Methylene Diphenyl Diisocyanate (MDI)
And Related Compounds
Action Plan
[RIN 2070-ZA15]

I. Overview

This Action Plan addresses the use of methylene diphenyl diisocyanate (MDI) and related compounds (See Appendix 1) in products that may result in consumer and general population exposures, particularly in or around buildings, including homes and schools. Diisocyanates are well known dermal and inhalation sensitizers in the workplace and have been documented to cause asthma, lung damage, and in severe cases, fatal reactions. This Action Plan focuses on the potential health effects that may result from exposures to the consumer or self-employed worker while using products containing uncured (unreacted) diisocyanates (e.g., spray applied foam sealants, adhesives, and coatings) or incidental exposures to the general population while such products are used in or around buildings including homes or schools. In conducting this review of MDI compounds, EPA considered a number of potential actions, including regulatory actions under TSCA sections 4, 5, 6, and 8; cooperative actions with other federal agencies; and voluntary actions.

II. Introduction

As part of EPA's efforts to enhance the existing chemicals program under the Toxic Substances Control Act (TSCA)[1], the Agency identified an initial list of widely recognized chemicals, including MDI, for action plan development based on their presence in human blood; persistent, bioaccumulative, and toxic (PBT)[2] characteristics; use in consumer products; production volume; and other similar factors. This Action Plan is based on EPA's initial review of readily available use, exposure, and hazard information[3] on MDI. EPA considered which of the various authorities provided under TSCA and other statutes might be appropriate to address potential concerns with MDI in developing the Action Plan. The Action Plan is intended to describe the courses of action the Agency plans to pursue in the near term to address its concerns and does not constitute a final Agency determination or other final Agency action. Regulatory proceedings indicated by the Action Plan will include appropriate opportunities for public and stakeholder input, including through notice and comment rulemaking processes. In a concurrent action, a separate Action Plan is under development for Toluene Diisocyanate (TDI), a substance chemically related to MDI with similar hazard and exposure concerns.

[1] 15 U.S.C §2601 et seq.
[2] Information on PBT chemicals can be found on the EPA web site at http://www.epa.gov/pbt/.
[3] Sources initially consulted for basic background information for all the action plan chemicals, including MDI, include Inventory Update Report (IUR) submissions; Toxic Release Inventory (TRI) reporting; data submitted to the HPV Challenge Program; existing hazard and risk assessments performed by domestic and international authorities including but not limited to U.S. Federal government agencies, the Organization for Economic Cooperation and Development, the Stockholm Convention on Persistent Organic Pollutants, Health and Environment Canada, the European Union; and others. Details about the specific sources used for this Action Plan can be found in the reference list in Section XI. of this document.

III. Scope of Review

Diisocyanates (also commonly known as isocyanates) are highly reactive and versatile chemicals with widespread commercial and consumer use. Over 90% of the diisocyanates' market is dominated by two diisocyanates and their related polyisocyanates: MDI and toluene diisocyanate (TDI) (Allport *et al.*, 2003). They have unique properties and functional versatility, and contain free isocyanate functional groups (-N=C=O). When isocyanates are combined with other compounds that contain free hydroxyl functional groups (i.e. –OH) they react and begin to form polyurethane polymers. This chemical reaction is completed when all of the initially free –N=C=O groups are bound within the polymer network. This process is commonly referred to as "curing." Products that contain free –N=C=O groups are intended to react and undergo "curing" in the process of use. An example would be an adhesive, which is sold to be initially applied in an uncured form and as it cures (hardens), bonds two pieces of wood together. Other polyurethane products, such as mattresses, pillows, and bowling balls, are considered completely cured products before they are sold. Completely cured products are fully reacted and therefore are considered to be inert and non-toxic (Krone & Klinger, 2005). This Action Plan focuses on concerns for unreacted uncured products.

Because of their reactivity and the diversity of uses, MDI and its related polyisocyanates (see Appendix 1) are generally supplied by their manufacturers as raw materials to formulators who take advantage of the diisocyanates' chemistry to combine them with other chemicals to create different polyurethanes with a wide diversity of applications. This diversity of applications also means that exposures to diisocyanates can occur in a broad range of production facilities from small workshops to automated production lines. Diisocyanates are potent dermal and lung sensitizers and a major cause of work-related asthma worldwide (NIOSH, 2006). Diisocyanates are also commonly available in unreacted forms as part of product mixtures widely used in construction, automotive, and other similar applications that require an end-use reaction as part of the functional performance of these products. Such applications occurring beyond the confines of a controlled production facility could result in exposures unless there is careful observance of best practices and controls to prevent exposures, including the use of protective equipment, containment, ventilation, proper clean-up practices, and medical surveillance of anyone who may be exposed.

In the past, consumer exposures have not been a focus of concern with respect to diisocyanates, because it has been assumed that consumers were generally exposed to products containing cured polyurethanes, which have been generally considered to be inert and non-toxic (Krone & Klinger, 2005). However, an increase in the consumer availability of polyurethane products intended to further react and undergo "curing" has occurred in the marketplace (see additional discussion in section on *Consumer/General Population Exposure*). For example, installation of spray polyurethane foam insulation in homes, schools and other public buildings is a source of potential exposure to uncured isocyanates by building occupants, as well as in do-it-yourself (DIY) consumer projects. Readily available consumer products, such as adhesives (including glues) and sealants also contain diisocyanates that are not completely reacted when applied and can provide potential exposures (Krone, 2004; Bello *et al.*, 2007). In addition, certain workers (e.g., self-employed) are not subject to the applicable OSHA exposure limits, and are not legally required to receive health and safety training and chemical hazard information, or wear personal protective equipment (PPE) or undergo medical surveillance and therefore could potentially be overexposed to uncured polyurethane products.

EPA is concerned about the presence of uncured MDI in products used by or around consumers, as well as other unprotected building occupants, and the lack of guidance or regulations to protect them, this action plan focuses on the potential health effects that may result from exposures to the consumer or self-employed worker while using products containing uncured MDI, or incidental exposures to the general population while such products are used in or around buildings, including homes or schools.

IV. Uses and Substitutes Summary

MDI and TDI are the largest volume aromatic diisocyanates, are high production volume chemicals, and are predominantly used in the production of polyurethanes. In 2008, the U.S. demand for pure MDI was 192.1 million pounds and for polymeric MDI was 1,418 million pounds (ACC, 2009). There are many types of polyurethane products in the marketplace, with foams representing the largest sector of the polyurethane industry. Non-foam polyurethane use sectors of MDI and polymeric MDI include coatings, adhesives, binders, and sealants. However, these products comprise a small amount of the total production volume. Polyurethane foams take two forms: flexible and rigid. Flexible foam is primarily used for cushioning, while rigid foam is used mainly for insulation. The majority of polyurethane products undergo curing prior to reaching the consumer. However, other polyurethane products such as spray foams, coatings, sealants and adhesives may be sold and used, most often in a mixture of formulated product, in an uncured form. Researchers looking at workplace exposures to diisocyanates have noted an increase in the number of isocyanate-containing products used by consumers. These researchers also noted that community exposures to isocyanates could potentially result from industrial exposures as well as the use of consumer products containing isocyanates (Redlich, et al, 2006).

The 2006 Inventory Update Reporting (IUR) database indicates that MDI chemicals are used in the following consumer/commercial categories: adhesives and sealants; paints and coatings; transportation products; rubber and plastic products; and lubricants, greases and fuel additives (EPA, 2010). The vast majority of these products contain forms of MDI as the diisocyanate components. To reduce vapor hazards, polyisocyanates and pre-polymer forms of isocyanates were developed; however, many products contain a mixture of MDI monomer and a MDI-based polyisocyanate.

The use of polyurethane foam for insulation is greatly expanding as many federal and state government programs create incentives for their use in increasing energy efficiency. In addition to their traditional uses by commercial applicators to insulate roofs and walls of buildings, pour-in-place foam, spray polyurethane foam (SPF) and one-component foam (OCF) have a variety of other uses. Pour-in-place, SPF, and OCF cans are all used in the arts arena for sculpture, mold making, and designing movie and theater sets. They are similarly used in theme parks, shopping malls, and parade floats (ACC, 2009). In addition, these types of foams are popularly used by arts and crafts hobbyists.

Other major types of non-foam polyurethane products sold for use in an uncured form include coatings and adhesives. The terms “coatings”, “sealants”, “binders”, and “adhesives” are sometimes used interchangeably when referring to various polyurethane products and some industry sectors use some or all of those four types of products. In particular, the auto refinishing and repair, the marine leisure craft maintenance and repair (ACC, 2009), and the floor and deck maintenance and repair (Jarand *et al.*, 2002; ACC, 2009) sectors have all had a variety of uncured polyurethane products available to both the professional applicator as well as the DIY consumer. Additionally, the synthetic recreational surfacing industry uses a variety of polyurethane components in formulating its products for both indoor and outdoor surfaces (Advanced Polymer Technology Corporation, 2010). Polyurethane coatings are available for use by industry and consumers to seal concrete, waterproof walls and refinish floors. Polyurethane sealants have a variety of uses in the automotive sector, the largest being glass installation of windshields and side windows. Polyurethane adhesives are used in numerous industrial and consumer applications. Some of these products are specifically marketed to DIY consumers for general multi-purpose applications as well as for specialty uses in woodworking, bookbinding and other hobbies. Consumer use of adhesives and sealants is a growth sector as noted by an industry overview of this sector in late 2009. This growth reflects increasing numbers of DIY energy-conscious homeowners doing more of their own home renovation and repair work in order to save money, as well as from craftsmen and consumers generally continuing to use adhesives (Pianoforte, 2009). The spray foam industry, recognizing the growing use of these products by DIYers, recently developed a website on the use of spray foam with guidance directed specifically to DIYers, in addition to homeowners and professionals (ACC, 2010).

Replacement of diisocyanates in an environmentally and economically friendly manner presents a significant challenge. However, a new class of non-isocyanate polyurethanes that offers potentially safer alternatives to conventional polyurethanes has been reported by two research groups (Figovsky & Shapovalov, 2006; Javni *et al.*, 2008). Other reported technologies include an isocyanates-free expanding foam product (Soudal, 2010) and a faster curing “isocyanates-free” flexible food packaging adhesive that reportedly prevents potential migration of isocyanates into non-dry food. Of note, a soy-based adhesive intended to replace formaldehyde-urea adhesives received a Presidential Green Chemistry Award (EPA, 2009), but more research is needed to determine if soy-based adhesives would be an adequate substitute for polyurethane adhesives. While research and development of appropriate alternatives is underway with a goal of direct product substitutions, it is important to focus on the safe use of existing polyurethane products through hazard communication and educating product users.

V. Hazard Identification Summary

The toxicity studies discussed in this summary were carried out on MDI chemicals with unreacted (uncured) isocyanate functional groups.

Environmental and Ecological Hazards. Although there is a moderate acute ecotoxicity profile for MDI, the hazards associated with exposures to MDI chemicals have centered on human health effects not ecological effects. Experimental ecotoxicological data for MDI and its degradation products indicate moderate to low toxicity to aquatic organisms (Bayer, 1992; Bayer, 2000a; Bayer, 2000b; Bayer, 2000c; Bayer, 2009). Other toxicity data suggest low likelihood of effects to terrestrial biota such as plants and earthworms (Van der Hoeven *et al.*, 1992a; Van der Hoeven *et al.*, 1992b).

<u>*Toxicity in Humans*</u>. Most of the data on human health hazards resulting from diisocyanate exposures are based on occupational populations. These data indicate that exposure to diisocyanates can cause contact dermatitis, skin and respiratory tract irritation, immune sensitization, and asthma (NIOSH, 2006). It is well documented that isocyanate exposure is the leading cause of work-related asthma, and prevalence in the exposed workforce is estimated at 1-20% (Ott *et al.*, 2003; Bello *et al.*, 2004). Both inhalation and dermal exposures to diisocyanates are thought to contribute to the development of isocyanate asthma (Bello *et al.*, 2007; Liljelind *et al.*, 2010). Once a worker is sensitized to diisocyanates, subsequent exposures can trigger severe asthma attacks. Higher incidences of asthma are typically associated with processes that generate higher exposures, such as spray application or heated processes that generate airborne vapors and mists that can expose workers via respiratory and dermal routes. For example, the UK Health and Safety Executive reported that vehicle refinishers who spray coatings containing isocyanates have an 80 times higher risk of getting asthma compared with the UK working population. (HSE 2009) [http://www.hse.gov.uk/mvr/priorities/isocyanates.htm/].
Fewer cases of diisocyanate asthma have been reported in work settings with lower isocyanate airborne exposures, and most workers who developed diisocyanate asthma have experienced long periods of exposure (months or longer). However, the minimum exposure to isocyanates that can elicit sensitization responses or asthma is not known. In addition, immune response and subsequent disease in humans can be quite variable (Redlich *et al.*, 2006). Fatalities linked to diisocyanate exposures in sensitized persons have been reported (NIOSH, 1996; ACC, 2005).

There are very few reports of non-occupational exposures to diisocyanates available; however, some incidents have been reported where diisocyanates in products are suspected of causing asthma reactions in humans (Dietemann-Molard *et al.*, 1991; NIOSH, 1996; Jan *et al.*, 2008).

<u>*Toxicity in Laboratory Animals*</u>. MDI has low acute toxicity via the oral and dermal routes, but is considered toxic via the inhalation route in animals (Collins, 2002; ECB, 2005). Dermal absorption of MDI has been experimentally demonstrated, and MDI is uniformly distributed throughout the body, following inhalation exposure (Collins, 2002; ECB, 2005) (Gledhill *et al.*, 2005). MDI causes skin, eye, and lung irritation, progressive impairment of lung function with long-term inhalation exposure and is a respiratory sensitizer via both the dermal and inhalation routes of exposure in animals (Collins, 2002; ECB, 2005). Cross-sensitization has been observed between MDI, TDI, hexamethylene diisocyanate (HDI) and dicyclohexylmethane diisocyanate (HMDI) in mice, and between MDI, TDI and HDI in humans (O'Brien *et al.*, 1979). MDI is negative in gene mutation assays in vitro and in chromosomal aberration assays *in vitro* and *in vivo* (ECB, 2005). Animal data indicate that MDI may be carcinogenic; however, a consistent association has not been reported in epidemiologic studies (IARC, 1987b; IARC, 1987a; ECB, 2005).

VI. Fate Characterization Summary

Hydrolysis is the dominant process in determining the overall environmental fate, transport, and bioaccumulation potential of diisocyanates. Commercially, diisocyanates react at room temperature with other chemicals (i.e. polyols) to form various polymers. Data shows that water from humidity in air can hydrolyze MDI thus forming the amine, methylene diphenyl diamine/toluene diamine (MDA), which also has hazards associated with it. Although their rapid hydrolysis in surface water will reduce persistence and bioaccumulation in the environment (Yakabe *et al.*, 1999), under conditions of low humidity, diisocyanates may be stable long enough to be transported some distances and inhaled. Data from the Toxics Release Inventory shows releases to all media (EPA, 2008b). Despite their apparent rapid reaction time, there is uncertainty regarding diisocyanate vapors and MDA in ambient air as a function of humidity (Dyson & Hermann, 1971). Air releases are of particular concern, because the hydrolysis products formed are irritants and there is a potential for inhalation exposure.

VII. Exposure Characterization Summary

Occupational Exposure. Approximately 280,000 U.S. workers were estimated to be potentially exposed to diisocyanates in 1996 (NIOSH, 1996) but given industry growth and new applications (Bello *et al.*, 2007), this estimate is expected to be higher today. OSHA regulates workplace exposures to MDI through its permissible exposure limits (PELs) (see Appendix 2). To reduce worker exposures when exposure levels exceed its PELs, OSHA requires use of PPE when engineering controls (e.g., ventilation) or administrative controls are infeasible or fail to reduce levels adequately.

Airborne MDI concentrations during manufacturing processes are influenced by whether the material is heated or sprayed, how the diisocyanate is reacted or cured, whether the process is conducted in an open or closed system, and the types of sampling methods used (Booth *et al.*, 2009). Exposures to MDI during SPF insulation and binder, coating, adhesive and sealant operations were found to be greater than MDI exposures from the production of other types of polyurethane products (e.g, mattresses) which reach consumers in a cured form (Booth *et al.*, 2009). Notably high MDI airborne exposures have been documented among workers during spray-on applications of truck bed liners and rigid foams for insulation (SPF) (Crespo & Galan, 1999; Lofgren *et al.*, 2003; Bonauto *et al.*, 2005; NIOSH, 2006; Lesage *et al.*, 2007). Certain NIOSH and OSHA evaluations have shown that worker exposures levels can be above OSHA PELs when spray applying MDI (NIOSH, 2004; Fairfax & Brooks, 2006) Airborne concentrations of MDI can also occur above established exposure limits in pour-in-place applications during process upsets (Booth *et al.*, 2009).

Occupational skin exposures in workers exposed to MDI are of concern because isocyanate sensitization and/or asthma has occurred in cases where the potential for skin exposure is substantial but measured airborne MDI monomer levels are below Occupational Exposure Levels (OELs) or below the limits of detection with the methods used, or where similar MDI levels would be expected but MDI air monitoring data is not available (Bernstein *et al.*, 1993; Ulvestad *et al.*, 1999; Petsonk *et al.*, 2000; Sommer *et al.*, 2000; Donnelly *et al.*, 2003). Skin exposure to MDI at work can occur even with use of personal protective equipment (Bello *et al.*, 2004).

In 132 OSHA inspections conducted between February 2004 and March 2005, approximately 46% of MDI samples collected during MDI-based spray-on urethane use in truck-bed lining exceeded OSHA's PEL (Fairfax & Brooks, 2006). The truck bed lining industry is primarily composed of small employers (six or fewer workers) with an estimated total of 10,000 workers (Lofgren *et al.*, 2003; Fairfax & Brooks, 2006). Since polyurethane coatings and sealants are marketed and used for truck trailers, house decks, walls, foundations and sports flooring and these applications use the same or similar chemicals, spray techniques, and equipment as the spray-on truck bed lining process and SPF insulation, excessive exposure to MDI may occur during these related applications, resulting in risk to spray gun users and other nearby workers (NIOSH, 2006). However, non-OSHA covered self-employed workers and small firms, may not have access to or be aware of the hazard information and appropriate precautions to take when using uncured polyurethane products (Krone, 2004). Also, non-occupational exposures of workers, self-employed or otherwise, that have been sensitized to diisocyanates at work deserve special attention (ECB, 2005).

EPA is aware that there is uncertainty about curing time of various products under different situations and that additional data are needed to address certain concerns, such as re-entry time, which are important for improving communication to prevent exposure. Additionally, while OSHA and NIOSH have developed methods to estimate air concentrations within workplaces, current methods underestimate air concentrations and may warrant the use of a compensation factor and/or development of improved analytical methods. Methods for detection of dermal exposure are in the early stages of development and will be key to estimating dermal exposures. There are several data gaps associated with dermal exposure, sensitization, and the availability of uncured isocyanate groups (Streicher *et al.*, 1998; Bello *et al.*, 2007). In the U.S., only isocyanate monomers (e.g., TDI and MDI) are regulated, although similar polyisocyanates that are widely used in commercial and consumer products contain the same reactive isocyanates. EPA is concerned that there does not appear to be sufficient recognition that potential exposures of consumers and non-OSHA regulated workers to MDI and its related polyisocyanates may need to be addressed with similar recommendations for use of engineering controls, PPE, and hazard communication as those required for OSHA-regulated occupational settings.

Consumer/General Population Exposure. The higher exposure operations identified in occupational settings (Booth *et al.*, 2009) use polyurethane products which are most commonly used by consumers (e.g., spray foam, adhesives). Thus, consumers, bystanders, building occupants (including children), hobbyists and DIY applicators may be exposed to uncured MDI when using similar products. Unlike workers who are protected by workplace regulations and, in most cases, have access to hazard information and training for working with diisocyanates, most consumers are unaware of the potential hazards of consumer products containing uncured MDI. Consequently, incorrect use because of insufficient and inadequate hazard communication may lead to increased consumer exposure. Even if consumers are aware of the hazards, they may not take appropriate precautions. The European Union assumed that "the systematic use of PPE by the consumer will be unlikely." (ECB, 2005). Concerns for potential consumer exposure to MDI-containing products ultimately resulted in a regulation requiring the inclusion of appropriate gloves and precautionary statements in consumer products containing MDI (European Union, 2009).

Consumer use of uncured polyurethane products that contain MDI has increased rapidly as the market for consumer products has expanded (Krone, 2004; Redlich *et al.*, 2006). In 2004, the National Institutes of Health Household Products database, which represents a random sampling of brand name products, listed 16 products containing MDI (Krone, 2004). In 2010, a search of the same database resulted in 43 products containing MDI (NIH, 2010). In addition, there is a growing availability of products, both consumer products and those labeled as "professional grade," that contain uncured MDI in retail and home improvement stores, as well as for purchase over the Internet that are available to the consumer (MPK Enterprises, 2010; NIH, 2010). Some professional art organizations have noted the common use of uncured polyurethane products by their members and warn their members of the potential hazards associated with these products in their safety library (United Scenic Artists, 2010). However, it is unclear whether amateur and school arts groups are similarly aware of the potential hazards resulting from the use of these same products.

Rigid foam products containing MDI are predominantly used to make spray foam insulation by a variety of systems. Exposures to consumers are not well characterized. The exposure potential varies with the method and quantity used, particle size distribution, and end-product curing time. With two-component high pressure spray polyurethane foam systems, chemical migration between floors was noted with certain conditions. Area samples show that occupants and bystanders, including sensitive populations, may be exposed at levels above the workplace exposure limits (Crespo & Galan, 1999; Lesage *et al.*, 2007; Bayer, 2009; IRSST, 2009). This is of special concern because exposure limits for the general population's exposure to hazardous chemicals are lower than workplace exposure limits, primarily because the general population also includes the sick, the disabled, sensitive and immuno-compromised individuals, and children (Redlich, *et al*, 2006). Several researchers have recommended establishing a work zone to minimize exposure of unprotected individuals during application. This is supported by data that show reduction of MDI (Lesage *et al.*, 2007) concentration with distance from the application site (Lesage *et al.*, 2007). Until polyurethane products fully cure, there may be the potential for inhalation and dermal exposure. However, limited information on the impact of such factors as product composition, temperature, humidity, and application technique on curing times affects determination of safe re-entry time after application.

Children exposed to the same airborne concentrations of MDI as adults may receive a larger dose because they breathe more per pound body weight and per unit respiratory surface area. Additionally, children may be more highly exposed to environmental toxicants through dermal routes than adults. For instance, children may crawl, roll or sit on surfaces treated with chemicals (i.e., carpets and floors) and play with objects such as toys where residues may settle. Similarly, children have a higher surface area relative to body weight, which would result in a greater dose relative to body weight for a child than for an adult with equivalent skin exposure (EPA, 2008a), and children are more likely to crawl, lay, or spend time on the floor. Children may have a greater potential for exposure if they use or are bystanders to the use of uncured MDI products, because they may not have fully developed judgment for following labeling instructions and safety precautions and may not cease activity even when they are experiencing symptoms of exposure. An accidental acute exposure of children to high levels of MDI in a polyurethane sealant used on a school athletic track was associated with asthma-like symptoms, including among children with no prior history of respiratory dysfunction (Jan *et al.*, 2008). This observation is consistent with MDI being a well known source of occupational asthma. Children with asthma are an especially vulnerable population for exposure; they are more susceptible to inflammatory narrowing of the airways, which results in a proportionally greater obstruction of their smaller respiratory system (NIH, 2011; Trasande & Thurston, 2005).

In contrast to the large amount of exposure data available for professional workers who work with diisocyanates, there is limited exposure data available characterizing the use and exposure scenarios of consumer and commercial products containing uncured MDI. Additional data characterizing the concentration of MDI in the air is needed. It is unknown to what extent factors such as application techniques, product composition, and method of measurement influence the availability of uncured MDI. In addition, comparing concentrations to existing workplace exposure limits is not appropriate because the worker PEL is not sufficiently protective for the consumer (Redlich, *et al*, 2006).

IX. Risk Management Considerations

Similar quantities of uncured products are available for purchase by either professionals or consumers. Numerous authors have noted the versatility of polyurethane as well as its increasing uses. EPA is concerned that the potential exists for similar exposures in non-OSHA-regulated situations. Both primary users and bystanders should be made aware of the potential risks and appropriate precautions to take when uncured MDI is being used. In addition, personal and health care products, such as bandages and orthopedic casts could contain uncured MDI but are beyond the scope of this action plan. However, exposures from use of such products could contribute to cumulative diisocyanate exposures (Sommer *et al.*, 2000; Donnelly *et al.*, 2003). The factors described above suggest that a heightened concern for potential risks of diisocyanate exposure to children should be addressed during actions taken to manage these chemicals.

Current and Ongoing Regulatory and Related Activities

MDI and its related polyisocyanates are the subjects of a variety of regulatory and related activities, some of which are summarized below. Additional details, including numerical values, are provided in Appendix 2.

EPA Regulatory Activities. MDI is regulated under the Clean Air Act as a hazardous air pollutant and under RCRA and CERCLA as a hazardous waste. Diisocyanates as a category are subject to Toxics Release Inventory reporting. Under TSCA, EPA has previously used its authority under TSCA sections 8(a) and 8(d) to request information from industry (see 40 CFR parts 712 and 716). EPA has also received submissions regarding diisocyanates under TSCA section 8(c) and TSCA section 8(e). Diisocyanates are a TSCA New Chemicals Program Chemical Category and any new chemical substance falling in that category may be further regulated after a TSCA section 5 premanufacture notice has been submitted (EPA, 2002).

Spray Polyurethane Foam (SPF) Federal Partnership Promoting Stewardship & Research. In 2009, EPA convened a multi-agency partnership with OSHA, NIOSH, and the Consumer Product Safety Commission (CPSC) to evaluate and address potential exposures to isocyanates and other chemicals during installation of spray polyurethane foam (SPF) insulation and air sealants in homes and schools. Commercial and DIY applicators, as well as building occupants are often unaware of inhalation and dermal hazards. Applicators and others at the work site may not wear adequate PPE. Building occupants, who remain on the premises during the operations or re-enter the site before the product is fully cured may be at risk. The federal agencies are working with the polyurethanes industry to ensure accessible hazard communication, applicator training, and best workplace practices to prevent exposure to isocyanates and other SPF chemicals. In addition, the federal group has identified critical research needs to assess and measure exposures to total reactive isocyanate groups (TRIG) during use and curing of SPF products. EPA will continue to work with its federal partners, the polyurethanes industry, and others to ensure improved labeling and product safety information for polyurethane products containing unreacted isocyanates, especially products targeted to consumers. EPA is also considering a green chemistry challenge to encourage the development of safer alternative chemicals.

European Union. Following publication of an MDI risk assessment which identified risks to human health for consumers, the European Union (EU) amended its REACH regulation to include restrictions on certain consumer uses of MDI. Effective December 27, 2010, all consumer products manufactured and imported into the EU containing concentrations of 0.1 percent or more MDI must include specific types of protective gloves and specific warnings and use instructions (European Union, 2009).

X. Next Steps

In conducting this review, EPA considered a number of potential actions, including regulatory actions under TSCA sections 4, 5, 6, and 8; cooperative actions with other federal agencies; and voluntary actions as described above. Based on EPA's screening level review of MDI and its related polyisocyanates (Appendix 1), EPA intends to:

1. Issue a data call-in for uncured MDI under TSCA section 8(c) to determine if there are allegations of significant adverse effects and initiate a TSCA section 8(d) rulemaking for one-time reporting of relevant unpublished health and safety studies for uncured MDI.

2. Consider initiating a TSCA section 4 test rule to require exposure monitoring studies on uncured MDI and its related polyisocyanates in consumer products and exposure monitoring studies in representative locations where commercial products with uncured MDI and its related polyisocyanates would be used.

3. Consider initiating rulemaking under TSCA section 6 for
   a. Consumer products containing uncured MDI, and
   b. Commercial uses of uncured MDI products in locations where the general population could be exposed.

4. Consider identifying additional diisocyanates and their related polyisocyanates that may be present in an uncured form in consumer products that should be evaluated for regulatory and/or voluntary action.

XI. References

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Appendix 1

<u>Tier 1: MDI monomers and related isomers and polymers</u>

No	CASRN	CA Index Name	Acronym	Common Name
1	101-68-8	Benzene, 1,1'-methylenebis[4-isocyanato-	4,4’-MDI	4,4’-Methylenediphenyl diisocyante
2	5873-54-1	Benzene, 1-isocyanato-2-[(4-isocyanatophenyl)methyl]-	2,4’-MDI	2,4’-Methylenediphenyl diisocyante
3	2536-05-2	Benzene, 1,1'-methylenebis[2-isocyanato-	2,2’-MDI	2,2’-Methylenediphenyl diisocyante
4	26447-40-5	Benzene, 1,1'-methylenebis[isocyanato-	MDI	Methylenebis(phenyl isocyanate)
5	9016-87-9	Isocyanic acid, polymethylenepolyphenylene ester	Polymeric MDI	Poly(Methylenebis(phenyl isocyanate)

<u>Tier 2: MDI dimers, trimers and polymers</u>

No	CASRN	CA Index Name	Acronym	Common Name
6	17589-24-1	1,3-Diazetidine-2,4-dione, 1,3-bis[4-[(4-isocyanatophenyl) methyl]phenyl]-	4,4’-MDI dimer	4,4’-Methylenediphenyl diisocyante dimer
7	31107-36-5	1,3-Diazetidin-2-one, 1,3-bis[4-[(4-isocyanatophenyl)methyl]phenyl]-4-[[4-[(4-isocyanatophenyl)methyl] phenyl]imino]-	4,4’-MDI trimer	4,4’-Methylene diphenyl diisocyante trimer (or Uretonimine of 4,4’-MDI)
8	25686-28-6	Benzene, 1,1'-methylenebis[4-isocyanato-, homopolymer	4,4’-MDI homo-polymer	4,4’-Diphenyl methanediisocyanate homopolymer

Appendix 2 – Regulatory and Exposure Limits for MDI

<u>EPA</u>. The EPA’s Integrated Risk Information System (IRIS) program has developed a reference concentration (RfC) for MDI of 6 x 10^{-4} mg/m^3 using histopathological changes in the upper respiratory system in animals as the critical effect (EPA, 1998).

OSHA. Diisocyanate hazards are addressed by OSHA in specific standards for the general industry, shipyard employment, and the construction industry, including PELs for workplace exposure.

OSHA's PEL for the MDI monomer is 0.2 mg/m^3 (0.02 ppm) as a ceiling limit (29 CFR § 1910.1000). OSHA also requires the use of PPE to reduce worker exposure to hazards when engineering and administrative controls are not feasible or effective in reducing exposure below its PELs.

NIOSH. In 1996 and 2006, NIOSH issued Alerts to prevent asthma and death from diisocyanate exposure to workers in certain situations (NIOSH, 1996; NIOSH, 2006). NIOSH considers SPF insulation application to present hazards similar to other spray polyurethane applications and recommends use of the same safety procedures and PPE.

NIOSH's Recommended Exposure Limit (REL) for the MDI monomer is a Time Weighted Average (TWA) of 0.05 mg/m^3 (0.005 ppm) for up to a 10-hour workday during a 40-hour workweek with a ceiling limit of 0.2 mg/m^3 (0.02 ppm) for any 10-minute period (NIOSH, 2005). The NIOSH REL is intended to prevent acute and chronic irritation and sensitization of workers but not to prevent health effects in workers who are already sensitized. Per NIOSH, available data do not indicate a concentration at which MDI fails to produce adverse reactions in sensitized persons (NIOSH, 2006).

ACGIH. American Conference of Governmental Industrial Hygienists. Threshold Limit Values (TLVs) for MDI address respiratory sensitivity but not dermal sensitivity. It has been suggested that there is now sufficient information to recommend the addition of a "skin notation" to the TLVs for MDI to bring attention to the potential for absorption of diisocyanates through the skin.

ACGIH has assigned the MDI monomer a TLV of 0.05 mg/m^3 (0.005 ppm) as a Time-Weighted Average (TWA) for a normal 8-hour workday and a 40-hour workweek. The ACGIH TLV for MDI is based, among other things, upon the potential for sensitization and meant to protect workers from induction of this effect (ACGIH, 2009).

California, OEHHA. In April 2010, California's Office of Environmental Health Hazard Assessment (OEHHA) released "for comment" draft documents describing proposed Reference Exposure Levels (RELs) for MDI which have been revised to include consideration of possible differential effects on the health of infants, children and other sensitive subpopulations (California EPA, 2010).

EU. Following publication of an MDI risk assessment which identified risks to human health for consumers, the EU amended its REACH regulation to include restrictions on certain consumer uses of MDI. Effective December 27, 2010, all consumer products manufactured and imported into the EU containing concentrations of 0.1 percent or more MDI must include specific types of protective gloves and specific warnings and use instructions (European Union, 2009).