	~1.07 @ 20°C
Vapor Pressure	~0.011 mmHg @ 25°C	0.00048 mmHg @ 20°C	0.000015 mmHg @ 25°C
Saturate Vapor Concentration	14.47 ppm @ 25°C	0.63 ppm @ 20°C	0.019 ppm @ 20°C
Viscosity	2.4 mPa.s @ 20°C	10 mPa.s @ 25°C	12.7 mPa.s @ 55°C
Solubility in Water	Insoluble - Reacts slowly	Insoluble - Reacts slowly	Insoluble - Reacts slowly
Flash Point	130°C (266°F)	150°C (302°F)	200°C (392°F)
Autoignition Temperature	454°C (849°F)	430°C (806°F)	225°C (437°F)
Flammability Limits	Not established	Not established	Not established

Source: ADI Panel website: www.americanchemistry.com/adi

ADI Health and Safety Information

As with all chemicals, precautions must be taken to help protect anyone handling ADIs during production, transportation, or processing. ADI producers have a long history of providing safe use and handling information through Safety Data Sheets (SDS), formerly known as Material Safety Data Sheets (MSDS). Safety Data Sheets provide information about important health and safety topics, including:

- Potential hazards, how to protect against them, and steps to take in an emergency;
- Occupational exposure limits (OELs)², including permissible exposure limits (PELs);
- Handling, storage, transportation, spills, and disposal advice; and
- Regulatory information such as Occupational Health and Safety Administration (OSHA) classification and labeling.

Importance of Safety Data Sheets and Hazard Labels: Before working with an ADI, one should obtain the SDS from the manufacturer and become familiar with it. In addition, ADI containers are labeled with appropriate hazard warning information. Similarly, during transportation, appropriate Hazard warning signs and placards are used on trucks, tank cars, containers, and during marine transportation.

Recognizing Potential Health Hazards

Exposure to airborne ADI vapors or aerosols above their occupational exposure limit (OEL) can be harmful to your health. There are four possible routes of exposure:

- Breathing it in
- Getting it in your eyes
- Getting it on your skin
- Ingestion

Here are the potential effects of overexposure and some first-aid considerations:

Inhalation:

Professional organizations such as those listed below help develop limits for ADI airborne exposure:

- [American Conference of Governmental and Industrial Hygienists \(ACGIH\)](#) Threshold Limit Value (TLV)
- [National Institute for Occupational Safety and Health \(NIOSH\)](#) Recommended Exposure Limit (REL)

If an ADI is sprayed as a mist, heated, or handled in a poorly ventilated area, there is a greater chance of overexposure.

ADI polyisocyanates have low vapor pressures so inhalation is not likely to be an issue unless they are sprayed. In that case, precautions must be taken to avoid exposure.

OSHA has stated that OELs are intended to set the airborne concentrations of substances to which workers can be exposed on a daily basis for a working lifetime without significant risk of adverse effects from the material. OELs are normally set for an eight-hour day and are expressed as an eight-hour time-weighted average (TWA). In some cases, a short-term (15-minute) exposure limit (STEL) or Ceiling (C) limit is also established. See Table 2 for exposure limits for HMDI, HDI and IPDI.

Table 2: Exposure Limits for HMDI, HDI and IPDI

Isocyanate	ACGIH-TLV (ppm)	NIOSH-REL (ppm)
HMDI	0.005 (8-hr TWA)	0.010 (C)
1,6-HDI	0.005 (8-hr TWA)	0.005 (8-hr TWA) 0.020 (STEL)
IPDI	0.005 (8-hr TWA)	0.005 (8-hr TWA) 0.020 (STEL)

Source: ACGIH TLVs and BEI Book, 2016 Edition

C = Ceiling Limit (concentration that should not be exceeded during any part of the work shift)

TWA = Time Weighted Average (average airborne concentration over an 8-hour work shift)

STEL = Short Term Exposure Limit (15-minute average airborne concentration that should not be exceeded at any time during the work shift)

PPM = Parts Per Million (0.020 ppm is equivalent to 20 parts per billion or 20 ppb; 0.005 ppm is equivalent to 5 ppb)

NOTE: OSHA does not currently have permissible exposure limits (PELs) established for the ADIs.

First-Aid: If a person is overexposed (to levels above the TLV or REL), ADIs can irritate his/her nose and lungs and asthmatic-type symptoms may develop. The person may feel a tightening in the chest and have difficulty breathing. Gross overexposure to ADIs may cause more serious problems including pulmonary edema which requires immediate medical attention.

If you suspect that someone has been overexposed, remove the person to an area with fresh air, and try to keep them calm and warm. Seek immediate medical attention. If the person is having difficulty breathing, a properly trained person may provide oxygen. If they stop breathing, a properly trained person may give artificial resuscitation. **Seek medical attention at once.**

Note: Overexposure may also cause a person to become sensitized or “allergic” to ADIs, which may cause asthma-like attacks if the person breathes the ADI vapors again. If this happens, any further exposure must be avoided. The onset of symptoms may occur immediately following an accidental overexposure, may occur shortly after overexposure, or can develop several hours after overexposure if sensitization has developed. Difficulty breathing may occur the evening after overexposure if sensitization has developed. HDI, HMDI and IPDI are respiratory irritants and potential respiratory sensitizers. There are no specific antidotes and treatment is essentially symptomatic for primary irritation or bronchospasm.

Eye Contact: Eye contact with an ADI can be painful and may cause tearing and irritation. If not immediately addressed, ADI exposure to the eye can cause more serious problems, including corneal burns and possible permanent damage. Wear chemical goggles or safety glasses with side shields whenever there could be potential exposure to the ADI liquid, vapor, or mist.

First-Aid: If eyes come in contact with an ADI, flush them immediately with the contents of several sterile eye-wash bottles or a continuous flow of low pressure water from a tap (preferably from an eyewash fountain). Then remove contact lenses, if present and easily removable, and continue eye irrigation for not less than 15 minutes. **Seek medical attention at once.**

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Skin Contact: Skin contact with an ADI may play a role in the development of skin sensitization. In addition, animal tests have indicated that respiratory sensitization may occur from skin contact with ADIs. Repeated skin contact with an ADI may also cause discoloration, redness, swelling, or itching. It is best to avoid skin contact at all times.

First-Aid: Monomeric ADIs may be difficult to wash off with just water or soap and water, so extra effort is required:

- Wash off thoroughly with large amounts of water and then wash well with soap and water (preferably warm water if available). Do not use solvents.

-OR-

- Wash off with soap and water. After washing, cover affected area with polyethylene glycol (300-500 molecular weight) and wash again with soap and water to thoroughly remove polyethylene glycol and residual isocyanate. Repeat if necessary.

For severe exposures (significantly above the TLV or REL), obtain medical attention immediately. Get under a safety shower and begin rinsing off. Properly dispose of items that have been contaminated, such as clothes, shoes, belts and watchbands.

Note: If skin is exposed to an aliphatic polyisocyanate, wash it off thoroughly with large amounts of water and then wash well with soap and water.

Ingestion: Swallowing an ADI can cause irritation to the mouth, throat and stomach.

First-Aid: If an ADI is ingested, rinse the mouth with water. Do not try to induce vomiting. **Rest and seek medical attention at once.**

Note: HDI, HMDI, and IPDI have low oral toxicity.

Protecting Yourself from ADI Overexposure

In poorly ventilated environments, there is a greater chance of overexposure. If an ADI is sprayed, aerosolized, heated, or handled, there is a greater chance of overexposure. In addition, overexposure can occur when there is direct skin contact with liquid ADI. Where there is a risk of exposure to airborne ADI above applicable exposure limits, consider using (at a minimum):

- An approved respirator, either air-supplied or air-purifying. Consult your company safety professional, the product SDS or the manufacturer for guidance. The type of respiratory protection will depend upon the maximum exposure concentration.
- Eye protection may also be needed if not already provided by the respirator because elevated airborne concentrations may be irritating to the eyes. Chemical safety goggles or safety glasses with side shields are suggested.

Where there is a risk of skin contact with ADI, consider using at a minimum:

- Chemical-resistant gloves, examples are nitrile or butyl rubber gloves, neoprene gloves

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If there is potential for more extensive exposure, consider using the following:

- Permeation-resistant long-sleeve coveralls or full body suit with a permeation resistant barrier (e.g., butyl or nitrile rubber gloves, neoprene apron, chemical suit, etc.)
- Permeation-resistant fitted boots
- Head protection, such as a loose-fitting hood

When coatings, paints, or any other ADI-containing products are spray-applied, the use of respiratory protection, eye protection, and complete skin protection is necessary.

In all situations, you should first consult the supplier SDS to determine the appropriate PPE for the product.

Understanding Potential Reactivity Hazards

ADIs are reactive chemicals. A build-up of heat or pressure can result from improper mixing of ADIs with:

- Acids, inorganic bases (such as sodium hydroxide or potassium hydroxide), ammonia, and amines
- Magnesium, aluminum, and their alloys
- Other metal salts, especially halides (such as tin, iron, aluminum and zinc chlorides)
- All strong oxidizing agents (such as bleach or chlorine)
- Polyols
- Water (typically, a relatively slow reaction)

Caution: Resealing ADI containers contaminated with water can cause a build-up of pressure in the container and cause it to explode. All forms of ADIs can also self-react in a fire or at very high temperatures, releasing carbon dioxide and causing a build-up of pressure in sealed containers sufficient to cause an explosion.

Reaction of ADIs If Spilled:

HDI, HMDI or IPDI are routinely transported in a variety of dedicated containers ranging from ships' tanks to plastic drums under applicable transportation safety laws and regulations. In the unlikely event of a spill to the aquatic or soil environments, ADIs react with water to form predominantly insoluble, inert polyureas and release carbon dioxide. If a spill occurs, refer to applicable environmental laws and the manufacturer's SDS. Refer to the section below "Responding to Emergencies."

Considerations for ADI Handling, Unloading and Storing

When handling, unloading and storing an aliphatic diisocyanate, review the SDS and all federal, state and local laws and regulations. To minimize hazards, here are some considerations:

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- Wear proper PPE
- Follow employer's established procedures for normal operations, maintenance, loading/unloading, sampling, special operations, and emergencies
- Use appropriate checklists provided by the employer for specific procedures
- Inspect equipment to ensure it is in good condition and capable of operating properly. A preventative maintenance program is suggested
- Maintain good housekeeping
- Participate in relevant training programs

When handling drums, consider the following:

- Wear proper PPE
- Follow all safety precautions for handling ADI
- Handle and store drums in a well-ventilated area with secondary containment and protect from contact with water
- Check drum shipments for leakage
- Do not use pressure to empty drums
- Do not store in open-head drums
- Use plugs/caps on terminal valves or fittings and bleed valves
- Keep drum overpacks available
- Keep drums segregated from materials that are incompatible with ADI
- Do not cut empty drums with a torch
- Do not use empty ADI drums from a worksite for any other use (e.g., a barbecue pit, flower box, trash barrel, etc.)
- **Empty drums should be handled by a qualified drum reconditioner. Contact the manufacturer or the Reusable Industrial Packaging Association (RIPA –www.reusablepackaging.org) to locate a drum reconditioner near you**

Guidance for Liquid Decontaminant/Disposal of Empty ADI Containers:

HDI (CAS# 822-06-0), HMDI (CAS# 5124-30-1) and IPDI (CAS# 4098-71-9) are not listed as hazardous wastes under the Resource Conservation and Recovery Act (RCRA). Residual HDI, HMDI and IPDI material can be reacted with a liquid decontaminant. Drums destined for a scrap dealer, an incinerator, or alternative options must be decontaminated, then punctured or crushed to prevent reuse. **Refer to the manufacturer's recommendations on how to decontaminate HDI, HMDI or IPDI drums.**

There are five procedures for disposing of drums that have contained ADIs. They may be sent to:

- A reconditioner
- A scrap metal dealer
- An approved incineration facility
- A material reclamation processor
- An approved landfill that complies with all federal, state and local laws and regulations and that accepts these materials.

Regardless of the procedure used, empty all drums (as defined by RCRA, 40 CFR § 261.7) before they leave the HDI, HMDI, or IPDI user's facility. Drums to be sent to a reconditioner may also need to be decontaminated. However, since reconditioners use a variety of techniques to clean drums and to prepare them for reuse, consult with the reconditioner before using any drum decontamination procedure.

Responding to Emergencies

Fires, spills, bulging drums, and other emergencies involving ADIs require an immediate response. If you are not a trained, designated emergency responder, leave the immediate area and notify the appropriate emergency response personnel. **If you need assistance with a spill or other emergency involving HDI, HMDI or IPDI, call the emergency number listed on the supplier's SDS or call CHEMTREC at 1-800-424-9300.** CHEMTREC operators are available 24 hours a day, seven days a week.

1. Based on data in the ACC Center for the Polyurethanes Industry 2010 End-Use Market Survey.
2. OSHA has stated that OELs are intended to set the airborne concentrations of substances to which workers can be exposed on a daily basis for a working lifetime without significant risk of adverse effects from the material.

Legal Notice

This guidance document was prepared by the American Chemistry Council's Aliphatic Diisocyanates Panel. It is intended to provide general information to professional persons who may handle ADIs or their polyisocyanates. 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 involved in handling ADIs or their polyisocyanates 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 Aliphatic Diisocyanates Panel, 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.**

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