Product Safety Assessment

Toluene Diisocyanate

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Names
- CAS No. 26471-62-5 Mixed isomers
- CAS No. 91-08-7 2,6-TDI
- CAS No. 584-84-9 2,4-TDI
- Toluene diisocyanate
- TDI
- 2,4-Toluene diisocyanate
- 2,6-Toluene diisocyanate
- 1,3-Diisocyanatomethyl-benzene
- 2,4-Diisocyanatomethyl-benzene
- VORANATE™ T-80 TDI

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Product Overview

- Toluene diisocyanate (TDI) is a reactive chemical. TDI’s isocyanate groups (–N=C=O) can be reacted with polymers that have alcohol (–OH) groups to make polyurethanes.¹ For further details, see Product Description.
- TDI-based products are commonly used in automotive seating, furniture foam applications, mattress cushioning, and specialty foam applications.² For further details, see Product Uses.
- TDI is typically produced in closed systems with stringent process controls, which reduce the potential of workplace exposure. Consumers may be exposed to TDI via “do-it-yourself” applications in the United States (U.S.). For further details, see Exposure Potential.
- All diisocyanates are very reactive chemicals that are potentially hazardous to humans. The inhalation of diisocyanate vapors and aerosol mists represents the primary hazard in the use of diisocyanates; therefore, they must be handled carefully and with procedures designed to minimize exposure.¹ Although large quantities of diisocyanates are used without adverse health effects, some cases of bronchial hyper-reactivity have occurred. For further details, see Exposure Potential and Health Information.
- TDI can be a skin and respiratory sensitizer. Even concentrations below exposure guidelines may cause allergic respiratory reactions in individuals already sensitized.³ Excessive vapor concentrations of TDI may cause serious adverse effects when inhaled, even death. TDI is listed as a potential carcinogen based on studies by the National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC). These findings were based on oral ingestion studies in laboratory animals. However, TDI did not cause cancer in laboratory animals exposed to TDI by inhalation. TDI shows little, if any, mutagenic activity and no adverse effects on reproduction.¹ For further details, see Health Information.
In the aquatic and terrestrial environment, TDI reacts with water forming insoluble polyureas that are chemically and biologically inert. Studies show that bioconcentration (accumulation in the aquatic food chain) is unlikely. For further details, see Environmental Information.

FOR EMERGENCY RESPONSE INSIDE THE UNITED STATES: Call CHEMTREC (1-800-424-9300) for first response advice for handling TDI. CHEMTREC will make contact with the manufacturer.

TDI reacts with water to produce heat and carbon dioxide (CO₂) gas. For further details, see Physical Hazard Information.

Manufacture of Product

- **Capacity** – In 2008, worldwide production capacity of TDI was 2,201 thousand metric tons (4.85 billion pounds). Dow’s global capacity is reported as 160 thousand metric tons (352 million pounds) of TDI per year from the following locations: Freeport, Texas, in the U.S.; and Camacari, Brazil. However in 2010, Dow discontinued production of TDI in the U.S.

- **Process** – The current manufacturing technology for most isocyanates is based on the phosgenation of primary amines. The conventional phosgene-based process is outlined below:

  Synthesis of TDI begins with the nitration of toluene using a nitric acid-sulfuric acid mixture. Note: The reaction is shown for the 2,4-isomer only.

  \[
  \begin{align*}
  &\text{CH}_3 \text{C}_6\text{H}_4 \text{NO}_2 + 2 \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 \text{C}_6\text{H}_4 \text{N}_2\text{O}_2 + 2 \text{H}_2\text{O} \\
  \text{Toluene} &\quad \text{Nitric Acid} & \quad \text{Dinitrotoluene} &\quad \text{Water}
  \end{align*}
  \]

  The nitration product is reduced catalytically.

  \[
  \begin{align*}
  &\text{CH}_3 \text{C}_6\text{H}_4 \text{N}_2\text{O}_2 + 6 \text{H}_2 \xrightarrow{\text{catalyst}} \text{CH}_3 \text{C}_6\text{H}_4 \text{NH}_2 \text{NH}_2 + 4 \text{H}_2\text{O} \\
  \text{Dinitrotoluene} &\quad \text{Hydrogen} & \quad \text{Toluene Diamine} &\quad \text{Water}
  \end{align*}
  \]

  The diamine isomer mixture is dissolved in monochlorobenzene or ortho-dichlorobenzene and is reacted with phosgene to produce toluene diisocyanate.
Product Description
Toluene diisocyanate (TDI) is a colorless to pale yellow liquid with a pungent odor. TDI can have different forms or isomers. TDI isomers have the same chemical formula \( \text{C}_9\text{H}_6\text{N}_2\text{O}_2 \), but the atoms are arranged differently. So, the term “TDI” represents the isomeric compounds along with mixtures of these isomers. The two commonly used isomers of toluene diisocyanate are 2,4-TDI and 2,6-TDI. Mixtures of 80% 2,4-TDI and 20% 2,6-TDI are the most commonly used in industry, although TDI is commercially available in the following forms:

- 100% 2,4-TDI
- 80% 2,4-TDI, 20% 2,6-TDI
- 65% 2,4-TDI, 35% 2,6-TDI

Dow currently sells VORANATE™ T-80, which is an 80/20 mixture of the 2,4- and 2,6-isomers, respectively.

Product Uses
Toluene diisocyanate is commonly used to manufacture:

- **Flexible foam**: Flexible polyurethane foams constitute the largest market for TDI products. The largest end-use markets for TDI-based flexible foams are transportation, carpet underlay and furniture.
- **Rigid foam**: Most rigid foam applications use polymeric MDI as the isocyanate component. In the past, only small amounts of TDI were consumed in pour-in-place applications, primarily for appliances, but smaller amounts for construction, packaging and transportation segments. Only minor quantities continue to be used in small-volume rigid foam applications such as surfboards.
- **Adhesives, sealants, surface coatings and elastomers**: TDI is used predominantly for sealants in construction applications. TDI is used principally in urethane alkyds, reactive two-component systems and moisture-curing prepolymer products (mainly for construction coatings). In the past, TDI was used in small amounts in three types of elastomers – reaction-injection molding (RIM), cast and thermoplastic (TPU). Currently, TDI is only used for cast elastomers.
Exposure Potential

TDI is used in the production of industrial and consumer products. Based on the uses for TDI, the public could be exposed through:

- **Workplace exposure** – Exposure can occur either in a TDI manufacturing facility or in the various industrial or manufacturing facilities that use TDI. TDI is produced, distributed, stored and consumed in closed systems with stringent process controls. Those working with TDI in manufacturing operations could be exposed during maintenance, sampling, testing or other procedures. Each manufacturing facility should have a thorough training program for employees, appropriate work processes and safety equipment in place for employees to limit TDI exposure. Because of the potential hazards posed by TDI vapors, exposure limits have been established regarding allowable TDI vapor concentrations in the work environment. Workers should be examined for pulmonary function with particular emphasis on allergic history including asthma or other diseases. Employment in an isocyanate area may present a health risk to individuals with a history of respiratory problems or allergies. See Health Information.

- **Consumer exposure to products containing TDI** – Dow does not sell TDI for direct consumer use, but TDI is used as a raw material to make polyurethane coating materials. There may be the potential for consumer TDI exposure to some consumer products via “do-it-yourself” applications in the United States, primarily with adhesives and glues. Both inhalation and dermal exposures are possible, although concentrations in these instances are difficult to quantify. The opportunity for exposures to TDI would be relatively short due to its reactivity with moisture. Because of the risk of irritation and sensitization, the use of protective gloves, as recommended on product labels, will limit potential dermal exposures. Due to the risk of allergic respiratory reactions, the use of respiratory protection as suggested in the Safety Data Sheet (SDS) will limit potential inhalation exposure. See Health Information and the relevant SDS for more information about protective equipment.

- **Environmental releases** – All spills and leaks should be immediately contained to prevent contamination of soil, surface or ground water. The area should be ventilated; open all doors and windows. To avoid inhaling vapors of TDI or the decontamination byproducts, workers should wear approved, positive-pressure self-contained breathing apparatus (SCBA). For small spills, TDI should be absorbed with materials such as: sawdust, vermiculite, dirt, sand or clay absorbents. Shovel the absorbent into an open container and cover, but do not seal. Attempt to neutralize the absorbed mixture with a suitable decontaminant solution and then add more absorbent material. Consult the VORANATE™ T-80 Toluene Diisocyanates Safe Handling & Storage Guide and relevant Safety Data Sheet for more information about protective equipment and procedures. See Environmental, Health and Physical Hazard Information.

- **Large release** – Industrial spills or releases are infrequent and are generally contained. In the event of a large spill, local emergency response services should be contacted immediately, and a state of emergency should be declared for the affected area. Contingency arrangements should be discussed with local emergency response services, such as police and fire units, in advance of actual emergency situations. A written emergency plan for large spill control should be in place with periodic drill practices scheduled before actual emergency situations occur. A positive-pressure, self-contained breathing apparatus (SCBA) with a full-face mask approved by NIOSH is recommended for emergency work. Follow emergency plan guidelines and procedures carefully.

- **FOR EMERGENCY RESPONSE INSIDE THE UNITED STATES:** Call CHEMTREC (1-800-424-9300) for first response advice for handling TDI. CHEMTREC will make contact with the manufacturer. The material should be neutralized, captured, collected and re-processed, or disposed of according to applicable governmental requirements. Consult the VORANATE T-80 Toluene Diisocyanates Safe Handling & Storage Guide and relevant Safety Data Sheet for more information. See Environmental, Health and Physical Hazard Information.

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Health Information ²⁻⁵

**Eye Contact:** TDI may cause severe eye irritation and moderate corneal injury. Vapor may cause eye irritation experienced as mild discomfort and redness.

**Skin Contact:** Prolonged contact with TDI may cause severe skin irritation with local redness and discomfort. Skin contact may cause an allergic skin reaction. Animal studies have shown that skin contact with isocyanates may play a role in respiratory sensitization.

**Inhalation:** Easily attainable vapor concentrations may cause serious adverse effects, even death. Excessive exposure to TDI may cause severe irritation of the upper respiratory tract and lungs, fluid in the lungs, permanent decrease of lung function, neurological disorders, cholinesterase depression and gastrointestinal distress.

**Respiratory Sensitization:** TDI may cause allergic respiratory response. Re-exposure to extremely low isocyanate concentrations may cause allergic respiratory reactions in individuals 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. Effects may be delayed.

**Ingestion:** TDI has low toxicity if swallowed. Small amounts swallowed incidentally as a result of normal handling operations are not likely to cause injury; however, swallowing larger amounts may cause injury. Swallowing may result in gastrointestinal irritation or ulceration. Good personal hygiene must be followed and hands washed before eating. Food should not be consumed or stored in the work area.

**Other:** An oral study in which high doses of TDI were reported to cause cancer in animals has been found to contain numerous deficiencies which compromise the validity of the study. TDI did not cause cancer in laboratory animals exposed by inhalation, the most likely route of exposure. TDI did not cause birth defects in laboratory animals. Slight effects were observed in the fetus but only at doses which caused toxic effects to the mother.

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

Environmental Information ³

When an isocyanate group reacts with water, it forms an amine, which itself reacts even faster with another isocyanate group to yield a urea. TDI reacts with water to form stable, insoluble polyureas, which are inert solids. So the reactivity of TDI with water dramatically limits its mobility in the event of a spill.

Because TDI reacts with water to form solids, biodegradation studies for TDI relate to the inert polyureas. These polyureas have not been found to be inherently biodegradable and they have not been found to bioaccumulate. Upon exposure to the environment (with and in water), unreacted TDI is practically unavailable. Nonetheless, TDI has been tested in a number of aquatic species with overall findings showing low to moderate toxicity.

Because released amounts of TDI are low, and exposure is further limited by the reactivity of TDI in water which severely limits its availability and environmental transfer in anticipated conditions, even accidental spills are localized and have only transient impact. Thus, the Organization for Economic Cooperation and Development (OECD) concluded that TDI does not present a significant risk to the environment.
However, TDI should be prevented from entering into soil, ditches, sewers, waterways and/or groundwater because of its reactivity with water. Spilled material should be contained if possible.

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

**Physical Hazard Information**

TDI is stable under recommended storage conditions. However, it can decompose at elevated temperatures. Gas generated during decomposition can cause pressure in closed systems. Pressure build-up can be rapid.

During a fire, smoke may contain TDI in addition to unidentified toxic and/or irritating compounds. Hazardous combustion products may include, but are not limited to: nitrogen oxides, isocyanates, carbon monoxide, carbon dioxide and hydrogen cyanide.

TDI can react violently with moisture, releasing carbon dioxide gas. The resulting pressure buildup can cause closed containers to rupture. Elevated temperatures can accelerate this reaction.

Hazardous polymerization of TDI can occur. Polymerization can be catalyzed by strong bases and water.²

Spills of TDI should be absorbed with material such as: vermiculite, dirt, sand, or clay. The absorbent mixture should be neutralized with a suitable decontaminant solution. Do not place in sealed containers because pressure could build up as TDI reacts with any moisture that is present. Wash the spill site with large quantities of water. Contact CHEMTREC (1-800-424-9300) for first response advice and cleanup assistance.²

Additional information on TDI physical hazards, reactivity and stability and accidental release measures such as TDI spill clean up guidance is available Safety Data Sheet that can be requested from the Dow Customer Information Group.

**Regulatory Information**

Regulations may exist that govern the manufacture, sale, transportation, use and/or disposal of TDI. These regulations may vary by city, state, country or geographic region. Information may be found by consulting the relevant Safety Data Sheet or Contact Us.

**Additional Information**

- Safety Data Sheet (request from the Dow Customer Information Group: www.dow.com/assistance/dowcig.htm)
- Contact Us (www.dow.com/polyurethane/contact/index.htm)
- Draft Organization for Economic Cooperation and Development (OECD) Screening Information Data Set (SIDS) Initial Assessment Report for SIAM, June 15, 2004
- *Safe Handling of Toluene Diisocyanate (TDI)*, Produced by PRIMEDIA Workplace Learning, Inc., Copyright 1999
Product Safety Assessment: Toluene Diisocyanate (TDI)


For more business information about TDI, visit the Dow Polyurethanes web site at www.dow.com/polyurethane/.

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References

2 VORANATE™ T-80 TDI Products, The Dow Chemical Company.
4 Video, Safe Handling of Toluene Diisocyanate (TDI), PRIMEDIA Workplace Learning, Inc., 1999.

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