



# Massachusetts Chemical Fact Sheet

## 4,4'-Methylene Diphenyl Isocyanate

Methylene Diphenyl Isocyanate (MDI) is a poison when inhaled. At room temperature MDI is a solid, but it is sold and used in molten form. Workplaces are the primary source of exposure to MDI, which is an intermediary chemical in the manufacture of polyurethanes. In Massachusetts MDI use is on the rise due to a single facility, which used over 10 million pounds in 1997 to manufacture roofing insulation.

### Hazards

#### Acute (Short-Term) Health Effects

- MDI is a poison by inhalation. It is highly irritating to the eyes and respiratory tract and can cause coughing, wheezing, chest tightness, or shortness of breath. MDI is immediately dangerous to life and health at concentrations of 7.5 parts per million (ppm).
- If MDI comes into contact with skin, it can irritate the skin and cause a rash.

#### Chronic (Long-Term) Health Effects

- The chronic inhalation of MDI can result in shortness of breath, asthma, and other respiratory ailments.
- MDI is an allergic sensitizer. The chronic inhalation or skin contact with MDI may cause allergic reactions. The inhalation of MDI can cause an asthma-like allergy, where future exposure to very low levels of MDI result in asthma attacks with shortness of breath, wheezing, coughing, or chest tightness. Chronic skin contact with MDI can cause a skin allergy, where future exposures to very low levels of MDI result in itching or skin rash.
- The International Agency for Research on Cancer (IARC) classifies MDI as a Group 3 carcinogen, not classifiable as to human carcinogenicity.

#### Life-Cycle Hazards

Manufacturers produce MDI using the "phosgenation process," where phosgene is an intermediary in the manufacture of MDI. MDI production begins with the condensation of aniline and formaldehyde, which forms diphenylmethane diamine. The phosgenation (addition of phosgene) of diphenylmethane diamine produces MDI.

#### FACTS

Other Names:	Methylene Bisphenyl Isocyanate
Chemical Formula:	$C_{15}H_{10}N_2O_2$
CAS Number:	101-68-8
Vapor Pressure:	0.05 mm Hg at 20°C (68°F)
Water Solubility:	Slightly soluble
Description:	Light yellow, fused solid

- Both formaldehyde and phosgene are considered high hazard chemicals in Massachusetts.
- Formaldehyde is a probable human carcinogen and potential reproductive hazard.
- Phosgene is a lethal gas at very low concentrations. To avert potential exposure manufacturers continuously monitor operating areas with a variety of alarm and shutdown systems.

(For Section references, see endnote #1.)

### Exposure Routes

Exposure to MDI, an intermediary chemical, occurs almost exclusively in the workplace through the inhalation of vapors and aerosols and dermal contact. Facilities using MDI must minimize worker exposure in the following manner:

- Use MDI in closed systems. If a closed production system is infeasible, enclose operations and use local exhaust ventilation.
- Take precautions to avoid MDI contact. If MDI contacts skin, wash immediately. If MDI exposure may exceed 0.005 ppm, use a Mine Safety and Health Administration/National Institute for Occupational Safety and Health-approved supplied-air respirator with a full facepiece.
- Do not dry sweep MDI; use a vacuum or wet method to reduce dust during cleanup.

(For section references, see endnote #1.)



**Table 1. Massachusetts 4,4'-Methylene Diphenyl Isocyanate (MDI) Use and Output Data for 1990 and 1994 & Diisocyanates Category Use and Output Data for 1998 (pounds)**

	MDI	MDI	Diisocyanates Category
<b>Use Data -- MA TURA</b>	<b>1990</b>	<b>1994</b>	<b>1998</b>
Manufactured or Processed	6,497,517	8,636,236	5,528,156
Otherwise Used	72,534	128,277	67,632
Total TURA Inputs	6,570,051	8,764,513	5,595,788
<b>Output Data -- MA TURA</b>	<b>1990</b>	<b>1994</b>	<b>1998</b>
Generated as Byproduct	17,819	25,632	52,904
Shipped In or As Product	1,057,297	7,905,939	610,176
Total TURA Outputs	1,075,116	7,931,571	663,080
<b>Releases and Transfers -- US EPA, TRI</b>	<b>1990</b>	<b>1994</b>	<b>1998</b>
Environmental Releases	3,541	356	915
Off-site Transfers	14,748	23,567	51,041
Total TRI R&T	18,289	23,923	51,956

Note: From 1990 to 1994, MDI was reported as a single CAS number (101-68-8). In 1995, a "diisocyanates category," which includes MDI and 19 other diisocyanates (but does not include toluene diisocyanates - they are reported separately), was added to the EPCRA list of reportable chemicals. Therefore, the 1998 quantities provided cannot be compared with the earlier years. Sources: MA TURA -- Massachusetts Toxics Use Reduction Act data, 1998; and US EPA, TRI -- US Environmental Protection Agency, Toxics Release Inventory data, 1998.

use), flexible foam, binders, elastomers, adhesives and sealants, surface coatings, and fibers.

- The primary uses of rigid polyurethane foam are as an insulating or cushioning material in construction applications, appliances, packaging, transportation, and industrial applications. "Transportation" includes board insulation used in trucks, trailers, and rail cars and energy absorbing foams in automobiles. "Industrial applications" includes insulation used on tanks, pipes, and ducts.

- Manufacturers occasionally use MDI in flexible polyurethane foams, often as a blend with TDI. End-users of flexible foam include producers of transportation equipment, furniture, bedding, carpet underlay, packaging, and textiles.

- MDI is used to produce polyurethane "binders" for linking wood chips and flakes together (e.g., oriented strandboard), sand together for use in foundry molds, and rubber chips and flakes together to create surface materials (e.g., outdoor sport tracks).

## Use Nationally and in Massachusetts

MDI is part of a family of isocyanate-based chemicals called "diisocyanates" and "polyisocyanates." MDI and toluene diisocyanates (TDI) are the primary isocyanates, accounting for 94% of U.S. isocyanate production capacity in 1998. ARCO Chemical, BASF Corporation, Bayer Corp., Dow Chemical, and ICI are the principal global producers of MDI and TDI. They account for 80% of worldwide capacity and are the only producers of MDI and TDI in the U.S. MDI and TDI are primarily intermediaries in the manufacture of urethane-based materials, especially polyurethane foams.

In 1996, U.S. manufacturers consumed 1.17 billion pounds of MDI in the production of polyurethane rigid foams (53% of total

- Polyurethane elastomers include cast elastomers, microcellular products, and thermoplastic elastomers. Cast elastomer products include gaskets, shoe soles, mechanical parts, and wheels. Microcellular products include automobile parts (such as body panels, bumper covers, modular windows, and spoilers) and furniture. Thermoplastic elastomer products include extrusion-produced electrical cable jackets, flexible tubing and hose, film, and sheet and injection-produced cattle tags, hydraulic seals, instrument panels, and sport and recreational items.

- Polyurethane adhesives and sealants are used in automobile production, construction applications, packaging applications, and shoe production.
- Manufacturers also use MDI to produce polyurethane surface coatings and fibers .

Under the Massachusetts Toxics Use Reduction Act (MA TURA), MDI was reported as a specific chemical from 1990 to 1994.

**Table 2. Massachusetts 4,4'-Methylene Diphenyl Isocyanate (MDI)  
Consumption for 1990 & 1994,  
Diisocyanates Category Consumption for 1998**

Use Category [1]	Facility Name	Use (pounds)		
		MDI 1990	MDI 1994	Diisocyanates Category 1998
Polyurethane Binders	Charles G Allen	11,495	0 [2]	0
	Crest Foam	0	230,658	0
	Wollaston Alloys Inc	29,469	35,216	67,632
	subtotal	40,964	265,874	67,632
Liquid Isocyanates	Hapco Inc	0	0	101,642
	General Latex And Chemical Corp	419,223	0	0
	subtotal	419,223	0	101,642
Rigid Foam	<b>Insulation</b>			
	Firestone Building Products	5,099,761	6,956,702	0
	Heat Transfer Products	14,000	103,043	0
	<b>Packaging</b>			
	General Electric Company	31,570	25,740	72,160
	Lucent Technologies Inc	12,000	0	28,600
	Wang Labs Inc	20,701	0	0
	<b>Cushions</b>			
	Modu Form Inc	0	56,588	49,500
	subtotal	5,178,032	7,142,073	150,260
Polyurethane Elastomers	Acushnet	0	12,000	118,710
	Castall Inc	28,604	76,227	156,810
	GI Plastek Limited Partners	345,938	322,300	939,920
	New Balance Athletic Shoes	111,278	122,410	144,600
	Spalding Sports Worldwide	129,266	81,061	0
	subtotal	615,086	613,998	1,360,040
Polyurethane Fiber (Spandex)	Globe Manufacturing	128,641	407,647	798,000
	subtotal	128,641	407,647	798,000
Polyurethane Adhesives	Bostik Inc	88,605	168,886	111,072
	CL Hawthaway & Sons	99,500	120,400	613,267
	ITW Devcon	0	0	55,660
	Key Polymer Corporation	0	0	22,808
	Mace Adhesives & Coatings Co	0	0	21,329
	subtotal	188,105	289,286	824,136
Miscellaneous Liquid Urethanes	Stahl USA	0	11,365	1,144,432
	Surface Coatings Inc	0	0	84,109
	Union Specialty	0	0	67,376
	Zeneca Resins	0	34,270	998,161
	subtotal	0	45,635	2,294,078
<b>Total</b>		<b>6,570,051</b>	<b>8,764,513</b>	<b>5,595,788</b>

Note: From 1990 to 1994, MDI was reported as a single CAS number (101-68-8). In 1995, a "diisocyanates category," which includes MDI and 19 other diisocyanates (but does not include toluene diisocyanates - they are reported separately), was added to the EPCRA list of reportable chemicals. Therefore, the 1998 quantities provided cannot be compared with the earlier years; [1] Use Categories were assigned based on the Institute's examination of TURA data and in some cases may not represent the actual use; [2] "0" indicates that the facility is either not using the chemical or has dropped below the reportable threshold; Source: Massachusetts Toxics Use Reduction Act data, 2000.



(CAS 101-68-8) In 1995, a “Diisocyanates Category,” which includes MDI and 19 other diisocyanates, was added to the list of reportable chemicals. This category does not include toluene diisocyanates (TDIs); they are still reported as specific chemicals. For this fact sheet, specific MDI data for 1990 and 1994 is provided, as well as Diisocyanates Category data for 1998 in Tables 1 and 2. Facilities listed in Table 2 which reported only in 1998 may be users of other diisocyanates, not MDI.

Between 1990 and 1994 MDI use in Massachusetts grew by 2.2 million lbs., or 33%, with Firestone Building Products accounting for 1.9 million lbs. In 1990, 15 facilities used MDI to produce polyurethane binders for foundry core sand molds, polyurethane elastomers for shoe soles and the inner cores of softballs, polyurethane adhesives, rigid foam for insulation and packaging, and spandex (see Table 2).

In 1998, 19 facilities reported using 5.6 million lbs. of Diisocyanates Category. The largest difference compared with earlier MDI quantities was the decrease due to Firestone Building Products, which ceased operations in Massachusetts. Increases relative to previous MDI quantities occurred in miscellaneous liquid urethanes, and polyurethane elastomers, fiber and adhesives.

Table 1 includes two sources of “output” data: MA TURA and U.S. Environmental Protection Agency (EPA), Toxics Release Inventory (TRI) data. The MA TURA database includes all non-product material created by a process line prior to release, on-site treatment, or transfer (“byproduct”) and the amount of toxic chemical incorporated into a product (“shipped in or as product”). The U.S. EPA, TRI database includes information on the waste materials generated by a facility after on-site treatment including: releases to air, land, and water (“environmental releases”) and transfers off-site for treatment or disposal (“off-site transfers”).

Reported TURA Outputs of MDI increased dramatically between 1990 and 1994, due primarily to Firestone Building Products’ change in how they reported MDI “shipped in or as product.”

- Firestone reported no MDI as shipped in or as product in 1990, but reported all MDI used (7 million lbs.) as shipped in product in 1994.

In 1998, approximately 50,000 lbs. of Diisocyanates Category were reported as byproduct.

- Bostik, Inc. reported 19,000 lbs., and New Balance Athletic Shoes and Globe Manufacturing each reported approximately 10,000 lbs. of byproduct.

TRI environmental releases and transfers of MDI increased by 30% between 1990 and 1994.

- Environmental releases decreased by 90% between 1990 and 1994. Offsetting that were increases in off-site transfers.

(For section references, see endnote #2.)

## Regulatory Context

The U.S. Occupational Safety and Health Administration (OSHA) and U.S. EPA regulate MDI.

- The OSHA permissible exposure limit (PEL) for MDI is 0.02 ppm and should not be exceeded at any time.

The U.S. EPA regulates MDI under the authority of three environmental statutes. Under the:

- Clean Air Act, MDI is a “hazardous air pollutant.”
- Comprehensive Environmental Responsibility, Compensation and Liability Act (popularly known as “Superfund”), MDI is a “hazardous substance.”
- Emergency Planning and Community Right-to-Know Act, TRI program, all large quantity users of MDI must submit data on environmental releases and off-site transfers.

For related information, see the Toxics Use Reduction Institute Formaldehyde and Toluene Diisocyanates Chemical Fact Sheets.

### Endnotes

- 1 Environmental Defense Fund (EDF), 1999, “Chemical Profile: 1,1’Methylenebis(4-Isocyanatobenzene)” (New York: EDF; see webpage: <http://www.scorecard.org/chemical-profiles/>); Richard J. Lewis, Sr. (ed.), 1993, *Hazardous Chemicals Desk Reference* (New York: Van Nostrand Reinhold); New Jersey Department of Health and Senior Services, 1998, “Hazardous Substance Fact Sheet: Methylene Bisphenyl Isocyanate” (Trenton, New Jersey; see webpage: <http://www.state.nj.us/health/eoh/rtkweb/rtkhsfs.htm>); and U.S. EPA, Office of Air Quality Planning and Standards, 1998, “4,4’-Methylenediphenyl Isocyanate” (Washington, D.C.: U.S. EPA; see webpage: <http://www.epa.gov/ttn/uaatw/hlthef/methyl-d.html>); Stanford Research Institute (SRI) International, *Chemical Economics Handbook*, “Diisocyanates and Polyisocyanates” (1998) and “Phosgene” (1997) (Palo Alto, California: SRI).
- 2 SRI International, 1998, “Diisocyanates and Polyisocyanates” (see endnote #1 for complete citation); Massachusetts Department of Environmental Protection (MA DEP), 1998, “Massachusetts Toxics Use Reduction Act Chemical Reporting Data” (Boston: MA DEP).
- 3 EDF, 1999; and New Jersey Department of Health and Senior Services, 1998 (see endnote #1 for full citations).