Product Safety Assessment

DOW™ 3019 Isocyanate


Select a Topic:
Names
Product Overview
Manufacture of Product
Product Description
Product Uses
Exposure Potential
Health Information
Environmental Information
Physical Hazard Information
Regulatory Information
Additional Information
References

Names
- CAS No. 9016-87-9 (Polymeric MDI)
- DOW™ 3019 Isocyanate
- Diphenylmethane diisocyanate
- Methylene bisphenyl isocyanate
- CAS No. 101-68-8 (4,4′-Methylene diphenyl diisocyanate)
- Methylene diphenyl diisocyanate (MDI)
- Methylene bis(p-phenyl isocyanate)
- pMDI

Product Overview
- DOW™ 3019 Isocyanate is a polymeric form of methylene diphenyl diisocyanate (MDI), typically composed of 30 to 70% monomeric MDI, with the balance, higher molecular weight fractions. For further details, see Product Description.
- DOW 3019 Isocyanate is used primarily as a component in the production of STYROFOAM™ Brand Spray Polyurethane Foam (SPF) Insulation for use in the construction industry. For further details, see Product Uses.
- There is a potential for workplace exposure to DOW 3019 Isocyanate in industrial, commercial, construction, or manufacturing settings. The Dow Chemical Company (“Dow”) sells DOW 3019 Isocyanate only for use by trained building contractors and spray foam insulation applicators. Other than in the workplace, exposure is unlikely. For further details, see Exposure Potential.
- Eye contact with isocyanates may cause moderate eye irritation and slight, temporary corneal injury. Brief skin contact may cause slight irritation with local redness. Prolonged skin contact may stain the skin and cause slight irritation with local redness or an allergic skin reaction, but is not likely to result in absorption of harmful amounts. Inhalation exposure may cause allergic respiratory response. Asthma-like symptoms may include coughing, difficult breathing and a feeling of tightness in the chest; occasionally, breathing difficulties may be life threatening. This product has low toxicity if swallowed. For further details, see Health Information.
- If released to the environment, DOW 3019 Isocyanate reacts rapidly with water to form insoluble polyureas which are expected to slowly degrade in the environment. Due to their high molecular weight, these polyureas do not accumulate in the food chain, and are practically non-toxic to aquatic organisms on an acute basis. For further details, see Environmental Information.
- DOW 3019 Isocyanate is stable under recommended storage conditions, but can decompose at elevated temperatures. Contamination of any MDI product with water may have potentially hazardous consequences. This product reacts with water, forming an insoluble polyurea and releasing carbon dioxide and heat, which can cause pressure build-up, plugging of lines and

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Created: June 3, 2013 The Dow Chemical Company Page 1 of 7
Product Safety Assessment: DOW™ 3019 Isocyanate

valves, and rupture of closed containers.\textsuperscript{13} Even relatively small amounts of water can cause notable problems. For further details, see Physical Hazard Information.

Back to top

Manufacture of Product\textsuperscript{14}

- **Location** – In 2011, global production capacity of MDI was estimated to be 5,810 metric kilotonnes (12.8 billion pounds). The Dow Chemical Company has a global capacity of 660 metric kilotonnes (1.5 billion pounds) annually. Dow and its global affiliates manufacture this product in facilities in the U.S., Europe, and Asia.
- **Process** – The manufacture of MDI begins with the condensation of aniline and formaldehyde to form diphenylmethane diamine.

\[
\begin{align*}
\text{aniline} & \quad + \quad \text{HCHO} \quad \xrightarrow{\text{HCl}} \quad \text{diphenylmethane diamine} \\
\text{formaldehyde} & \quad \text{water}
\end{align*}
\]

Subsequent phosgenation yields an aromatic isocyanate product mix largely corresponding to the composition of the polyamine; in the case of the p,p'-diphenylmethane diamine, MDI is obtained.

\[
\begin{align*}
\text{diphenylmethane diamine} & \quad + \quad 2 \text{ COCl}_2 \quad \xrightarrow{\text{hydrogen chloride}} \quad \text{MDI} \\
\text{phosgene} & \quad \text{MDI}
\end{align*}
\]

Typically, a mixture consisting of MDI and its dimer and trimer is produced. Some tetramer and higher adducts are also formed. The polyamine adduct, often referred to as polymethylene polyphenylamine (PMPPA), after phosgenation produces polymethylene polyphenyl isocyanate (or polymeric MDI). These polyisocyanates are represented in a simplified manner as follows:

```
NCO
CH\_2\[\text{NCO}
\]
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Pure MDI can be recovered via distillation from an MDI/polymeric MDI reaction mixture, leaving a product with a slightly lower MDI content.

Back to top

Product Description\textsuperscript{15,16}

DOW™ 3019 Isocyanate is a polymeric form of methylene diphenyl diisocyanate (MDI), typically composed of 30 to 70% monomeric MDI, with the balance, higher molecular weight fractions. Pure MDI is a solid at room temperature with a melting point of 39°C (102°F) to 43°C (109°F). Polymeric MDI is a brown liquid with a musty odor and an indefinite melting point around 0°C (32°F).

Back to top

Product Uses\textsuperscript{17,18,19}

In general, MDI products are used in applications such as building materials and construction, appliances, packaging, automotive trim and seating, insulation and laminated panel cores, structural foam, furniture, industrial products, coatings, adhesives, binders, sealants, and elastomers.

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Created: June 3, 2013

The Dow Chemical Company

Page 2 of 7
Most DOW™ 3019 Isocyanate is mixed and reacted with specific polyols and blowing agents using specialized spray equipment to produce STYROFOAM™ Brand Spray Polyurethane Foam (SPF) Insulation, a closed-cell foam for use as thermal insulation and air sealant in interior and exterior building construction.

U.S. Consumption of MDI in Rigid Foam (2011)\textsuperscript{17}

<table>
<thead>
<tr>
<th>Category</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>Construction</td>
<td>63%</td>
</tr>
<tr>
<td>Appliances</td>
<td>17%</td>
</tr>
<tr>
<td>Packaging</td>
<td>6%</td>
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<tr>
<td>Industrial</td>
<td>6%</td>
</tr>
<tr>
<td>Transportation</td>
<td>2%</td>
</tr>
<tr>
<td>Other</td>
<td>6%</td>
</tr>
</tbody>
</table>

Exposure Potential\textsuperscript{20,21,22,23,24}
DOW™ 3019 Isocyanate is used almost exclusively by trained construction contractors and spray foam insulation applicators. Based on the uses for this product, individuals could be exposed through:

- **Workplace exposure** – Although there is a potential for workplace exposure to DOW 3019 Isocyanate in facilities where the product is manufactured, the potential is reduced because this product is produced, transported, and stored in closed systems with stringent process controls. Other engineering controls and the use of appropriate safety equipment also mitigate the potential for injury in industrial settings. Those working with DOW 3019 Isocyanate in manufacturing operations could be exposed during maintenance, sampling, testing, or other procedures. Each manufacturing facility should have a thorough training program for employees and appropriate work processes, ventilation, and safety equipment in place to limit exposure. See Health Information.

- **Consumer exposure to products containing DOW 3019 Isocyanate** – DOW 3019 Isocyanate is sold primarily as a component of STYROFOAM™ Spray Polyurethane Foam (SPF) insulation. These products are only applied by trained and experienced construction contractors and spray foam insulation applicators. Carefully reading and following application instructions and using the appropriate safety equipment will minimize the exposure potential. Exposure of building occupants or other individuals is unlikely since only the professional and trained applicators and support workers are to be in the area during application. The ventilation systems of the application areas are to be isolated from other occupied areas of the building during application. The material is fully cured within 24 hours. Contact with the dried and cured product is not considered to represent a risk to consumers. See Health Information.

- **Environmental releases** – In the event of a spill, the focus is on containing the spill to prevent contamination of soil, surface water, or groundwater. Respiratory protection is necessary for cleaning up spills and leaks. Eliminate all sources of ignition immediately. For small spills, DOW 3019 Isocyanate should be absorbed with materials such as soil, sand, or clay. Do not use cement as an absorbent. Release of DOW 3019 Isocyanate to the atmosphere is unlikely due to its low vapor pressure. If released to the environment, it will rapidly react with water to form insoluble polyureas which will tend to float on water and ultimately bind to soil and sediments. These polyureas will likely be removed in wastewater treatment facilities by adsorption to biosolids. See Environmental, Health, and Physical Hazard Information.

- **Large release** – Industrial spills or releases are infrequent and generally contained. If a large spill does occur, the product should be captured, collected, and reprocessed or disposed of according to applicable governmental requirements. Containment and clean up should only be done by properly trained and equipped personnel. All others should leave the contaminated area. See Environmental, Health, and Physical Hazard Information.

- **In case of fire** – Deny any unnecessary entry into the area and consider the use of unmanned hose holders. Use water spray or fog, carbon-dioxide or dry-chemical extinguishers, or foam to fight the fire. Use of a direct water stream may spread the fire. Firefighters should wear positive-pressure, self-contained breathing apparatus (SCBA) and protective firefighting clothing. Individuals should be warned of downwind vapor explosion hazards. Vapors are heavier than air and may travel a long distance and accumulate in low-lying areas. Keep vapors out of sewers. Immediately withdraw all personnel from the area in case of rising sounds from venting safety device or discolorations of the container. Keep fire water out of waterways and sewers to minimize the potential for environmental damage. Follow emergency procedures carefully. See Environmental, Health, and Physical Hazard Information.

For more information, request the relevant Safety Data Sheet from the Dow Customer Information Group.
Health Information²⁵,²⁶

**Eye contact** – Contact may cause moderate eye irritation and slight, temporary corneal injury. Chemical goggles should be used when working with this product and an eye wash fountain should be located in the immediate work area.

**Skin contact** – Prolonged contact may cause slight skin irritation with local redness or may stain skin. Skin contact may cause an allergic skin reaction. Animal studies have shown that skin contact may play a role in respiratory sensitization.

**Inhalation** – At room temperature, vapors are minimal due to low vapor pressure. However, certain operations may generate vapor or mist concentrations sufficient to cause respiratory irritation and other adverse effects. Such operations include those in which the material is heated, sprayed, or otherwise mechanically dispersed, such as drumming, venting, or pumping. Excessive exposure may cause irritation to the upper respiratory tract (nose and throat) and lungs or pulmonary edema (fluid in the lungs.) Effects may be delayed. Decreased lung function has been associated with overexposure to isocyanates. Inhalation may result in an allergic respiratory response. Concentrations below the exposure guidelines may cause allergic respiratory reactions in individuals who are already sensitized. Asthma-like symptoms may include coughing, difficult breathing, and a feeling of tightness in the chest. Occasionally, breathing difficulties may be life threatening.

**Ingestion** – This product has low toxicity if swallowed. Small amounts swallowed incidental to normal handling operations are not likely to cause injury. However, swallowing larger amounts may cause injury.

**Other** – Lung tumors have been observed in laboratory animals exposed to respirable aerosol droplets of MDI products for a lifetime. These tumors occurred along with respiratory irritation and lung injury. Current exposure guidelines are expected to protect against these effects. In laboratory animals, exposure to MDI products did not cause birth defects, with other fetal effects occurring only at doses that were toxic to the mother.

For more information, request the relevant Safety Data Sheet from the Dow Customer Information Group.

Environmental Information²⁷,²⁸

Release of DOW 3019 Isocyanate to the atmosphere is unlikely due to its low volatility. If released to the aquatic or terrestrial environment, DOW™ 3019 Isocyanate reacts rapidly with water forming insoluble polyureas. This reaction limits the mobility of this product in soil and water.

Although the polyureas are essentially non-biodegradable, they are expected to slowly degrade in the environment, including degradation by physical action or by exposure to sunlight. The polyureas will likely be removed in wastewater treatment facilities by adsorption to biosolids.

Due to their high molecular weight, the polyureas do not accumulate in the food chain and are practically non-toxic to aquatic organisms on an acute basis (LC₅₀/EC₅₀ >100 mg/L in the most sensitive species tested).

For more information, request the relevant Safety Data Sheet from the Dow Customer Information Group.

Physical Hazard Information²⁹

DOW™ 3019 Isocyanate is stable under recommended storage conditions. However, it can decompose at elevated temperatures. Decomposition products depend upon temperature, air supply, and the presence of other materials. Gases may be released during decomposition. Generation of gas during decomposition can cause rapid pressure build-up in closed systems.

DOW 3019 Isocyanate reacts with water, releasing carbon dioxide and heat, which can cause pressure buildup, plugging of lines and valves, and rupture of closed containers. Elevated temperatures can accelerate this reaction and cause hazardous polymerization.
Avoid contact with acids, alcohols, amines, water, ammonia, bases, metal compounds, moist air, moist organic absorbents and strong oxidizers. DOW 3019 Isocyanate will react with many materials – sometimes violently – and the rate of reaction increases with temperature and increased contact.

For more information, request the relevant Safety Data Sheet from the Dow Customer Information Group.

Additional Information
- Safety Data Sheet – request from the Dow Customer Information Group at www.dow.com/assistance/dowcig.htm
- "Methylene diphenyl disocyanate (MDI):CAS No. 9016-87-9," Screening Information Data Set (SIDS) Initial Assessment Profile for SIAM 17, Organisation for Economic Co-operation and Development (OECD), ORTEP, Jeju, South Korea, November 11–14, 2003 (http://webnet.oecd.org/HPV/UI/handler.axd?id=1ce6c2a2-97f0-40fd-9ea5-2d21de174a1e)


References


NOTICES

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[Back to top]