

Product Stewardship Summary

4,4'-Methylenediphenyl diisocyanate

General Statement

4,4'-methylenediphenyl diisocyanate (MDI) is a sensitizer with several industrial and commercial uses. It is used in the production of polyurethane resins and high-strength adhesives. MDI in commercial form typically exists as a mixture of the MDI monomer and polymeric forms of MDI (PMDI). This mixture typically contains between 45% and 65% MDI monomer by weight.

Chemical Identity

Name: 4,4'-methylenediphenyl diisocyanate (MDI) / Polymeric MDI (PMDI)

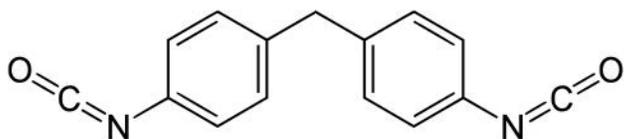
Chemical name (IUPAC): 1,1'-methylenebis(4-isocyanatobenzene)

CAS number(s): 101-68-8 / 9016-87-9

EC number: 202-966-0

Molecular formula: C₁₅H₁₀N₂O₂

Structure:



Uses and Applications

MDI is used in the production of rigid polyurethane plastics and high-strength adhesives. Ashland uses MDI to produce polyurethane "prepolymers" for use by customers in the adhesives and composite markets. The MDI prepolymer is reacted with a polyol to produce the final polyurethane. MDI is also used in high-strength adhesive products (for example, "super glues") for consumer use.



RESPONSIBLE CARE[®]

[®] Registered trademark, Ashland or its subsidiaries, registered in various countries

[™] Trademark, Ashland or its subsidiaries, registered in various countries

* Trademark owned by a third party

© 2018, Ashland



Physical/Chemical Properties

Phys/Chem Safety Assessment

Property	Value
Form	Crystalline solid
Physical state	Solid
Color	White to yellow
Odor	Aromatic
Density	1.32 g/cm ³ @ 20°C
Melting / boiling point	39°C / >300°C
Flammability	Not classified
Explosive properties	Not classified
Self-ignition temperature	>601°C
Vapor pressure	0.0000049 hPa @ 20°C
Mol weight	250.3 g/mol
Water solubility	~6.8 mg/L @ 25°C
Flash point	211°C @ 1000 hPa
Octanol-water partition coefficient (Log _{k_{ow}})	4.51 @ 22°C

Exposure, Hazard and Safety Assessment

The following section describes possible exposures scenarios and hazards associated with MDI. The exposure assessment describes both the amount of and the frequency with which a chemical substance reaches a person, a population of people, or the environment. Hazard refers to the inherent properties of a substance that make it capable of causing harm to human health or the environment. The safety assessment reports the possibility of a harmful event arising from exposure to a chemical or physical agent under specific conditions. Just because a substance may possess potentially harmful properties does not mean that it automatically poses a risk. It is not possible to make that determination without understanding the exposure.

Human Health Effects

Human Exposure Assessment

Consumer: Consumers may be exposed to MDI in the form of commercial high-strength adhesive preparations, or "super glues". Exposure to these adhesives may cause skin sensitization. When cured, these adhesives form very strong bonds and may lead to physical damage when attempting to separate joined body parts.

Worker: Workers may additionally be exposed to MDI-containing dust in polyurethane manufacturing processes. This potential exposure should be mitigated by workplace controls such as respiratory protection equipment.

Human Hazard Assessment

Effect Assessment	Result
Acute Toxicity Oral / inhalation / dermal	H332: Harmful if inhaled.
Irritation / corrosion Skin / eye / respiratory test	H315: Causes skin irritation. H319: Causes serious eye irritation. H335: Causes respiratory irritation.
Sensitization	H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled. H317: May cause an allergic skin reaction.
Toxicity after repeated exposure Oral / inhalation / dermal	H373: May cause damage to respiratory system through prolonged or repeated exposure by inhalation.
Genotoxicity / Mutagenicity	Does not affect genetic system
Carcinogenicity	Not considered as a carcinogen
Reproductive / Developmental Toxicity	Not toxic to reproduction or to unborn children
Aspiration hazard	Not applicable

Human Health Safety Assessment

Consumer: MDI can produce both skin and respiratory sensitization upon overexposure. Once sensitized, individuals can experience allergic-type responses of the skin (e.g., "poison ivy") and the respiratory system (e.g., asthma-like symptoms) at much lower levels of exposure. Because MDI has a very low vapor pressure, consumer inhalation of sensitizing concentrations of MDI vapor is highly unlikely. Inhalation of MDI dust can cause respiratory irritation and sensitization. Use of MDI-containing adhesives can cause skin sensitization if not handled properly. There is limited evidence in animal experiments for the carcinogenicity of a mixture containing monomeric and polymeric MDI. There is inadequate evidence for the carcinogenicity of MDI in humans; therefore, MDI is not classifiable as to its carcinogenicity in humans (Group 3).

Worker: MDI can produce skin and respiratory sensitization upon occupational overexposure. Because MDI has a very low vapor pressure, worker inhalation of sensitizing concentrations of MDI vapor is highly unlikely. Inhalation of MDI dust can cause respiratory irritation and sensitization. Use of MDI-containing adhesives can cause skin sensitization if not handled properly. Chronic exposure to MDI dust can lead to respiratory damage.

Environmental Effects

Environmental Exposures

As MDI hydrolyzes rapidly in aqueous environments and has a very low vapor pressure, significant environmental exposure to MDI is unlikely except in cases of significant spills.

Environmental Hazard Assessment:

Effect Assessment	Result
Aquatic toxicity	Not toxic to aquatic organisms

Fate and behavior	Result
Biodegradation	Readily biodegradable
Bioaccumulation potential	Substance does not bioaccumulate (log Kow = -0.17)
PBT / vPvB conclusion	This substance is not considered to be persistent, bioaccumulating and toxic (PBT) or very persistent and very bioaccumulating (vPvB)

Environmental Safety Assessment

MDI has a low half-life in the environment. MDI hydrolyzes rapidly in aqueous environments into an insoluble polyurea.

Risk Management Recommendations

Exposure to MDI in the workplace can be controlled by sufficient ventilation and proper handling and storage techniques. Respiratory protection should be worn in applications with the potential to generate airborne MDI dust.

A selection of occupational exposure limits are below.

US OSHA PEL (8h TWA): 0.02 ppm

ACGIH TLV: (8h TWA): 0.005 ppm UK OELV: (8h TWA): 0.02 mg / m³

China: (8h TWA): 0.05 mg/m³ (0.005 ppm)

Regulatory Agency Review

MDI is on the list of REACH registered substances (EC) 1907/2006

MDI is classified under Annex VI of Regulation (EC) 1272/2008 (CLP Regulation) with the following classification:

- Skin irritation Category 2
- Skin sensitization Category 1
- Eye irritation Category 2
- Acute inhalation toxicity Category 4
- Respiratory sensitization Category 1
- Specific target organ toxicity – Single Exposure Category 3 – respiratory irritation
- Carcinogenicity Category 2
- Specific target organ toxicity – Repeated Exposure Category 2
- Has use restrictions under REACH

MDI is on the ECHA CoRAP list

MDI is on the US TSCA inventory

MDI is listed on Canada's DSL list

MDI is on the Australia Index of Chemical Substances

MDI is on the China Inventory of Existing Chemical Substances

MDI is on the Japan Inventory of Existing and New Chemical Substances

MDI is on the Korea Existing Chemicals Inventory

MDI is regulated as toxic chemical in Korea (mixtures > 25%)

MDI is on the New Zealand Inventory of Chemicals

MDI is on the Philippines Inventory of Chemicals and Chemical Substances

MDI has been listed by IARC as group 3 (not classifiable as to carcinogenicity in humans)

Regulatory Information / Classification and Labeling

Under the Globally Harmonized System for classification and labeling (GHS), substances are classified according to their physical, health, and environmental hazards. The hazards are communicated via specific labels and the (Extended) SDS. GHS attempts to standardize hazard communication so that the intended audience (workers, consumers, transport workers, and emergency responders) can better understand the hazards of the chemicals

in use.

GHS Classification:

Acute toxicity (inhalation): Category 4

Skin corrosion/irritation: Category 2

Serious eye damage/eye irritation: Category 2

Respiratory sensitization: Category 1

Skin sensitization: Category 1B

Carcinogenicity: Category 2

Specific target organ toxicity (single exposure): Category 3 (inhalation – respiratory system)

Specific target organ toxicity (repeated exposure): Category 2 (inhalation – respiratory system)

Hazard Statements:

H315: Causes skin irritation

H317: May cause an allergic skin reaction

H319: Causes serious eye irritation

H332: Harmful if inhaled

H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled

H335: Causes respiratory irritation

H373: May cause damage to respiratory system through prolonged or repeated exposure by inhalation

H351: Suspected of Causing Cancer

Signal Word:

Danger

Precautionary Statements:

P260: Do not breathe dust / fume / gas / mist / vapors / spray P264: Do not breathe dust / fume / gas / mist / vapors / spray.

P271: Wash skin thoroughly after handling.

P272: Use only outdoors or in a well-ventilated area.

Contaminated work clothing should not be allowed out of the workplace.

P280: Wear eye protection/ face protection.

P280: Wear protective gloves.

P284: Wear respiratory protection.

P301 + P352: IF ON SKIN: Wash with plenty of water.

P304 + P340 + P312: IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER or doctor / physician if you feel

P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P333 + P313: If skin irritation or rash occurs: Get medical advice / attention.

P337 + P313: If eye irritation persists: Get medical advice / attention.

P342 + P311: If experiencing respiratory symptoms: Call a POISON CENTER or doctor/ physician.

P362 + P364: Take off contaminated clothing and wash it before reuse.

P403 + P233: Store in a well-ventilated place. Keep container tightly closed.

P405: Store locked up.

P501: Dispose of contents / container to an approved waste disposal plant.

Hazard Pictograms:



Conclusion

MDI is a useful chemical in the production of polyurethane resins and high-strength adhesives. When handled responsibly, the potential for skin and respiratory sensitization can be minimized, allowing consumers and workers to use materials containing MDI safely.

Contact Information with Company

Ashland LLC
5200 Blazer Parkway
Dublin, Ohio 43017
<http://www.ashland.com/contact>

Date of Issue: December 15, 2018

Revision: 2

Additional Information

For more information on GHS, visit <http://www.osha.gov/dsg/hazcom/ghsguideoct05.pdf> or http://live.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html.

Ashland product stewardship summaries are located at <http://www.ashland.com/sustainability/product/product-stewardship>

Disclaimer

All statements, information and data presented herein are believed to be accurate and reliable, but are not to be taken as a guarantee, an express warranty, or an implied warranty of merchantability or fitness for a particular purpose, or representation, express or implied, for which Ashland and its subsidiaries assume legal responsibility.

REACH registration is specific to Importers/Manufacturers that place the chemical on the EU market, and is specific to registered uses. Inclusion on the list of REACH Registered Substances does not automatically imply registration by Ashland.

Inclusion on the New Zealand Inventory of Chemicals applies only to the pure substance listed. The importer of

record must determine whether or not their substances are in compliance.