# Massachusetts Chemical Fact Sheet

## Toluene Diisocyanates

*This fact sheet is part of a series of chemical fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand the chemical's use and health and environmental effects, as well as the availability of safer alternatives.*

| TABLE 1: TDI FACTS [6, 7, 8] | |
|---|---|
| **TOLUENE-2,4-DIISOCYANATE** | |
| **Chemical Formula** | $CH_3C_6H_3(NCO)_2$ |
| **CAS Number** | 584-84-9 |
| **Vapor Pressure** | 0.01 mm Hg at 20°C |
| **Solubility** | Insoluble/reactive in water |
| **Flash-point** | 127°C (260°F) |
| **Description** | Colorless to pale yellow solid or liquid (above 71°F) with a sharp, pungent order |
| **TOLUENE-2,6-DIISOCYANATE** | |
| **Chemical Formula** | $CH_3C_6H_3(NCO)_2$ |
| **CAS Number** | 91-08-7 |
| **Vapor Pressure** | 0.02 mm Hg at 25°C |
| **Solubility** | Insoluble/reactive in water |
| **Flash-point** | 127°C (260°F) |
| **Description** | Colorless to pale yellow solid or liquid (above 71°F) with a sharp, pungent order |
| **COMMERCIAL GRADE TOLUENE DIISOCYANATE (MIXED ISOMERS)** | |
| **Chemical Formula** | Not available: Usually 80% 2,4-TDI:20% 2,6-TDI |
| **CAS Number** | 26471-62-5 |
| **Vapor Pressure** | 0.02 mm Hg at 25°C |
| **Solubility** | Insoluble/reactive in water |
| **Flash-point** | 132°C (270°F) |
| **Description** | Clear pale yellow liquid with a sharp, pungent odor |

# Overview

Toluene diisocyanate (TDI) monomer is commercially available as toluene-2,6-diisocyanate (2,6-TDI), toluene-2,4-diisocyanate (2,4-TDI), and toluene diisocyanate mixed isomers (a mixture of 2,4 and 2,6 isomers). Exposure to TDIs can result in severe skin, eye, lung, and throat irritation, and skin and respiratory sensitization. TDIs are strong sensitizers and are classified as possible carcinogens. Workplaces are the primary source of exposure to TDIs. TDIs are used as intermediate chemicals in the manufacture of polyurethanes, among other applications. In Massachusetts, businesses used 6.6 million pounds of TDIs in 2014.

**TDI is designated as a Higher Hazard Substance under the Toxics Use Reduction Act (TURA), which lowers the reporting threshold to 1,000 lbs/year, effective January 2017.**

# Hazards

## Acute (Short-Term) Health Effects

*Inhalation.* Inhalation of TDI can cause severe irritation, asthma, and hypersensitivity pneumonitis,[1] and may progress to a chemical bronchitis with severe bronchospasm.[2] Exposure to high levels of 2,4-TDI can cause pulmonary edema (fluid build-up in the lungs).

*Eyes, Nose, Throat and Skin.* Contact with TDI can cause severe skin, mucous membrane,[3] and eye irritation and contact dermatitis. Both inhalation and dermal exposures to diisocyanates are thought to contribute to the development of isocyanate asthma.[4, 5]

## Chronic (Long-Term) Health Effects

- 2,4-TDI and 2,6-TDI are sensitizers and may cause an asthma-like allergy, where future exposure to very low levels of TDI results in asthma attacks with shortness of breath, wheezing, coughing, or chest tightness; fatalities have also been reported.[9] It is possible to be sensitized after a single exposure; however, sensitization usually takes place after months or years of exposure, after which even low exposures may be life threatening.[10]
- TDIs are classified as "possibly carcinogenic to humans" by the International Agency for Research on Cancer (IARC Group 2B)[11] and "reasonably anticipated to be human carcinogens" by the National Toxicology Program, based on evidence of carcinogenicity from oral exposure studies in experimental animals.[12]

## Exposure Routes

### Worker Health

Facilities using TDIs must minimize worker exposure. The American Conference of Governmental Industrial Hygienists (ACGIH) has recently adopted new time-weighted average (TWA) and short-term exposure limit (STEL) threshold limit values (TLVs) for TDI to:

- 8 hr TWA: 0.001 parts per million (ppm) (inhalable fraction and vapor - IFV) (previously 0.005 ppm)
- 15 min STEL: 0.005 ppm (IFV) (previously 0.02 ppm)

At 2.5 ppm, 2,4-TDI is immediately dangerous to life and health.[13]

With support from the Centers for Disease Control and Prevention (CDC), Massachusetts conducts surveillance of work-related asthma. Over the period 1993-2008, disease surveillance programs in Massachusetts, California, Michigan and New Jersey combined their data on work-related asthma. From these data, isocyanates were the ninth most frequently reported exposure among all the cases of work-related asthma.[14]

The Occupational Safety and Health Administration (OSHA) implemented a National Emphasis Program that works to prevent occupational disease associated with isocyanate exposure.[15]

### Public Health

TDI is primarily a concern for occupational health, but public exposures are possible via consumer products. Unreacted TDI is not typically present in consumer products, but some adhesives or sealants are available that contain TDI compounds that are not completely reacted when applied. Thus, users and bystanders can potentially be exposed.[16] It is also possible that residual amounts of unreacted TDI may be found in some polyurethane products. The unreacted TDI seeps out of products ("off-gases"), exposing people to small concentrations of TDI. Indoor products that could release TDI monomer include polyurethane coatings, foams and adhesives.

## Life-Cycle Hazards

Manufacturers produce TDI using the "phosgenation process," where phosgene is an intermediate in the manufacture of TDI.[17] Phosgene is a lethal gas at very low concentrations[18] and is categorized as a "more hazardous chemical" by the TURA Science Advisory Board. To avoid exposing workers to phosgene, manufacturers of TDI continuously monitor operating areas and employ a variety of alarm and shutdown systems.

## Use in the US

TDIs are part of a family of isocyanate-based chemicals called diisocyanates. TDIs and 4,4'-methylene diphenyl isocyanate (MDI) are the primary isocyanates. Currently, there are only two US producers of TDI, BASF Corporation and Bayer Corporation with a combined annual capacity of 840 million pounds.[19] TDIs and MDI are primarily used as intermediates in the manufacture of urethane-based materials, especially polyurethane foams.

In 2015, U.S. manufacturers consumed 478 million pounds of TDIs in the production of flexible polyurethane (PU) foams (85%), surface coatings (7%), cast elastomers (3%), and adhesives and sealants (5%).[20]

The primary end-uses for TDI-based PU flexible foams are (in order of highest to lowest levels of demand) bedding, transportation, furniture, carpet underlay, textiles and packaging.[21]

- End-uses for TDI-based PU surface coatings include floor and wood finishes and paints.
- Cast elastomer products made with isocyanates include gaskets, shoe soles, mechanical parts, and wheels.
- The primary end-uses for TDI-based PU adhesives and sealants are construction applications, automobile production, and shoe production.

## Use in Massachusetts

Currently, the predominant uses of TDI in Massachusetts follow national patterns. In 2014, Massachusetts facilities used 6.6 million pounds of TDIs. The major end uses for TDI in Massachusetts are polyurethane foam (88%) and surface coatings (11%) (see Table 2). TDI use is also reported in the manufacture of adhesives and sealants.

The following information is based on use reporting to the TURA program:

- Businesses subject to TURA reported a 25% increase in the use of TDI from 1990 to 2014, from 5.2 million pounds in 1990 to 6.6 million pounds in 2014 (Figure 1).
- Four facilities reported using TDI in 2014, a considerable decrease from 11 facilities in 1990 (Table 2).
- Among the facilities reporting use in 1990 and 2014, use increased among three of the four users.

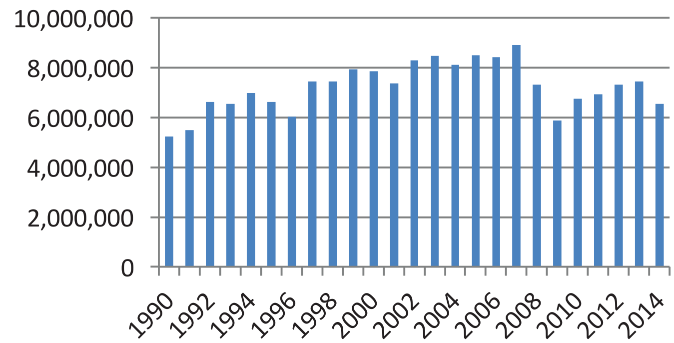
**Table 2: TDI use reported under TURA, 1990 and 2014**

| Industry Sector/Use | Facility Name | Location | Use (pounds) 1990 | Use (pounds) 2014 |
|---|---|---|---|---|
| Adhesives & Sealants | *Bostik Findley Inc* | Middleton | 97,525 | 0 |
| | *CL Hauthaway & Sons* | Lynn | 66,900 | 89,145 |
| | *Mace Adhesives* | Dudley | 108,171 | 0 |
| Photographic Equipment & Supplies | *Polaroid* | Assonet | 17,470 | 0 |
| Polyurethane Fiber (Spandex) | *Globe Manufacturing* | Fall River | 706,600 | 0 |
| Flexible Polyurethane Foam | *Advanced Urethane Technologies Inc* | Newburyport | 3,315,664 | 5,768,956 |
| | *Hasbro Inc* | Salem | 430,941 | 0 |
| | *Boston Whaler Inc* | Rockland | 105,685 | 0 |
| Surface Coatings | *Allcoat Technology Inc* | Wilmington | 101,401 | 69,703 |
| | *Zeneca Resins (DSM)* | Wilmington | 149,919 | 627,973 |
| | *Stahl USA* | Peabody | 143,001 | 0 |
| **Total TDI Use** | | | **5,243,277** | **6,555,777** |

[1] Use Categories were assigned based on the Institute's interpretation of information by the facility under TURA; [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. (2016).

- One company accounted for 88% of the reported use of TDI in 2014: Advanced Urethane Technologies (formerly Crest Foam and Leggett and Platt), a manufacturer of polyurethane foam.

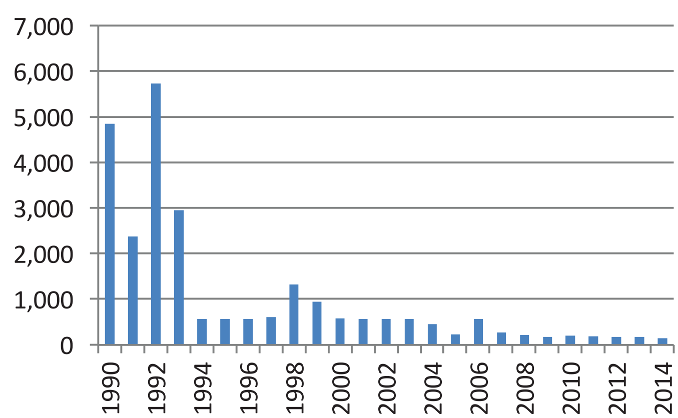
**Figure 1. TDI Use (lb), TURA Program, 1990-2014**




## Environmental Releases in Massachusetts

Massachusetts facilities reported significant reductions in environmental releases of TDI (Figure 2). From 1990-2014, releases declined 97%, from 4,843 pounds in 1990 to 146 pounds in 2014.

**Figure 2. TDI Releases (lb), TURA Program, 1990-2014**



# Alternatives

## Flexible Polyurethane Foam

Almost 88% of the TDI used in Massachusetts in 2014 was associated with the manufacture of flexible PU foams for bedding, furniture, industrial, medical, packaging and transportation applications.

Density of material and ability to recover height after compression are two key performance indicators associated with these applications. Substitute materials that do not require the use of TDI include, but are not limited to, short staple polyester fiber, cotton, coconut coir and latex foam rubber.

Short staple polyester fiber and cotton both have poor height recovery and typically require augmentation with steel springs for bedding or furniture applications. These materials also compress with time, becoming more rigid and less comfortable. Conversely, natural and synthetic latex foam rubbers can exceed flexible PU foam's performance.[22] These materials, however, are typically considerably more expensive to produce.

Alternative methods for producing flexible PU without the use of isocyanates have been investigated. At this time, non-isocyanate polyurethanes (NIPU) and hybrid NIPUs (a combination of NIPU and isocyanate-formed PU) are showing promise primarily for applications other than for flexible PU foams. Flexible NIPU foams for applications such as mattresses and furniture have not yet been commercialized.[23, 24]

## Surface Coatings, Resins, Adhesives and Sealants

*Coatings.* Alternatives to PU coatings are available for certain surface coating applications. These alternative materials, such as acrylic resins, polyesters, alkyd resins, urethane acrylate hybrids or powdered polyester resins, may not provide equivalent functionality to PU coatings and therefore must be evaluated for the specific application.

One company in Massachusetts creates coatings using a number of alternative technologies, including another alternative material, powder polyester resins, as well as alternative waterborne resin technologies and UV curable coatings. The waterborne technologies include alternative polyester materials as well as acrylic resins, urethanes, alkyd resins, and urethane acrylate hybrids.

*Powdered polyester resin coatings.* Powdered polyester resin coatings use non-isocyanate cross-linkers at lower loadings than PU powder coatings. The polyester resins are cured with triglycidyl isocyanurate (TGIC) or hydroxyl alkyl amide (HAA) cross-linkers.[25] TGIC is associated with asthma, skin sensitization, reproductive toxicity and mutagenicity,[26] along with moderate aquatic toxicity and the potential to persist and bioaccumulate in the environment. HAA causes skin irritation and serious eye irritation, and may cause respiratory irritation. These systems require less cross-linker (typically 5 to 10 percent) than the typical PU powder coating, which can call for isocyanate cross-linkers ranging from 15 to 60 percent. Polyester powder coating systems also function with decreased curing temperatures.[27]

*Non-Isocyanate Polyurethanes (NIPUs).* Significant effort to develop NIPU formulations that can be used in coatings and sealant applications is on-going. Per Figovsky *et.al,* 69 NIPU coatings have been patented since the 1950s.[28] One of the primary methods for synthesizing NIPU is from the reaction of cyclic carbonates with amines to yield hydroxyurethanes. Other methods include chemical reactions with halohydrins, halogenated carbonates and substituted propargyl alcohols.[29] These reactants are not without their own environmental and human health concerns.

An example of a NIPU coating currently on the market is from Hybrid Coating Technologies, which won the 2015 US EPA Presidential Green Chemistry Challenge for developing a plant-based PU for use in UV-cured acrylic polymer based coatings.[30] This coating is formed from a reaction of a mixture of mono and polycyclic carbonates and epoxy oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. The company utilizes hydroxyalkyl urethane modifiers based on vegetable oils, which it claims have improved performance (weathering, chemical and moisture resistance) and hazard characteristics (due to its higher molecular weight than isocyanate-based PU coatings).

Research on bio-based NIPUs that can function well in surface coatings continues to progress. For instance, researchers are working with carbonated plant seed (soy bean and linseed) oils, blends of both components, and cyclic limonene carbonates.[31, 32] In this research the plant seed oils are cured with slightly less toxic diamines to produce NIPUs that demonstrate good characteristics for surface coatings and, potentially, adhesives. While not as severe as the human health implications associated with TDI, most of the reactants in these studies have eye and skin irritation and/or sensitization concerns, and some also show evidence of reproductive toxicity. More recent research indicates that both glycerol- and sorbitol-based intermediates may be viable for preparing 100% bio-based NIPUs which can be cured at ambient temperatures in the absence of catalysts,[33] though this process is not yet commercially available.

## Regulatory Context

Due to its toxicity, TDI is subject to a number of regulations. Selected federal and state regulations, as well as related non-regulatory initiatives, are noted in the tables below.

| **TABLE 3: MASSACHUSETTS REGULATIONS & GUIDELINES** | |
|---|---|
| **Toxics Use Reduction Act** | • Listed under TURA. Designated as a Higher Hazard Substance under TURA, effective January 1, 2017. |
| **Environmental & Public Health** | • Subject to Massachusetts Right-to-Know requirements.[34]<br>• Massachusetts Ambient Air Guidelines: Threshold Effect Exposure Limit (TEL) for 2,4-TDI: 0.01 ppb (24-hour average).[35] |
| **Releases & waste cleanup** | • Reportable under 310 CMR 40.0000, the Massachusetts Contingency Plan (2,4-TDI and 2,6-TDI).[36] |

| **TABLE 4: OTHER STATE REGULATIONS (*Not Comprehensive*)** | |
|---|---|
| **California** | • Regulated as a carcinogen under Proposition 65.[37] |

| **TABLE 5: U.S. REGULATIONS AND GUIDANCE VALUES (*Not Comprehensive*)** | |
|---|---|
| **EPCRA** | • 2,4-TDI, 2,6-TDI, and TDI (mixed isomers) are all reportable under TRI.[38]<br>• Subject to US EPA Tier II reporting requirements.[39]<br>• 2,4-TDI and 2,6-TDI are regulated as Extremely Hazardous Substances (EHS) under EPCRA Section 302.[40] |
| **U.S. Safe Drinking Water Act (SDWA)** | • TDI (mixed isomers) is on EPA's SDWA Contaminant Candidate List 3. This is a list of chemicals that may be present, and are not currently regulated, in drinking water and thus are candidates for possible future regulation under SDWA.[41] |
| **U.S. RCRA** | • Regulated as a hazardous waste.[42] |
| **U.S. Clean Air Act (CAA)** | • 2,4-TDI is regulated as a Hazardous Air Pollutant (HAP). Regulated under CAA Section 112(r) List of Substances for Accidental Release Prevention with a threshold quantity of 10,000 lb per process.[43]<br>• 2,4-TDI is regulated under standards of performance for equipment in the Synthetic Organic Chemicals Manufacturing Industry (SOCMI).[44]<br>• MACT standard for flexible polyurethane foam fabrication facilities.[45] |
| **CERCLA** | • Reportable quantity: 100 lb.[46] |
| **U.S. OSH Act & Nonregulatory occupational guidelines** | • OSHA Permissible Exposure Limit (PEL) for 2,4-TDI: 0.02 ppm ceiling. (Note: This PEL was established in 1971. A more protective PEL of 0.005 ppm TWA for 2,4-TDI was set by OSHA in 1989 but vacated by a 1992 decision by the $11^{th}$ Circuit Court of Appeals.)[47] |
| **FDA** | • 2,4-TDI and 2,6-TDI: Indirect food additive for use only as a component of adhesives.[48] |
| **NIOSH IDLH** | • Immediately Dangerous to Life or Health: Ca [2.5ppm].[49] |
| **NIOSH REL** | • 2,4-TDI: Carcinogen[50] |
| **ACGIH TLV (8 hr TWA)** | For 2,4-TDI, 2,6-TDI and mixed isomers:<br>• *8 hr TWA:* 0.001 ppm (IFV)<br>• *STEL:* 0.005 ppm (IFV)[51]<br>*Basis:* asthma; pulmonary function; eye irritation. |
| **TSCA** | • The US EPA has identified TDI and related compounds as priorities for action under TSCA, publishing an Action Plan for these chemicals in 2011.[52] EPA's Action Plan focuses on exposures experienced by consumers, self-employed workers, and the general population. |

| **TABLE 6: INTERNATIONAL REGULATIONS** | |
|---|---|
| **Canada** | • Canadian Domestic Substance List (DSL): Meets human health |

| TABLE 6: INTERNATIONAL REGULATIONS | |
|---|---|
| | categorization criteria; designated as a high priority for human health.<br>• Canada has issued a Pollution Prevention Planning Notice for the Polyurethane and Other Foam Sector (P2 Planning Notice) regarding TDIs, effective as of November 2011. This notice requires affected companies to analyze and, if necessary, create plans to reduce their releases of TDIs to air.[53] |
| **European Union** | • 2,4-TDI, 2,6-TDI and TDI (mixed isomers) are all included in the EU Cosmetic Products Regulation, Annex II (list of substances prohibited in cosmetic products).[54] |

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