Department of Toxic Substances Control

SAFER CONSUMER PRODUCTS

California Environmental Protection Agency
DEPARTMENT OF TOXIC SUBSTANCES CONTROL

PRIORITY PRODUCT PROFILE

SPRAY POLYURETHANE FOAM SYSTEMS CONTAINING UNREACTED DIISOCYANATES

MARCH 2014

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

The mission of DTSC is to protect California's people and environment from harmful effects of toxic substances through the restoration of contaminated resources, enforcement, regulation and pollution prevention.

NOTES TO READERS OF DTSC'S PRIORITY PRODUCT PROFILES

This product profile is a summary of information compiled by DTSC as of March 13, 2014. It explains the department's preliminary rationale for proposing this chemical-product combination as a Priority Product with a Chemical of Concern. Its purpose is to inform the public of the department's thinking as of that date. The Department intends to use the profile to frame conversations with interested stakeholders that will enable us to refine the descriptions of the product and chemical(s) in the regulations that will establish the Initial Priority Products List. As the department receives additional information on the chemical and product described in this document, it may modify the description of the chemical(s) or product or both prior to issuing a public notice for rulemaking. Any such changes will be reflected in the rulemaking file. Therefore, readers should consider the following:

1. This product profile is not a regulatory document and has no force of law.
2. The department requests that interested stakeholders provide data on the chemical and product described in this document to assist us in the discernment process that will lead to our regulatory proposal.
3. By proposing to list this product-chemical combination as a Priority Product with a Chemical of Concern, the department is not asserting that the product cannot be used safely, only that there is a potential for exposure of people or wildlife to the Chemical of Concern in the Priority Product and that such exposure has the potential to cause or contribute to significant or widespread adverse impacts.
4. Possible alternatives mentioned in this document that may meet one or more of the product's functional requirements are not a determination by the department that these alternatives are safer than the product-chemical combination and should not be construed as an endorsement of any alternative or product.

INTRODUCTION

Under the Department of Toxic Substances Control's (DTSC) Safer Consumer Products regulations, DTSC must publish a proposed initial Priority Products list by March 28, 2014. This draft list imposes no new regulatory requirements on product manufacturers until DTSC finalizes it by adopting regulations. This profile provides DTSCs rationale for proposing this Priority Product. To the extent practical, it follows the organization of the regulations. The section titled "Hazard Trait of the Chemical of Concern" identifies the authoritative lists[1] of chemicals on which diisocyanates appear and provides additional information on the chemical's hazard traits. The "Exposures" section identifies the chemical types specified in the regulations[2] into which diisocyanates fall.

Priority Product Identification

The Department of Toxic Substances Control here identifies spray polyurethane foam ("SPF") systems containing unreacted diisocyanates as a Priority Product.

Problem Identified

Diisocyanates are a group of low-molecular-weight organic compounds used in the production of polyurethanes in SPF systems. Diisocyanates are known respiratory, skin, and mucus membrane toxicants, capable of irritating, sensitizing, and causing asthma or triggering severe asthma attacks in sensitive populations.

Exposure to unreacted diisocyanates and other chemical ingredients in SPF systems may harm both workers who are not using exposure controls or personal protective equipment, and consumers or bystanders at the time of application and after the materials have been installed. Major exposure routes include inhalation of vapors, aerosols, and dusts, and exposure to the products and other particles containing diisocyanates through direct skin and eye contact.

Scientific studies have shown that diisocyanates are the leading attributable cause of asthma in the workplace, and asthma is common among workers in the polyurethane industry. A recent review found that 5-15% of polyurethane industry workers exhibit adverse health effects related to isocyanates exposure, and this percentage has remained stable in the last decade while use of SPF systems has been steadily increasing (Verschoor and Verschoor, 2014). Another study found that approximately 12% of polyurethane spray painters develop occupational asthma (Seguin et al., 1987).

The National Institute for Occupational Safety and Health (NIOSH) has implicated diisocyanates in the occupational deaths of U.S. workers following repeated respiratory exposures to polyurethane products (NIOSH, 1996a, 2006).

DTSC is particularly concerned about the increasing number of both independent contractors and do-it-yourselfers using SPF systems. These workers and consumers may not be aware of

[1] Identified in subsection (a)(1) of section 69502.2 of title 22 of the California Code of Regulations.
[2] Identified in subsection (a)(2) of section 69502.2 of title 22 of the California Code of Regulations.

the serious health risks associated with these products, and may not follow NIOSH or industry recommendations for engineering controls and the use of personal protective equipment when applying SPF systems (U.S. EPA, 2014). In addition, these users may not be aware of or have access to safety training recommended by the industry.

Priority Product Identification Description

Spray polyurethane foam systems for use as insulation, roofing, sealing, filling of voids and gaps, and for other uses such as in the creative arts are classified as a Priority Product if they contain one or more of the diisocyanates specified below:

- Generic methylene diphenyl diisocyanate (MDI) mixed isomers, Chemical Abstract Service Registry Number (CAS #): 26447-40-5
    - 4,4'-methylenediphenyl diisocyanate, CAS #: 101-68-8
- Toluene Diisocyanates, mixed (TDI), CAS #: 26471-62-5
    - 2,4-Toluene diisocyanate, CAS #: 584-84-9,
    - 2,6-Toluene diisocyanate, CAS #: 91-08-7
- Hexamethylene-1,6-diisocyanate (HDI), CAS #: 822-06-0

Other structural and stereochemical isomers of diisocyanates may be found in SPF systems in commerce today, and they share some common traits (U.S. EPA, 2013b; Bernstein, 1996). However, only the diisocyanates listed in this profile are identified as Chemicals of Concern by DTSC for the identified Priority Product.

Under the Global Product Classification ("GPC") System, these SPF systems may be assigned to the following bricks (GS1, 2013):

> Brick 10002456 Insulation – Loose Fill/Spray Foam: Includes any products that may be described/observed as a form of insulation poured or blown into cavities to reduce heat loss. These products when applied correctly can virtually eliminate energy wasting air filtration in lofts. Excludes products such as rigid foam board.
>
> Brick 10002692 Roofing Other: Includes any products that may be described/observed as Roofing/Exterior Trim products, where the user of the schema is not able to classify the products in existing bricks within the schema. Excludes all currently classified Roofing/Exterior Trim products.

This Priority Product designation includes any SPF material, whether professional grade or DIY products, containing the specified diisocyanates. Use of GPC Brick codes, where available, to identify California's Priority Products, may assist stakeholders in identifying such products. However, all SPF systems placed in the stream of commerce in California are classified as a Priority Product if they contain the specified diisocyanates, regardless of whether the manufacturer has assigned them to Brick 100024356 and 10002692 of the GPC.

SPF systems typically contain MDI including MDI mixed isomers, polymeric MDI, and HDI. TDI may be found in SPF systems either as a minor component or as a residual constituent, particularly in systems containing polyurethane-based materials such as coatings, which may contain TDI.

SPF systems consist of materials that are dissolved or suspended in liquid media and have not undergone the curing process to form a finished solid or rigid foam. Such liquid media may be solvent mixtures, water, or any other organic liquid combinations or mixtures. These SPF materials may be sold as one-, two-, or multiple-component systems, kits, or individual pressurized cans. At or after mixing or application, the product undergoes chemical reactions and further physical processes ("curing") to become the finished product.

SPF systems are widely available in California. Although these systems are known to differ slightly in composition, their precise product formulations are proprietary. For illustrative purposes, this profile describes two broad categories of SPF systems in more detail:

- Two-component drums/kits, and
- One-component kits/cans.

Two-component SPF drums/kits

These SPF systems are distributed in two separate mixtures, commonly referred to as "sides" (U.S. EPA, 2013a).

Side A contains diisocyanates as the active ingredient. Common diisocyanates include (U.S. EPA, 2013a):

- 4,4′-Methylene diphenyl diisocyanate (MDI), CAS # 101-68-8
- Polymeric MDI, CAS # 9016-87-9
- Generic MDI mixed isomers, CAS #26447-40-5
- Other chemicals

Side B contains proprietary chemicals that offer application-specific properties of the products. These chemicals may include (U.S. EPA, 2013a):

- Polyols
- Flame retardants
- Blowing agents
- Amine or metal catalysts
- Surfactants

When the two sides are mixed in a spray applicator, a series of chemical reactions and physical processes occur, and a polyurethane foam is generated that will 'cure' into a rigid foam. In the process, human exposure to diisocyanates is likely. Curing time may range from hours to weeks depending on the type and conditions of application (U.S. EPA, 2013c).

The polyols in Side B traditionally come entirely from petroleum sources. However, some recent product formulations substitute a fraction of the petroleum- based polyols with those derived from natural sources, such as soy- or sucrose-based oils (U.S. EPA, 2013a, BASF, 2010). Regardless of where the polyols originate, and how these products are marketed, all SPF foams contain approximately 50% diisocyanates (BASF, 2010).

Two component systems vary by pressure (high and low), density, and different types of uses or applications. For example, SPF-based roofing systems are high pressure systems and typically use the higher density 3 pound, rigid, closed cell SPF. See Table 1 for an overview of the different types of two component systems referred to in this profile.

One-component SPF kits/cans

These SPF products are premixed as a one-component mixture under pressure. They are typically sealed in 16-ounce cans, and are widely available in home improvement centers, hardware stores, and other retail locations.

The following table summarizes additional information on these systems (next page).

TABLE 1. OVERVIEW ON THE SPRAY POLYURETHANE FOAM SYSTEMS (SOURCE: U.S. EPA, 2013C)

SPF Types	**Two-Componets**		**One Component**
	High-Pressure	Low-Pressure	
	Open-Cell (low density, half lb.) Closed-Cell (medium density, 2 lb.) Closed-Cell (high density, 3 lb.)		
Uses	Larger insulation applications; Air sealant in hybrid insulation installation with fiberglass or other insulation materials; Roofing applications (Closed-Cell, high density,3 lb.)	Air sealant; Adhesive; Smaller insulation applications; Weatherization activities	Sealant for filling cracks, holes, gaps, and crevices: - Around windows and doors; ' - For sealing up small gaps (0.5" - 3") in a building to create an energy efficient building envelope
Applicator	Professional Installer	Professional Installer; Weatherization worker; Do-it-yourself (DIY) applicators	Professional Installer; Weatherization worker; DIY applicators
Container size	55 gallon drum containers	Typically three to five gallons per container from the system house, but can be purchased in larger containers over the internet or in some retail markets	Available in retail and hardware stores nationwide in a variety of sizes ranging from 12 oz. to 24 oz. cans
Chemical Exposure Potential	May be exposed to chemicals: During application After application During heat-generating processes such as drilling, welding, or sanding During fires Through: Aerosols Vapors Dust that may contain unreacted chemicals	May be exposed to chemicals: During application After application During heat-generating processes such as drilling, welding, or sanding During fires Through: Aerosols Vapors Dust that may contain unreacted chemicals	May be exposed to chemicals: During application After application During heat-generating processes such as drilling, welding, or sanding During fires Through: Aerosols Vapors Dust that may contain unreacted chemicals
Hazards	Asthma Sensitization Lung damage Other respiratory and breathing problems Skin and eye irritation	Asthma Sensitization Lung damage Other respiratory and breathing problems Skin and eye irritation	Asthma Sensitization Lung damage Other respiratory and breathing problems Skin and eye irritation
Re-Entry	Some manufacturers estimate that it can take 23 to 72 hours for the foam to fully cure after this type of application, but curing rates can vary.	Some manufacturers estimate that it can take 23 to 72 hours for the foam to fully cure after this type of application, but curing rates can vary.	Some manufacturers estimate that it can take 8 to 24 hours for one component foam to cure, but curing rates can vary.

RATIONALE FOR PRIORITY PRODUCT SELECTION

Evaluation of Adverse Impacts and Exposures

(See California Code of Regulations, title 22, section 69503.2(b)(1) and section 69503.3)

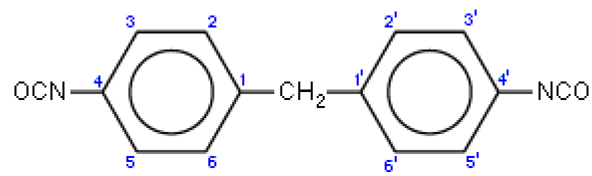
1. Chemicals of Concern: Diisocyanates

The terms "diisocyanates" and "isocyanates" may be used interchangeably throughout this profile, as both terms appear in source literature. For the most part, when the term "isocyanates" is used in this profile, it refers to isomers of diisocyanates.

Below is a brief description of the individual Chemicals of Concern:

Methylene diphenyl isocyanate or 4,4'-methylenediphenyl diisocyanates (MDI)

- CAS #s: 101-68-8 or 26447-40-5
- Chemical Abstract Name: 1,1′-Methylenebis(4-isocyanatobenzene)
- IUPAC Systematic Names for 101-68-8: isocyanic acid, methylenedi-paraphenylene ester
- Synonyms - See Appendix B
- Molecular formula: $C_{15}H_{10}N_2O_2$
- Chemical Structure (CAS #: 101-68-8):



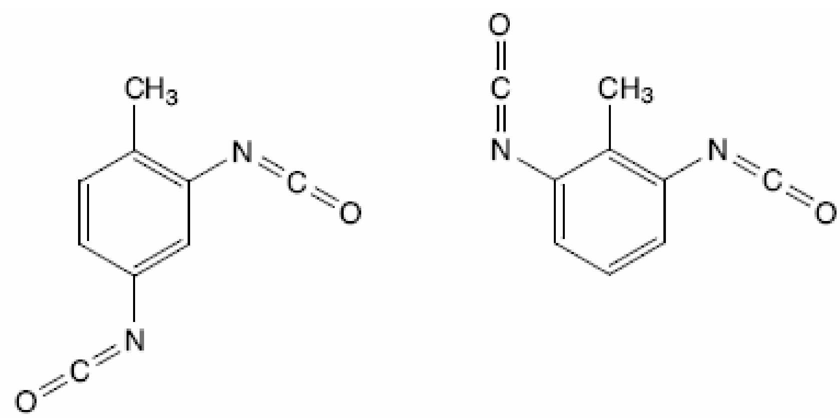
- MDI[3] meets the conditions specified in California Code of Regulations, title 22, section 69503.6(a) in that it appears on one or more of the authoritative lists in California Code of Regulations, title 22, section 69502.2(a)(1) and is one or more of the types of chemicals listed in California Code of Regulations, title 22, section 69502.2(a)(2):
    - classified by the European Commission as respiratory sensitizers Category 1 in Annex VI to Regulation (EC) 1272/2008
    - listed by the Office of Environmental Health Hazard Assessment (OEHHA) with an inhalation Reference Exposure Level (OEHHA 2014a)
    - identified as Toxic Air Contaminant (California Code of Regulations, title 17, sections 93001)

Toluene Diisocyanates (TDI)

- CAS #s:
    - 26471-62-5 (mixed isomers)
    - 584-84-9 (2,4-Toluene diisocyanate)
    - 91-08-7 (2,6-Toluene diisocyanate)
- Chemical Abstract Names:

[3] In this instance, MDI refers to CAS # 101-68-8. The basis for listing the CAS # 26447-40-5 is available on DTSC's informational list of Candidate Chemicals (DTSC, 2013)

    - 2,4-Toluene diisocyanate
    - 2,6-Toluene diisocyanate
- IUPAC Systematic Names:
    - 2,4-diisocyanato-1-methyl-benzene
    - 2,6-diisocyanato-1-methyl-benzene
- Synonyms - see Appendix C
- Molecular Formula: $C_9H_6N_2O_2$ (HSDB, 2011)
- Chemical structure (NTP, 2011):



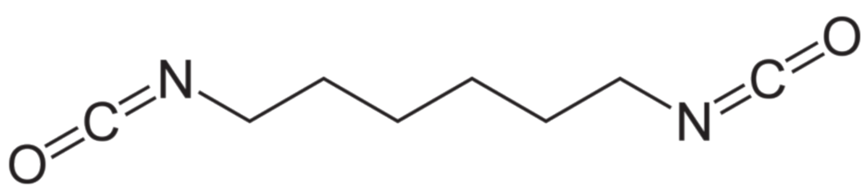
2,4-Toluene diisocyanate
CAS No. 584-84-9

2,6-Toluene diisocyanate
CAS No. 91-08-7

- TDI[4] meets the conditions specified in California Code of Regulations, title 22, section 69503.6(a) in that it appears on one or more of the authoritative lists in California Code of Regulations, title 22, section 69502.2(a)(1) and is one or more of the types of chemicals listed in California Code of Regulations, title 22, section 69502.2(a)(2). TDI is listed on four of the lists described in 69502.2(a)(1) for carcinogenicity or respiratory toxicity. It also appears on two of the lists described in 69502.2(a)(2) for respiratory toxicity.

Hexamethylene-1,6-diisocyanate (HDI)

- CAS #: 822-06-0
- CAS/IUPAC name
    - 1,6-Hexamethylene Diisocyanate (U. S. EPA, 1992)
    - 1,6-diisocyanatohexane (IUPAC name)
- Synonyms - see Appendix D
- Molecular formula: $C_8H_{12}N_2O_2$ (HSDB, 2011)
- Chemical Structure:



[4] In this instance, TDI refers to refers to CAS # 26471-62-5. The basis for listing the other TDI isomers is available on DTSCs informational list of Candidate Chemicals (DTSC 2013)

- HDI meets the conditions specified in California Code of Regulations, title 22, section 69503.6(a) in that it appears on one or more of the authoritative lists in California Code of Regulations, title 22, section 69502.2(a)(1) and is one or more of the types of chemicals listed in California Code of Regulations, title 22, section 69502.2(a)(2):
  - classified by the European Commission as respiratory sensitizers Category 1 in Annex VI to Regulation (EC) 1272/2008
  - identified as Toxic Air Contaminant (California Code of Regulations, title 17, sections 93001)

2. Physicochemical properties of the Chemicals of Concern

(See California Code of Regulations, title 22, section 69503.3(a)(1)(D))

TABLE 2. PHYSICOCHEMICAL PROPERTIES OF THE CHEMICALS OF CONCERN (HSDB, 2011; NTP, 2011)

Property	MDI	TDI			HDI
		Toluene Diisocynates Mixed	2,4-Toluene diisocynate	2,6-Toluene diisocynate	
Molecular weight (g/mol)	250.3	174.2	174.2	174.2	168.20
Specific gravity at 25°C (g/mL)	1.23	1.22 or 0.01	1.22 or 0.01	1.22 or 0.01	1.04
Melting point	37 °C	11°C to 14°C (Freezing Point)	19.5°C to 21.5°C	18.3°C	-67 oC
Boiling point	196 °C	251°C	251°C	129°C to 133°C at 18 mm Hg	213 oC
Log Kow	5.22 (est)	3.74	3.74	3.74	3.20 (est)
Water solubility at 25°C	1.51 mg/L	37.6 mg/L	37.6 mg/L	decomposes	decomposes
Vapor pressure*	5.0×10^{-6} mm Hg at 25°C	2.30×10^{-2} mm Hg at 25°C	8.0×10^{-3} mm Hg at 20°C	2.1×10^{-2} mm Hg at 25°C	5.0×10^{-2} mm Hg at 25°C
Vapor density relative to air	8.6	6	6	6	5.81

* This profile kept "mm Hg" for vapor pressure to be consistent with the cited source literature. Use the following formula and conversion factor for conversion - to kPa: 1 mm Hg = 00.133322368 kPa.

3. Environmental fate

(See California Code of Regulations, title 22, section title 22, section 69503.3(a)(1)(E))

The production and use of diisocyanates may result in their release to the environment through various waste streams (HSDB, 2011).

Air

If released to air, MDI will exist in both the vapor and particulate phases in the atmosphere as indicated by a vapor pressure of 5.0×10^{-6} mm Hg at 25°C; TDI and HDI will exist solely as vapor phases in the ambient atmosphere as indicated by vapor pressures of 2.30×10^{-2} mm Hg at 25 °C and 0.05 mm Hg at 25°C, respectively.

Vapor phase diisocyanates will be degraded in the atmosphere via reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 11 hours for MDI, 20 hours for TDI, and 1.3 days for HDI.

As these diisocyanates do not contain chromophores that absorb at wavelengths >290 nm, they are not expected to be susceptible to direct photolysis by sunlight (HSDB, 2011). Particulate-phase MDI will be removed from the atmosphere by wet or dry deposition. Atmospheric degradation may also occur through contact with clouds, fog, or rain for TDI and HDI while HDI hydrolyzes to form amines and polyureas (HSDB, 2011).

Land/Water

If released to water or moist soil, these diisocyanates are not expected to leach or adsorb to solids, volatilize from water surfaces, nor bioconcentrate due to its rapid hydrolysis due to their rapid hydrolysis(HSDB, 2011).

Biodegradation data for MDI in soil or water were not available. It reacts with water to form amines and urea. As a result, accumulation in the food chain should be low or non-existent (HSDB, 2011).

In one experiment simulating a spill, 5.5% of the original TDI remained after 24 hours, and in a field situation, the concentration declined to the ppm level in 12 weeks (HSDB, 2011). TDI is not expected to bioconcentrate in aquatic organisms.

Once SPF is installed and cured, most diisocyanates will remain as part of a rigid material, which does not show much environmental release potential. However, diisocyanates are known to undergo thermal degradation and release toxic chemicals (ACC, 2008). Any heat-generating processes such as drilling, welding, soldering, grinding, sawing, or sanding on or near SPF insulation may generate a range of airborne degradation chemicals, including isocyanates, hydrogen cyanide, and others (ACC 2008, U.S. EPA, 2013a).

4. Hazard traits of Chemicals of Concern

(See California Code of Regulations, title 22, section 69501.1(a)(36) and section 69503.3(a)(1)(A))

Respiratory Toxicity

The diisocyanates, MDI,HDI and TDI, are structurally similar chemicals, however they exhibit different chemical and toxicological properties. When assessing the toxicological effects of this class of chemicals it is generally understood that exposure to any of the three isomers can result in respiratory illness, most notably asthma (Bernstein, 1996). However, most studies involving the toxicity of diisocyanates focus on TDI because it has been shown to be a more significant inducer of asthma as compared to MDI and HDI (Butcher et al., 1986). MDI, TDI, and

HDI are classified by the European Commission as respiratory sensitizers Category 1 in Annex VI to Regulation (EC) 1272/2008.

- Acute exposure
    - Exposure to MDI resulted in an immediate, moderate, asthmatic reaction associated with significant hypoxemia (Marczynski et al., 1992).
    - Respiratory irritation in previously non-exposed individuals exposed to TDI:
        - Can range from upper airway irritation to toxic bronchitis (Ott et al., 2000; OEHHA, 2010).
        - Eye, nose and throat irritation followed by dry cough, chest pain and tightness (OEHHA, 2010).
        - Patchy infiltrates may be seen on chest X-rays possibly indicating bronchiolitis, bronchial asthma, or pneumonitis (Peters and Wegman, 1975).
        - Potential for allergic sensitization; subsequent acute inhalation exposure may provoke a pulmonary hypersensitivity response (OEHHA, 2010).
    - Acute hypersensitivity pneumonitis after exposure to MDI, HDI, or TDI:
        - Primary symptoms mimic those of flu, with fever, muscle aches and headaches (Charles et al., 1976; Fink and Schlueter, 1978; Baur et al., 1984; Selden et al., 1989).
    - In Infants and Children:
        - Headache, persistent cough, shortness of breath, and nausea can result from MDI exposure (Jan et al., 2008, OEHHA, 2010).
        - Reactive airway dysfunction (no previous asthma-like symptoms reported) after TDI exposure (OEHHA, 2010).
- Chronic exposure
    - Increased asthma in female workers and chronic bronchitis in male and female workers following chronic occupational exposure to MDI (<0.02 ppm) (Pham et al., 1988).
    - A workplace death of a foundry worker was ascribed to occupational asthma induced by MDI exposure (Carino et al., 1997).
    - Allergic sensitization, including chronic hypersensitivity pneumonitis after TDI exposure.
        - Progressively more difficult breathing (even with mild exertion), fatigue and weight loss (Parker et al., 1992).
    - Diisocyanate-induced asthma after MDI, HDI, or TDI exposure
        - Characterized by bronchial inflammation with lymphocytic infiltration and eosinophilia, airway hyper-responsiveness, and airway remodeling (Chan-Yeung, 1990).
        - Subsequent exposures can trigger severe and even life threatening asthma attacks (OEHHA, 2010).
        - Persistence of pulmonary symptoms for months to years following cessation of diisocyanate exposure is not uncommon (Paggiaro et al., 1990, 1993; Piirila et al., 2008; OEHHA, 2010).

  - Antibodies to TDI have been detected in some residents living near a facility that manufactured polyurethane foam, indicating that exposures may be occurring from environmental releases from the plant and sensitizing some individuals (Orloff et al., 1998; Darcey, 2002).

- Carcinogenicity of TDI

Most authoritative bodies generally accept that TDI is a reasonably anticipated human carcinogen (WHO, 1987; IARC, 1999; NIOSH, 2006)

  - TDIs are reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (NTP, 2011).
  - TDI is classified as a Group 2B, possible human carcinogen (IARC, 1999).
  - TDI is listed as a carcinogen under the State of California's Proposition 65 law (OEHHA, 2014b).
  - Oral exposure to TDI results in TDI hydrolysis in the gut, thereby generating toluene-2,4-diamine (TDA), a carcinogen. These oral route studies found that TDI exposure caused tumors at several different tissue sites in rats and mice (Timchalk et al., 1994; OEHHA, 2009, 2010).
  - Inhalation and dermal exposure to TDI produces much less TDA compared to oral exposure (Collins, 2002; OEHHA, 2010).

3. Human Populations Potentially Impacted and Sensitive Subpopulations

(See California Code of Regulations, title 22, section 69503.3(a)(1)(F) and section 69503.3(a)(2))

- Exposure to isocyanates is a leading attributable cause of occupational asthma (Mapp et al., 1988; U.S. EPA, 1998b). TDI-induced asthmatic symptoms may occur immediately upon exposure, be delayed for several hours after exposure, or consist of both an immediate and delayed reaction (Moscato et al., 1991).
- The polyurethane industry fully recognizes the hazardous nature of the SPF systems (ACC, 2014b). Through the American Chemistry Council and industry alliances and trade associations, the industry has developed training materials and health and safety guidance for workers (ACC, 2014c; CPI, 2014).
- The industry also maintains a certification program for professional workers (Rudman, 2013, SPFA, 2013).
- Frequent violations have occurred and been documented for the Occupational Safety and Health Administration (OSHA) regulated workers (Rudman, 2013).
- Independent contractors who do not belong to any industry alliances or trade associations and consumers (such as DIY users of diisocyanate-containing products) are populations of particular concern, as they may not understand the potential hazards associated with product usage. These populations may not take the precautions used in a regulated industrial environment, such as utilizing engineering controls, and personal protective equipment (U.S. EPA, 2011a, 2011b, and 2014).

Sensitive Subpopulations

- Workers
  - Workers in industries that utilize or work around diisocyanates are of primary concern, due to both acute and chronic exposure via inhalation and dermal routes.
  - Inhalation exposures in excess of the OSHA permissible exposure limit have been documented among workers during spray-on applications of truck bed liners, foam roofs, and insulation foam (NIOSH, 1996a, 2005, 2006; U.S. EPA, 2011b; Karlovich, 2010; Hosein and Farkas, 1981; Crespo and Galan, 1999; Lesage et al., 2007).
  - During spray foam application, approximately 20% of the spray foam aerosol was found to be in the respirable size range (Lesage et al., 2007).
  - Inhalation exposures have been documented after thermal degradation (welding or grinding) of isocyanate-containing products (OEHHA, 2010; U.S. EPA, 2011a, b; EPA 2013b).
  - Dermal exposure has been associated with isocyanate sensitization and/or asthma, even when airborne isocyanate concentrations were below occupational exposure levels (U.S. EPA, 2011a, b).

4. Exposures

(See California Code of Regulations, title 22, section 69503.3(b))

- Market Presence
  - The global market for building insulation is projected to grow from $18.5 billion in 2011 to $24 billion by 2016 (Markets and Markets, 2014a). The market for plastic insulation foams will have a compound annual growth rate (CAGR) of 5.8% from 2011 to 2016, and is projected to reach $10 billion by 2016 (Markets and Markets, 2014a).
  - Within the polyurethane industry, the SPF sector is currently estimated to be worth $800 million, and is projected to grow to $1.1 billion by 2015 (Business Wire, 2013).
  - In North America, the polyurethane foam market revenue was $203 million in 2009, and is projected to reach $273 million by 2016, with a CAGR of 4.2% (Markets and Markets, 2014b).
  - At least 83 polyurethane-related facilities, with a total of $616.6 million in sales, are located in California (C. Barnes & Co., 2010).
  - The Spray Polyurethane Foam Alliance (SPFA), an independent trade association in the US, currently lists 44 California SPF contractors as its members (SPFA, 2014).
  - The SPF industry is rapidly expanding due to financial incentives for energy upgrades offered by various government organizations. These incentives are generally offered as a tax break, or as monetary offers through contractors and utilities to increase energy efficiency in residential and commercial establishments (Energy Upgrade California, 2013).
  - The number of businesses and individual consumers that are trying to conserve energy through upgrades is also growing, due to educational outreach by governments, non-profit organizations, and advocacy groups. In Northern California, new homes are being built in Placer County using SPF insulation (Personal communication with Payam Bozorgchami, California Energy Commission, July 2013).

- It has been projected that demand for SPF insulation will grow 13% per year from 2013 to 2015 (Business Wire, 2013).

- Potential exposures to the Chemicals of Concern in the product during the product's life cycle

  SPF systems typically contain MDI including both MDI mixed isomers and polymeric MDI. TDI is mainly used in the manufacture of other polyurethane products including flexible foams, coatings, sealants, and adhesives. However, TDI may be found in SPF systems either as a minor component or as an residual constituent. For example, TDI is declared in the MSDS of one manufacturer in California (UPI Inc., 2012). TDI remains one of the largest volume aromatic diisocyanates, and is a high production volume chemical predominantly used in the production of polyurethanes (U.S. EPA, 2011b). U.S. EPA has expressed concerns about the presence of uncured TDI in products used by or around consumers, as well as other unprotected building occupants, and the lack of guidance or regulations to protect them (U.S. EPA, 2011b). Some SPF systems on the market today are SPF systems containing polyurethane-based coatings, sealants, or adhesives, which are likely to contain TDI. For these reasons, TDI is included in this Priority Product listing.

Worker Exposures

- Potential for exposure to isocyanates comes from inhalation of or dermal contact with the material in these ways (Petsonk et al., 2000; NIOSH 2006; U.S. EPA, 2013b, 2013c, and 2014; Rundman, 2013):
  - Vapors and aerosols when a product is sprayed. Inhalation exposures during spray foam insulation typically exceed OSHA occupational exposure limits, and require skin, eye, and respiratory protection.
  - Dust that may contain unreacted isocyanates, generated from cutting or trimming the foam as it hardens.
  - Degradation products, including isocyanates, from heat-generating processes such as drilling, welding, soldering, grinding, sawing, or sanding on or near foam insulation.
  - Isocyanates and other toxic chemicals release during fires (Blomqvist, 2005; Karlovich et al., 2011).
- The rapid increase in production and use of SPF materials may result in increased risk of exposure to workers involved in manufacturing, formulating, distributing, transporting, and installing the SPF. Additional exposures to electricians, welders and emergency response personnel such as firefighters, police, and others are expected.
- Independent contractors in the construction and weatherizing industries are at a greater risk, as they are not subject to the protection of OSHA or Cal/OSHA requirements.
- Even with personal protective equipment, workers involved in manufacturing, pouring, mixing, spraying, applying, or working around polyurethane materials, moving waste materials, fighting fires, or installing or welding around polyurethane materials may be exposed to diisocyanates either by accident or intentional violations (Rundman, 2013).

Worker fatalities:

- A maintenance worker developed isocyanate-induced hypersensitivity pneumonitis and died after repairing an MDI foaming system at a facility that made artificial plants with polyurethane foam bases (NIOSH, 1994a).

- An asthma attack in a 37-year-old man led to death from chronic exposure to TDI in spray paints (Fabbri et al., 1988).
- A 45-year old man died due to acute asthma attack after 12 months on the job spraying MDI-based bed liners onto the floor and sides of cargo vans (NIOSH, 2006).

Occupational asthma cases

Diisocyanate exposures have been the leading attributable cause of work-related asthma (Mapp et al., 1988; U.S. EPA, 1998b; Creely et al., 2006; U.S. EPA, 2011a,b). NIOSH has repeatedly issued hazard summaries and alerts warning of asthma and deaths resulting from occupational exposure to isocyanates (NIOSH, 1996a; 2004, 2006). Harmful or fatal incidents cited involved workers spray painting cars, applying spray-on truck bed liners, installing foam, and exposed to adhesives used in coal mining.

- Ten workers with no preexisting asthma developed MDI-related asthma after 1-8 months on the job (NIOSH, 1996b).
- Nine spray paint workers suffered asthma in one plant (Seguin et al., 1987).
- A 29-year-old male working in a truck bed lining company spraying truck bed liners developed diisocyanate-induced asthma (Bonauto and Lofgren, 2004).
- Diisocyanate-induced asthma reported in a 30-year old man who worked for a truck bed lining company (NIOSH, 2006; Bonauto and Lofgren, 2004).
- A 22-year-old worker who was employed in the truck bed lining industry for 18 months developed diisocyanate-induced asthma (NIOSH, 2006; Bonauto and Lofgren, 2004).
- Coal miners at a longwall mine complained of respiratory difficulties, asthma, shortness of breath, dizziness, headache, sore throat, fatigue, and contact dermatitis after exposure to MDI-based polyurethane rock glues (NIOSH, 1994b).

Nonoccupational exposure potential

- Individual consumer use of uncured polyurethane products has been increasing rapidly. In 2004, the National Institutes of Health Household Products Database listed 16 products containing MDI (U.S. EPA, 2011a). Today, the Household Products Database lists 58 consumer products containing MDI (Household Products Database, 2013).
- Unlike workers who are protected by OSHA regulations and have access to hazard information, training, personal protective equipment, and engineering controls, most consumers may not be aware of the potential hazards of SPF systems containing MDI and other isocyanates (U.S. EPA, 2011a).
- Long-time researchers of isocyanates and asthma have become concerned about the potential relationship between isocyanates in consumer products, including SPF, and the increasing prevalence of asthma in the general population, especially children, and point to the urgent need for further research (Krone and Klingner, 2005).
- Although there is much evidence relating adverse health effects on workers to diisocyanate exposures, the evidence of harm to the general public and consumers is more limited. However, extrapolation from what is known about occupational exposure risks to the less-protected settings in which wet SPF is used by independent contractors and DIYers indicates a high

potential for adverse exposures to diisocyanates among the general population during the use of this product. A recent study found that rising use of isocyanate-based materials in consumer products is leading to an increased burden of disease, with an increase in nonoccupational exposure (Verschoor and Verschoor, 2014).

- A recent review study suggested a rise in nonoccupational asthma in response to consumer products containing diisocyanates (Verschoor and Verschoor, 2014).
- Diisocyanate exposures to bystanders, with subsequent adverse health effects, have also been reported both officially and unofficially through online social media.
    - A 1998 NIOSH report concluded that application of roofing material with MDI and TDI in a school could have contributed to the increased prevalence of asthma among school employees (Kullman et al., 1998).
- There are also anecdotal reports of strong odors and physiological reactions (headaches, dyspnea) following installation of insulation in various settings (Green Building Advisor, 2010).
- Research is ongoing to assess the full potential for exposure to diisocyanates in response to extensive use of SPF, including exposure from dermal contact as well as through inhalation exposure routes (Redlich, 2010).
- Large quantities of polyurethane foams and isocyanate coating materials applied to school roof led to as many as 34 staff members experiencing asthmatic symptoms (NIOSH, 1994c).
- Incidental exposure to MDI and xylene caused asthma-like symptoms in 203 students in Taiwan, where students from two adjacent schools were exposed to MDI and xylene (Jan et al., 2008).
- Two police officers developed asthma-like illness after a single exposure to TDI in the immediate vicinity of a tank car that had overturned on a highway (Luo et al., 1990).

OTHER RELEVANT PRODUCT-CHEMICAL IDENTIFICATION AND PRIORITIZATION FACTORS

(See California Code of Regulations, section 69503.2(b)(1)(C))

1. Availability and reliability of information

(See California Code of Regulations, title 22, section 69503.2(b)(1)(C))

- All toxicology and health-effects references in this profile meet the definition of "reliable information" pursuant to section 69501.1(a)(57), in that all reports and studies relied upon were either published in peer-reviewed literature, and/or published by a federal, state, or local agency that implement laws governing chemicals."
    - There is little dispute among authoritative bodies or in industry on both the irritating and sensitizing nature of diisocyanates. Exposure risks posed by diisocyanates have been well documented and are widely accepted. In addition, the danger of acute asthma attacks to workers has been well documented (NIOSH, 1996a, 2006).

2. Other regulatory programs

(See California Code of Regulations, title 22, section 69503.2(b)(2))

- Federal Regulations related to limiting exposures (NTP, 2011)
    - Clean Air Act:
        - National Emissions Standards for Hazardous Air Pollutants: 2,4-Toluene diisocyanate is listed as a hazardous air pollutant.
        - New Source Performance Standards: Manufacture of diisocyanates is subject to certain provisions for the control of volatile organic compound emissions.
    - Comprehensive Environmental Response, Compensation, and Liability Act, Reportable quantity (RQ) = 100 lbs.
    - Emergency Planning and Community Right-To-Know Act
    - Toxics Release Inventory: 2,4-Toluene diisocyanate is subject to reporting requirements.
    - Resource Conservation and Recovery Act
        - Listed Hazardous Waste: Waste codes for which the listing is based wholly or partly on the presence of toluene diisocyanates = U223, K027.
        - Listed as a hazardous constituent of waste.
    - OSHA:
        - Ceiling concentration = 0.02 ppm (0.14 mg/m3) for toluene-2,4-diisocyanate.
        - OSHA's National Emphasis Program for Isocyanates (Rundman, 2013; ACC, 2014a)
- NIOSH Guidelines:

        - Immediately dangerous to life and health (IDLH) limit = 2.5 ppm for toluene-2,4-diisocyanate.
        - Toluene-2,4-diisocyanate is listed as a potential occupational carcinogen.

- California State Regulatory Programs
    - Air Toxics "Hot Spots" Chemicals (Assembly Bill 2588)
    - Proposition 65 (OEHHA, 2014b)
    - Cal/OSHA requires engineering controls (ventilation, work process, work practices) and personal protective equipment when working with isocyanates. In addition, it has established ceiling limits for TDI, MDI, and HDI of 0.02 ppm, and an 8-hour time-weighted average of .005 ppm for TDI. Additionally, Cal-OSHA has promulgated a 15-minute Short Term Exposure Limit (STEL) of 0.02 ppm (DIR, 2014).
- Non-Regulatory Occupational Exposure Recommendations/Guidelines (ACGIH, 2013)
    - The American Conference of Governmental Industrial Hygienists (ACGIH) promulgates Threshold Limit Values (TLV's) to assist in the control of health hazards. TLV's are health-based values established by committees that review existing and peer-reviewed literature in various disciplines (e.g., industrial hygiene, toxicology, occupational medicine, and epidemiology). Based on available information, ACGIH formulates a conclusion on the level of exposure that the typical worker can experience without adverse health effects. The TLV's represent conditions under which ACGIH believes that nearly all workers may be repeatedly exposed, day after day, over a working lifetime, without adverse health effects.
    - The ACGIH has promulgated a TLV-Time Weighted Average (TLV-TWA) value of 0.005 ppm for HDI. It lists the basis for the TLV as "upper respiratory tract Irritation and respiratory sensitization"
    - The ACGIH has promulgated a TLV-Time Weighted Average (TLV-TWA) value of 0.005 ppm for MDI, and lists the basis for the TLV as being "respiratory sensitization."
- In the 2013 Notice of Intended Changes ((ACGIH, 2013)
    - the ACGIH is proposing a TLV-TWA of 0.001ppm for TDI, and a 15-Minute STEL of 0.003 ppm, and lists the basis for the TLV as being "Asthma." The ACGIH has also added the notations of "Dermal Sensitizer", "Respiratory Sensitizer", and "Skin." A "Skin" notation refers to the potential significant contribution to the overall exposure by the cutaneous route, including mucous membranes and the eyes, by contact with vapors, liquids, and solids. Furthermore, the ACGIH has modified the carcinogenicity classification for TDI to "Confirmed Animal Carcinogen with Unknown Relevance to Humans." In addition, ACGIH has published a "Biological Exposure Index" for TDI based upon toluene diamine in urine, collected at the end of the work shift.

3. Alternatives to SPF Systems [5]

(See California Code of Regulations, title 22, section 69503.2(b)(3))

- The industry acknowledges the health risks of polyurethane materials, but claims that there is currently no known substitute for the use of diisocyanates in spray polyurethane foam. The functional requirements vary based on specific application, but may include low thermal conductivity, physical strength, adhesion to substrates, efficiency, durability, and sometimes flammability and high temperature performance requirements (ACC, 2013).
- The following readily available materials are alternatives for insulation, although they are different materials and systems:
  - Cellulose (recycled paper)
  - Natural fibers (e.g., straw, hemp, cotton)
  - Plastic fibers (from recycled plastic milk bottles made with polyethylene terephthalate (PET), and polystyrene thermoplastic)
  - Phenolic foam
  - Rock and slag wool
  - Fiberglass

  These alternatives may be loose and bulky (blown-in), or in batts, rolls, blankets, or other more rigid foams.
- There exist very few isocyanate-free alternatives in the rigid spray foam market. The only reported commercialized product is an isocyanate-free expanding foam product for insulation applications utilizing a hybrid silane terminated polymer technology (Soudal, 2010).
- Recent research has focused on the development of non-isocyanate chemistries especially for polyurethane adhesives, sealant and coatings, such as soy-based polyurethane (Javni et al., 2008), and linear or network non-isocyanate-based polyurethane (NIPU) produced by reaction of cyclocarbonate resins and amines (Figovsky and Shapovalov, 2006). The researchers believe this new class of non-isocyanate polymers displays the equivalent high adhesion, elasticity, and strength properties of diisocyanate-based polyurethane materials, and exhibits improved hydrolytic stability and chemical resistance (Petrie, 2009). Several U.S. companies are commercializing this technology (Petrie, 2009). Although most NIPUs are used in applications such as adhesives, coatings, and sealants, some of them, such as cyclocarbonate technology, have the potential for use in additional market niches, including SPF insulation.
  In another effort to reduce isocyanate in polyurethane, Rohm and Haas Company (a subsidiary of

[5] Under the Safer Consumer Product regulations, when deciding whether to list a product-chemical combination, the Department may also consider whether there is a readily available safer alternative that is functionally acceptable, technically feasible, and economically feasible (see California Code of Regulations, title 22, section 69503.2(b)(3)). The potential alternatives identified below are provided as examples only, and do not constitute a comprehensive list of all available alternatives applicable to every Priority Product type. Furthermore, the Department is not asserting that these potential alternatives are necessarily safer, functionally acceptable, technically feasible, or economically feasible. The Department seeks information on these and any other alternatives in the marketplace. The Department expects that responsible entities and stakeholders will identify and provide reliable information on the safety, functionality, and technical and economic feasibility of these and other alternatives.

DOW Chemical), the Virginia Polytechnic Institute, and the U.S. Department of Agriculture have been partnering to develop new biomass derived, non-isocyanate based chemistries for various applications (Petrie, 2009).

- While alternative technologies and chemistries are emerging, it takes time to reach the market. An immediate near-term alternative to uncured SPF insulation exists: the use of factory-cured polyurethane foam materials for insulation, which pose relatively less risks to installers and consumers. The end-of- life waste disposal challenges of cured and installed SPF remain to be addressed.

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