Toxics Use Reduction Institute
Policy Analysis
Revised December 8, 2014
Higher Hazard Substance Designation Recommendation:

Toluene Diisocyanates

listed as: 2,4-TDI (584-84-9) 2,6-TDI (91-08-7); and TDI mixed isomers (26471-62-5)

The following document analyzes the implications of designating toluene diisocyanates (listed as: 2,4-TDI [584-84-9]; 2,6-TDI [91-08-7]; and TDI mixed isomers [26471-62-5]) as Higher Hazard Substances (HHS). TDI is on the TURA Science Advisory Board (SAB) list of More Hazardous Chemicals and has been recommended for HHS designation by the SAB.

With this designation, the reporting threshold for these chemicals would be lowered from 10,000/25,000 lb/year to 1,000 lb/year for companies in TURA-covered industry sectors with ten or more employees. New companies entering the program under the lower reporting threshold would be required to file annual toxics use reports, pay annual toxics use fees, and develop a toxics use reduction plan every two years.

This policy analysis summarizes key scientific information on TDI, estimates the number of facilities that are likely to enter the program as a result of the lower reporting threshold, notes opportunities and challenges that new filers are likely to face; and discusses the implications of this policy measure for the TURA program. Based on this analysis, the Toxics Use Reduction Institute supports the SAB's recommendation that toluene diisocyanates be designated as Higher Hazard Substances.

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Revised December 8, 2014[1]
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Toluene Diisocyanate (TDI)

(listed as: 2,4-TDI [584-84-9]; 2,6-TDI [91-08-7]; and TDI mixed isomers [26471-62-5])

1. State of the Science

TDI is known to have both acute and chronic effects on human health. It is a potent dermal and respiratory sensitizer and reasonably anticipated to be a human carcinogen. The main routes of exposure are inhalation and skin contact in both occupational settings and home construction and renovation settings. Sensitized individuals must not be allowed to work around TDI, as even concentrations below permissible exposure limits are capable of triggering an allergic response.[2]

Acute toxicity

- Exposure to diisocyanates, including TDI, can cause contact dermatitis, irritation of the skin, eyes, and respiratory tract, and asthma.[3]
- TDI can also affect the respiratory, gastrointestinal and central nervous systems.
- Exposure to high levels of 2,4-TDI can cause pulmonary edema (fluid build-up in the lungs) and at 2.5 parts per million (ppm) 2,4-TDI is immediately dangerous to life and health.[4]
- Asthma attacks induced by occupational exposure to TDI and other diisocyanates can be lethal.[5]

Chronic toxicity

- TDI is a potent respiratory irritant and sensitizer. Workers who have become sensitized to TDI or other diisocyanates through respiratory or skin exposure can develop severe asthma attacks in response to subsequent exposures. Exposure to diisocyanates, including TDI, is recognized as a leading cause of work-related asthma.[6] Spray applications or heated applications that generate vapors and mists are a particular concern, as these activities can lead to significant respiratory and skin exposures.[7]
- TDI exposure is also associated with other respiratory diseases, including chronic bronchitis, chronic restrictive pulmonary disease, and hypersensitivity pneumonitis.[8]
- The International Agency for Research on Cancer (IARC) classifies TDI in Group 2B (possible human carcinogen).[9] The National Toxicology Program (NTP) classifies TDI as "reasonably anticipated to be a human carcinogen," based on evidence from animal studies. Laboratory animals exposed to TDI developed liver tumors, benign tumors of the mammary gland and pancreas, and benign and malignant tumors of subcutaneous tissue and blood vessels, among other effects.[10]

Role of uncertainty

Uncertainty does not play a significant role in the development of our recommendations for this substance.

Nomenclature

TDI is commercially available as two isomers (2,4-TDI and 2,6-TDI). It is frequently marketed as 80:20 or 65:35 (2,4-TDI:2,6-TDI) mixtures of the two isomers.[11] It is reportable under TURA as 2,4-TDI; 2,6-TDI; or mixed isomers. TDI may also be referred to in the plural, as TDIs.

TDI belongs to the larger class of diisocyanates, often referred to in the literature simply as isocyanates. The most common diisocyanates are TDI, methylene bisphenyl isocyanate (MDI), and hexamethylene diisocyanate (HDI).[12]

2. Number of facilities affected

To develop an estimate of the number and type of companies likely to be affected by a 1,000 lb reporting threshold, the Institute consulted sources including the TURA data; facilities reporting under EPCRA Tier II requirements; RCRA hazardous waste data; and past experience with other HHS designations.

TDI is a feedstock for the manufacture of polyurethanes. Uses of TDI reported under TURA include production of resins, paints, adhesives and sealants, and foam products, among others.

a. Historical data on sectors using TDI in Massachusetts

Historically, the following sectors have reported TDI use under TURA:

2821	Plastics materials and resins
2824	Organic fibers, noncellulosic
2851	Paints and allied products
2891	Adhesives and sealants
2899	Chemical preparations, not elsewhere classified
3086	Plastics foam products
3732	Boat building and repairing
3861	Photographic equipment and supplies
3944	Games, toys, and children's vehicles
5169	Chemicals and allied products

b. Current TURA data on TDI use in Massachusetts

In 2012, the most recent year for which data are available, five companies reported the use of TDI under TURA, as shown in the table below.

SIC Code		No. of 2012 Filers	Type of Use
2821	plastics materials and resins	2	Processed
2851	paints and allied products	1	Processed
2891	adhesives and sealants	1	Processed
3086	plastics foam products	1	Processed

c. Storage & hazardous waste reporting data

Some additional information on TDI use can be obtained from the EPCRA Tier II data on hazardous chemical storage[13], as well as the RCRA data on hazardous waste shipments.

- The Tier II data for 2012 show a total of seven facilities reporting TDI storage. Of these, four also filed under TURA. Based on employment data and maximum amount codes, it is reasonable to expect that either one or two of these facilities would be brought into TURA by the HHS designation.
- The RCRA data for 2012 show that ten facilities reported hazardous waste shipments of TDI (mixed isomers). Two of the facilities reporting shipment of hazardous waste currently report TDI use under TURA and one has filed in the past.

d. Past experience with HHS designations

Experience since 2006 indicates that in general, an HHS designation brings in a number of new filers in the first couple of years of the designation, and this number falls in subsequent years as filers move to safer substitutes. Each sector is different, but this pattern may be indicative of future trends as well. For the six HHS for which data are currently available, the number of new filers in the first year the designation was effective ranged from 5 to 19.

e. Estimated number of companies that would be affected by a lower reporting threshold

The TURA program estimates that approximately 2 to 9 new filers would be brought in by the HHS designation. Of these, approximately half would be facilities that already file, or have filed in the past, for other chemicals.

3. Opportunities for New Filers

In this section, we briefly review trends in TDI use among existing TURA filers, and summarize basic information on TDI alternatives in selected applications.

a. Trends in TDI use

The three reportable forms of TDI (2,4-TDI; 2,6-TDI and TDI mixed isomers) have been reported under TURA at some point by a total of 10, 7, and 14 facilities, respectively.

TDI use reported under TURA has increased significantly since the program's inception. Use has increased from 5,243,277 lb in 1990 to 7,324,842 lb in 2012 (a 40% increase), and releases have declined 97%, from 4,843 lb in 1990 to 168 lb in 2012 (figures not adjusted for changes in production levels). The increase in use can be attributed to one filer that produces flexible polyurethane foam. This filer's use has doubled since 1990.

Massachusetts TURA TDI Use and Release Data: 1990 and 2012 (figures not adjusted for production)				
	Year		**Change In lbs**	**% Change**
	1990	**2012**		
TDI used (lbs)	5,243,277	7,324,842	2,081,565	+40%
TDI released (lbs)	4,843	168	4,675	-97%

b. Opportunities to reduce TDI use

TDI is used as a monomer to manufacture flexible polyurethane foams, which are used in a wide variety of settings, including furniture and bedding. It is also used as a monomer to manufacture rigid foams, and in production of elastomers and coatings, as a cross-linking agent in nylon-6, and as a hardener in polyurethane adhesives and finishes. Applications for TDI-based polyurethane include floor finishes, wood finishes and sealers, and coatings for aircraft and trucks, among others. [14]

Polyurethane coatings, adhesives and sealants

There are on-going efforts to develop isocyanate-free chemistries for polyurethane adhesives, sealants and coatings.[15]

Petrie (2009) describes efforts to develop non-isocyanate polyurethanes (NIPUs) based on cyclocarbonate resins, synthesized from epoxy precursors. The cyclocarbonates are reacted with amines to form polyurethanes. By eliminating isocyanates, this approach also eliminates the need for phosgene in producing isocyanates upstream. [16] The resulting polyurethane "displays the equivalent high adhesion, elasticity, and strength properties of diisocyanate-based polyurethane materials, and exhibits improved hydrolytic stability and chemical resistance." [17] Several companies are working to develop and test NIPUs. [18] An analysis by the California Department of Toxic Substances Control (DTSC) notes that although the focus of NIPU research has been coatings, adhesives and sealants, they could potentially also be useful for other applications, including spray foam insulation.

Another approach to producing polyurethanes without the use of TDI or other isocyanates is the use of carbonated soybean oil reacted with diamines.[19] Researchers have made progress in developing soy-based adhesives that could serve as alternatives for formaldehyde-urea adhesives; it may be worth investigating the utility of these products as substitutes for polyurethane adhesives as well.[20]

"Other reported technologies include an isocyanates-free expanding foam product and a faster curing "isocyanates-free" flexible food packaging adhesive that reportedly prevents potential migration of isocyanates into non-dry food." [21]

For polyurethane coatings of drivable and slip resistant surfaces, the Substitution Support Portal (Subsport) database identifies an alternative that can be used for crack bridging, trafficable, slip resistant wearing layers, and car park decks, garage floors and bridges.[22] Subsport is an NGO project designed to compile information on alternatives to a variety of chemicals.

Textile surface treatments

Subsport includes information on a TDI alternative for textile treatment. Subsport notes that mixtures of fluorinated compounds plus isocyanates are frequently used to make water repellent surface treatments for textiles. Alternatives to these products are of interest because of the toxicity of the fluorinated compounds as well as the toxicity of the isocyanates. One such alternative, OC-aquasil™, "presents an alternative surface treatment for applications where a high degree of repellency towards water and water-based soil is required." The product is described as "composed of a water-based solution of organic silicon compounds and organic acid."[23]

Marine coatings

The Pacific Northwest Pollution Prevention Resource Center (PPRC) conducted a rapid review of alternatives for isocyanate-based polyurethane for above-waterline marine coatings. PPRC found that a number of alternatives were available, but technical information on performance was limited, and there were a number of open questions about health impacts. There is a need for additional research.[24]

Alternatives for flexible polyurethane foam

End-uses for flexible polyurethane foams include transportation, furniture, bedding, carpet underlay, packaging, and textile applications, among others.[25] Alternatives for flexible polyurethane foam include natural latex foam, polyester fill, cotton, down, and other materials, depending on the application. Each of these materials presents its own performance characteristics, with some advantages and some disadvantages compared with polyurethane foam. For chairs, sofas, and mattresses, alternatives include natural latex, down and feathers, buckwheat hulls, and wool, felt, and cotton batting. EnviroTextiles produces a multi-purpose high-density fiber foam product from coconut fiber and natural latex for use in mattresses, upholstery, sound proofing and a variety of other applications.[26] One concern with natural latex foam is that it may be hazardous for individuals with latex allergies.

4. Regulatory context and exposure limits

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 below.

EPCRA	• Reportable under TRI[27] • Subject to US EPA Tier II reporting requirements[28] • Regulated as an Extremely Hazardous Substance (EHS) under EPCRA Section 302 (91-08-7; 584-84-9).[29]
CAA	• Regulated as a Hazardous Air Pollutant (HAP) (584-84-9)[30] • Clean Air Act Section 112(r) List of Substances for Accidental Release Prevention (Threshold quantity: 10,000 lb. per process)[31]
RCRA	• Must be managed as hazardous waste.[32]
CERCLA	• Reportable quantity: 100 lb.[33]
OSHA PEL	• OSHA PEL: 0.02 ppm Ceiling (Note: This PEL was established in 1971. A more protective PEL of 0.005 ppm TWA for toluene-2,4-diisocyanate was set by OSHA in 1989 but vacated by a 1992 decision by the 11th Circuit Court of Appeals.)[34]
IDLH	• Immediately Dangerous to Life or Health: Ca [2.5ppm][35]
NIOSH REL	• NIOSH REL: Carcinogen[36]
ACGIH TLV (TWA)	0.005 ppm[37]
ACGIH TLV-STEL	0.02 ppm[38]
Note: The ACGIH recommended TLV values noted above are based on respiratory sensitization. Note: In 2013, ACGIH issued a notice of intended changes, as follows: TLV (TWA) 0.001 ppm STEL 0.003 ppm The TLV basis is listed as Asthma.	

EPA TSCA Action Plan

- US EPA identified TDI and related compounds as priorities for action, publishing an Action Plan for these chemicals in 2011.[39] EPA's Action Plan focuses on exposures experienced by consumers, self-employed workers, and the general population.

Other states

- TDI is regulated under California's Proposition 65 due to its carcinogenicity.

International

- 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.[40]

5. Implications for the TURA program

Designating TDI as a Higher Hazard Substance would help to fulfill the intent of the 2006 amendments to TURA, providing important guidance and incentives to Massachusetts businesses to help them move away from the most hazardous chemicals and toward safer alternatives.

A focus on TDI in Massachusetts would also be consistent with efforts to address this chemical in other states and nationally. In particular, as noted above, specific uses of TDI have been proposed as priorities for action in California, and the US EPA has identified TDI as a priority for development of an Action Plan.

Avoiding adverse substitutions

Designating TDI as a Higher Hazard Substance in 2014 would also have important implications for additional HHS designations going forward. In particular, methylene diphenyl isocyanate (MDI) is a potential substitute for TDI in some applications, and also poses serious health concerns. Other diisocyanates are also a concern.

When the Science Advisory Board (SAB) categorized MDI as a More Hazardous Chemical, it was reportable as an individual substance. It is now reportable as part of the diisocyanates category. The SAB is now considering the diisocyanates category as a whole, to determine whether its other component substances are similar in toxicity to MDI.

Because the SAB is in the process of analyzing these other chemicals, they have not yet been brought before the Administrative Council for potential HHS designation. Should the Administrative Council decide to move forward on a HHS designation for TDI, it will be important to also consider the other diisocyanates as soon as the SAB has completed its review of the category.

Opportunities for interagency coordination

Exposures not directly subject to TURA can occur through use of commercially available household products containing unreacted TDI.[41] MassDEP is starting an outreach effort to provide additional education and guidance to large retailers that sell a variety of products containing high-priority toxic chemicals. With the designation of methylene chloride as a Higher Hazard Substance, outreach to this sector has been identified as a priority for protecting consumers from methylene chloride. It would be appropriate to include information on TDI and related compounds in this effort as well.

Other considerations: trends among existing filers

For some of the HHS designations the TURA program has undertaken in the past, existing TURA filers had already achieved significant reductions in use of the chemical. In the case of TDI, the opposite is the case: use by existing TURA filers has increased over time. Use of TDI and other diisocyanates has also been increasing in construction and do-it-yourself home owner uses, driven in part by increasing interest in energy efficient building practices.

TURA program projects on risk reduction

The TURA program has collaborated with industry associations on a program to provide training on risk reduction when using diisocyanate-based spray foam insulation. This effort could be broadened to include adhesives, sealants, and polyurethanes based on TDI.

Costs to businesses of reporting, planning, and fees

There would be some additional cost to companies that would begin reporting TDI based on a lower reporting threshold, including preparing annual toxics use reports and biennial toxics use reduction plans, and paying toxics use fees.

Based on the TIER II and RCRA data the TURA program estimates new reporting of TDI by 2 to 9 facilities. For the facilities for which employment data are available, the facilities are all under 50 employees.

Most of these filers would not be new to the program and already pay a base fee, but would begin to pay a per-chemical fee of $1,100. In addition, some facilities are already paying the maximum fee corresponding to their size; these facilities would not pay any additional fee. After two years of reporting toxics use, companies are required to engage in TUR planning. The cost of planning depends on the number of chemicals used and the complexity of the process.

Companies that want to have their own in-house TUR planner can qualify either by relying on past work experience in toxics use reduction or by having a staff member take the TUR Planners' training course. Those companies with experienced staff can become certified for as little as $100. For those that want staff to take a course the cost is $650. Companies with in-house toxics use reduction planners are likely to reap ancillary benefits from having an employee who is knowledgeable about methods for reducing the costs and liabilities of toxics use. Additionally, through the process of planning and reducing or eliminating TDI use, companies may be able to expand markets, improve compliance with other regulations, and achieve financial savings through process improvements.

Assuming 2 to 9 new TDI filers with the size distribution listed above, assuming that 2 of them are completely new to TURA, and assuming that 2 of the facilities currently reporting under TURA have already reached their fee maximum, the total additional cost in fees to filers (and revenue to the program) could be approximately $4,150 to $13,250.

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[1] The original version of this Policy Analysis was completed in August 2014. This revised version contains the following changes: In Section 1, endnote #4, and Section 3, endnote #25, the source has been updated. In Sections 3

and 4, information related to the California Safer Consumer Products Regulation and spray foam insulation have been deleted because TDI is not used as a major component of these products.

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[4] *NIOSH Pocket Guide to Chemical Hazards*, available at http://www.cdc.gov/niosh/npg/npgd0621.html, viewed November 24, 2014.

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[29] US EPA. 1999. 40 CFR Part 355, Appendix A. ("*Appendix A to Part 355: The List of Extremely Hazardous Substances and their Threshold Planning Quantities*"). Retrieved from http://www.gpo.gov/fdsys/pkg/CFR-2002-title40-vol24/pdf/CFR-2002-title40-vol24-part355-appA.pdf). EPCRA Section 302 requires facilities to notify the State Emergency Response Commission (SERC) and Local Emergency Planning Committee (LEPC) of the presence of such a substance above the threshold planning quantity, and directs the facility to appoint an emergency response coordinator.
US EPA. 2012. "*Emergency Planning and Community Right-To-Know Act,*" Retrieved from http://www.epa.gov/oecaagct/lcra.html, viewed May 29, 2014.

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