

**NEW CHEMICALS ENVIRONMENTAL TECHNOLOGY INITIATIVE**

**AUTOMOTIVE REFINISHING INDUSTRY  
ISOCYANATE PROFILE**

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This report as well as the companion reports, "Generic Scenario for Automobile Spray Coating" and "Control Technologies in the Autorefinish Industry", were developed as an information base for the ETI for Chemicals project to promote dialog between EPA and industry. These reports in preliminary draft form were shared with industry representatives at a meeting held on August 28, 1996. In response both to presentations at the meeting and the draft reports, the Agency received several sets of comments. The comments have been compiled in a Response to Comments document, "Response to Comments, Environmental Technology Initiative for Chemicals, Partners in Innovation in the Autorefinish Industry", April, 1997. The reports have been revised to incorporate comments where appropriate.

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***Editor's Note:*** EPA deleted references to diisocyanate polymers under TOXICOLOGY, Repeated Dose Respiratory Tract Toxicity and Conclusions, in response to comments received from the American Chemistry Council's Request for Correction #04025, dated September 8, 2004, and EPA's letter of response, dated December 21, 2004. In addition, two new Appendices were added. Appendix A-1 defines the terms monomer, prepolymer, polymer, and polyisocyanates. Appendix A-2 includes information on the monomer content in prepolymers and polymers. EPA also updated the Repeated Dose Respiratory Tract Toxicity and Conclusions to reflect additional toxicity data received by the Agency on prepolymeric diisocyanates. The correspondence from the American Chemistry Council and EPA's response can be accessed on EPA's website at <http://www.epa.gov/quality/informationguidelines/iqg-list.html>.

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# **AUTOMOTIVE REFINISHING INDUSTRY ISOCYANATE PROFILE**

## **INTRODUCTION**

Under the Environmental Technology Initiative for chemicals (“ETI for Chemicals”), the Environmental Protection Agency’s New Chemicals Program seeks to reduce human health and environmental risks that arise during the manufacture, processing, use and disposal of chemicals. The ETI for Chemicals encourages all types of risk reduction by working in partnership with industry to develop innovative, sensible approaches to risk management and by minimizing or eliminating regulatory requirements, as appropriate. With respect to isocyanates, the Agency would like to see the protective levels it requires for use of new compounds achieved by similar isocyanate chemicals already in commerce.

The Agency selected isocyanates as the first chemical class for in-depth review for a number of reasons. First, during the use of isocyanates in coating operations, workers are typically exposed to isocyanates and other substances in the form of mists; as a result, they are at risk for various health effects, including sensitization to skin and respiratory tract and lung effects. Second, the Agency receives many premanufacture notices (Toxic Substances Control Act, Section 5) for isocyanate chemicals and regulates those substances that may present an unreasonable risk to workers; plus isocyanates are subject to testing requirements under TSCA and other EPA and non-EPA related regulations. Finally, many manufactures of isocyanates and some of their customers have expressed a strong interest in working with the Agency to reduce risk and develop alternative approaches to risk management. For these reasons, the Agency believes an important opportunity exists to realize meaningful risk reduction during the use of isocyanates.

The purpose of this report is to investigate isocyanates, especially concerning their use in the automotive refinishing industry. The report provides information on automotive refinishing, control technologies employed to reduce exposures, and the regulatory status of a group of isocyanate compounds. The report also points out opportunities for innovation in reducing exposures and risks and promoting pollution prevention.

Automotive refinishing refers to paint products applied to any motor vehicle subsequent to the initial manufacturing process. Due to the nature of the manufacturing process, the original equipment manufacturer (OEM) can apply coating products that are cured at any temperature, commonly up to the 150 - 160°C range. However, once completely assembled (i.e., fitted with fabrics, plastics, rubber components, and possibly combustible petroleum products), finishes can not be cured at these temperatures. Thus, refinishing paint products must strive to be equivalent to OEM finishes but cure at ambient, or slightly higher than ambient (e.g., 80°C), temperatures (Howe-Grant, 1993).

The most commonly used automotive refinishing paint categories include: acrylic lacquers; acrylic enamels; acrylic urethanes; and polyurethanes. This report concentrates on the polyurethane-

based paint products used in the automotive refinishing market which are derived from diisocyanates.

## **AUTOMOTIVE REFINISHING INDUSTRY BACKGROUND**

Automotive refinishing includes operations in auto body repair/paint shops, production auto body paint shops, new car dealer repair/paint shops, fleet operator repair/paint shops, and custom-made car fabrication facilities. Refinishing work typically consists of structural repair, surface preparation and painting. Surface preparation includes grinding the paint off sheet metal, and applying, smoothing, shaping and sanding polyester resin body fillers. Painting involves matching paint colors, mixing paint formulations, and painting the repaired area using custom and conventional painting techniques. Workers involved in auto body repair, and refinishing can potentially be exposed to a wide range of air contaminants. During structural repair, activities such as sanding, grinding, and welding generate aerosols that are released into the worker's breathing zone. If the surface of the vehicle being repaired contains toxic metals such as lead, cadmium, or chromium, exposure to these metals is possible. Automobile painters can be exposed to organic solvents, hardeners that may contain isocyanate resins, and pigments that may contain toxic components. Within the automobile refinishing industry, the major air contaminant exposure appears to be polyisocyanates (Heitbrink, 1995).

Paints and coatings are comprised of binders, pigments, solvents, and various additives. Most automobile paint components for which PMNs have been submitted in the past are nonvolatile; a volatile PMN used for automobile paint may, in fact, be a monomer which would be consumed during the paint formulation step. During automobile refinishing and in many (but not all) automobile manufacturing operations, the paint is sprayed onto the automobile. This profile is most applicable to evaluating nonvolatile isocyanates that are part of paint solids.

Conventional coatings are typically comprised of three major components: a pigment for color; a polymer that acts as binder; and a liquid carrier-generally a solvent. In some coating formulations the solvent portion can account for two-thirds of the coating. Volatile organic compounds (VOCs) are solvents that evaporate or volatilize during the painting process and include thinners, reducers and cleaning solvents. Mixed in coatings, solvents provide proper viscosity, flow, and drying characteristics. These coats act as a shield for primers by resisting the penetration of solvents in topcoats and clear coats.

For the automotive refinishing industry, the paints can be set into different groups, which include pretreatments, primers, sealers, precoats, specialty coatings, and various topcoats. Topcoats can be pigmented (color coats) or clear (clearcoats). Pigmented topcoats can provide a high gloss ("single stage") or can be subsequently covered with a clearcoat which, provides gloss and protection ("basecoat"). Isocyanates are components of the hardeners used in topcoats, most notably the clearcoats. (BASF Corporation)

Automotive precoat can be defined as any coating that is applied to bare metal in order to deactivate the metal surface for corrosion resistance to a subsequent water-based primer. This coating is applied to bare metal solely for the prevention of flash rusting caused by the water in water-based primers. Automotive pretreatments are any coating that contains a minimum of 0.5% acid by weight and is applied directly to bare metal surfaces to etch the metal surface for corrosion resistance and primer adhesion. Specialty coatings include coatings that are used to perform unusual job requirements such as helping to prevent surface defects and improve desired coating properties. Examples include coatings for plastic parts, anti-glare coatings, and gloss flatteners (Kirk-Othmer, 1992 and TNRCC, 1995).

The spray coatings applied by body shops differ from those applied by original equipment manufacturer's (OEM's). OEM facilities use coatings that require temperatures up to 400°F (204°C) in order to cure the coating. This is possible because no temperature-sensitive materials have yet been installed in the automobile. Body shops, on the other hand, must use coatings that cure at temperatures less than 150°F (66°C) to avoid damaging the vehicle's upholstery, glass, wiring or plastic components.

Low VOC coatings have two distinct advantages when compared to higher VOC coatings. These two advantages are reduced occupational exposures to solvents and environmental releases of VOCs.

Polyisocyanates can be aliphatic or aromatic (a small number of compounds exist as a combination), and both types are commercially important depending on the use. The following general differences have been documented between these two general classes (Oertel, 1985):

- Coatings based on aliphatic polyisocyanates are more light stable than their aromatic counterparts.
- Coatings based on aromatic polyisocyanates lose their gloss relatively fast upon weathering, unlike their aliphatic counterparts.
- Coatings based on aromatic polyisocyanates are generally quicker drying than those based on aliphatic polyisocyanates.

Given these properties, it is expected that most paint used for automobile refinishing should be based on aliphatic rather than aromatic polyisocyanates since light stability and gloss retention are obviously very important characteristics. In fact, industrial hygiene surveys and occupational health literature reviewed by the Agency has shown this to be the case. Most of the resources EPA examined indicate that polyisocyanates sampled in automobile paint shops are based on the aliphatic compound hexamethylene diisocyanate (HDI).

A driving force behind the automotive refinishing industry converting to the use of low VOC coatings has been the introduction of state regulatory requirements reducing the amount of VOCs in paints. These state requirements are in response to the Clean Air Act Amendments passed by

Congress in 1990. In addition, the EPA is proposing new regulations on VOCs in the automotive refinishing industry through its Office of Air and Radiation. This proposed rule “the National Volatile Organic Compound (VOC) Emission Standards for Automobile Refinish Coatings was promulgated on April 30, 1996 and seeks to reduce emissions of VOCs from the use of automobile refinish coatings. The proposed standards are part of the Clean Air Act (Act) and require the EPA to control VOC emissions from certain categories of consumer and commercial products. Automobile refinish coatings are included under the definition of consumer and commercial products since the definition under section 183(e) of the Act specifically includes paints, coatings, and solvents. The regulation is required by March 1997. The compliance date of the rule is four months after the promulgation date of the rule. The criteria which contribute to the prioritization of automobile refinish coatings to be regulated include the availability of alternatives, the cost-effectiveness of controls, and the VOC emissions in ozone nonattainment areas.

The EPA believes that the proposed standards would reduce nationwide emissions of VOC from the use of automobile refinish coatings by an estimated 32,500 Mg (35,800 tons) in 1996. These reductions are compared to 1995 baseline emissions estimates. Since many regulated VOC species are also on the list of hazardous air pollutants (HAP) in section 112 of the Act, the proposed rule is expected to reduce some HAP emissions from the use of automobile refinish coatings.

The provisions of this proposed rule apply to automobile refinish coatings that are manufactured or imported for sale or distribution in the United States. The proposed standards do not apply to the following automobile refinish coatings:

1. Coatings manufactured exclusively for sale outside the United States;
2. Coatings manufactured or imported before the compliance date of the rule;
3. Coatings manufactured for use by original equipment manufacturers for assembly-line coating operations; and
4. Coatings supplied in nonrefillable aerosol containers.

The proposal sets VOC limits (grams-per-liter) by automotive refinish category and would phase out the U.S. sale of automotive refinish coatings with high VOC content. Products that exceed the limits could not be manufactured or imported for U.S. sale after the rule takes effect. Coatings subject to this proposed rule shall comply with the VOC content standards listed in the Table below. If a coating is marketed under more than one of the listed coating categories, the coating shall comply with the lowest applicable VOC content standard.

## VOC Content Standards for Automobile Refinish Coatings

Coating Category	VOC Content (grams/liter)
Pretreatment Wash Primer	780
Primer/Primer Surfacer	575
Primer Sealer	550
Single/2 Stage Topcoats	600
Topcoats of 3 or more stages	625
Specialty Coatings	840

Automobile refinish coating regulations are in place or under development in a number of States. For the companies that market automobile refinish coatings nationwide, trying to fulfill the differing requirements of State rules has created administrative, technical, and marketing problems. A Federal rule is expected to provide some degree of consistency, predictability, and administrative ease for the industry. In addition, State representatives have recommended that the EPA develop and implement nationwide Federal control measures to enhance enforceability and conserve State resources.

State regulations are also an important factor to consider when looking at the industry and its use of low VOC coatings. Some states have regulated the auto body refinishing industry while others have not, so the information is not representative. States like Texas, California, and Maryland have taken initiatives to require automotive refinishers to register for air permits and adopt new technologies within industry. Texas, for example, has specific guidelines established for the auto body coating industry. The California Air Resources Board (CARB) has actively endorsed technology through development of proposed regulations forcing VOC limits on many coatings market segments. In 1989, California issued several rules which required coating manufactures to produce coatings with little or no VOCs. At that time however, industry was not effective in creating the new compounds to meet the required deadlines. Revisions to the regulations were made and consequently, today there are several paint vendors in California that offer a variety of low VOC coatings (CARB, 1991). In 1992, additional regulations were issued requiring auto body shops in most CARB districts to incorporate the low VOC coatings. CARB was expected to complete a comprehensive survey of the auto body industry in California in May of 1996. The data will be used to develop generic chemical formulations for different categories of automotive coatings. These generic formulations will be used to track and evaluate emissions from auto body shops statewide (Watkins, 1996).

Maryland State regulations concerning the use of low VOC paint became effective on April 15, 1996. These new regulations limited the types of paints that shops can use and specific VOC concentrations are spelled out for specific types of paint. Discussions with automotive refinishers

and paint vendors indicate that in Maryland there was already a trend toward the use of low VOC paints. However, many of the older paints cannot be used in Maryland due to the regulations and the new paints are not as easy to apply and have longer drying time than some of the older lacquer paints. As a result, the amount of work (i.e., number of cars that can be painted) has been reduced drastically. The paints previously used dried in approximately 10 minutes at ambient temperatures.

Paints and coatings typically fall into four general end use categories as defined by the Bureau of the Census' Census of Manufactures - Industry Series for paints and allied products (SIC 2851 or Industry 2851). These categories include:

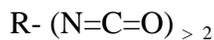
- *Architectural Coatings* (SIC 28511): are formulated for normal environmental conditions and general applications on new and existing commercial, residential, institutional, and industrial structures.
- *Original Equipment Manufacturer Product Finishes* (SIC 28512): for original equipment manufacturers are formulated to meet specific conditions of application and product requirements.
- *Special Purpose Coatings* (SIC 28513): are specifically formulated for refinishing and specialty applications or for environmental conditions such as extreme temperature or corrosive chemical atmospheres (NIOSH 1984). Automotive refinish coatings are covered under the special purpose coatings category.
- *Miscellaneous Allied Paint Products* (SIC 28515): such as cleaners, thinners, and preservatives.

The Special Purpose Coatings (SIC 28513) is the end use category of interest for automotive refinishing industry.

## CHEMISTRY ANALYSIS

### Definition

Any chemical substance containing two or more isocyanate (-N=C=O) functional groups (described below) is classified as a member of Isocyanates Category under EPA's New Chemicals Program (TSCA Section 5). Within this category, chemicals containing two isocyanate functional groups are commonly known as diisocyanates.



EPA has concerns with new isocyanate monomers as well as new oligomers, polymers, prepolymers, or reaction products of existing isocyanate monomers (such as methylenebis(phenyleneisocyanate))

(MDI), toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI)). They can be classified into two subgroups : the aromatic isocyanates, and the aliphatic isocyanates, respectively.

### Hazard Concerns

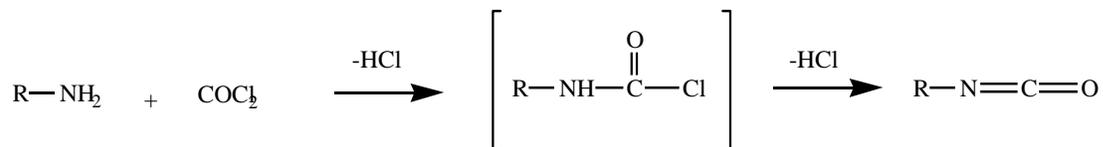
Isocyanates are of concern for potential dermal and pulmonary sensitization, and other lung effects. The aromatic isocyanates may be potential carcinogens based on analogy to TDI or 3,3'-dimethoxybenzidine-4,4'-diisocyanate (dianisidine diisocyanate, DADI).

### New Chemical Program Review Boundaries

The Agency has developed guidelines for the review of new chemicals under the New Chemical Program (TSCA Section 5). For isocyanates, chemicals with an isocyanate functional group equivalent weight (FGEW) equal to or greater than 5,000 dalton are presumed not to pose a hazard under any conditions. Typically, concerns are confined to those species with molecular weights less than 1,000 dalton. The Agency has thus far been concerned only with those isocyanates having potentially significant inhalation exposure.

### Manufacture of Isocyanates (Monomers)

Isocyanates may be synthesized by various methods. The most common method used commercially to produce isocyanates is the phosgene-based process (Elvers *et al*, 1989). Free amines are reacted with excess phosgene in an inert organic solvent at low temperature; the resulting slurry of carbamoyl chlorides and amine hydrochloride is then heated at elevated temperature in the presence of excess phosgene to give the desired isocyanates. The overall reaction scheme is:



However, the industrial use of this phosgenation process has a detrimental impact on health, safety, and the environment. Because phosgene is highly toxic and reactive, safety precautions and diligent care are required (to prevent accidental release of this chemical) in process design, plant operation, handling, storage and transport of this hazardous substance. The strong acid by-product, hydrochloric acid, is also a hazardous industrial chemical.

## Uses of Isocyanates

Isocyanates (di- and polyfunctional isocyanates) are commonly used as monomers to make various polymers, such as polyurethanes. The reaction of diisocyanates (or polyisocyanates) with polyols (molecules containing at least two free hydroxy groups) produces the corresponding polyurethanes. Among those diisocyanates, toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI) are commonly used to produce polyurethanes. Oligomers and prepolymers of isocyanates (with low molecular weight) are derived from existing or new isocyanates monomers and are widely used as feedstocks in the polyurethane industry.

Polyurethanes find significant application in the manufacture of rigid and flexible foams. They are also used in the production of adhesives, elastomers, and coatings. Polyurethane coatings find use where high-performance coatings are required, particularly in the automotive refinishing industries. These coating systems have three distinct advantages over other coatings systems: high mechanical resistance, outstanding chemical resistance, and excellent lightfastness and weather resistance (i.e., aliphatic diisocyanates). Also, many polyurethane coatings cure at ambient temperatures and their properties are so versatile that they can be formulated for use in many conditions, even extreme ones.

## Polyurethane Coating Classifications

Polyurethane coatings are often described as one-component or two-component systems; in two-component systems the coating system is formulated in two parts, which are combined prior to application commonly within the application equipment. Polyurethane coatings can also be described as being reactive (i.e., curing involves the isocyanate group) or non-reactive (i.e., curing does not involve the isocyanate group) (Gum *et al*, 1992; Oertel, 1985).

ASTM designations have been introduced to help categorize the variety of polyurethane coatings (Brandau, 1990 and LeSota, 1978):

Type I: One package urethane coating in which the polyisocyanate has been reacted.

Type II: One package moisture cured urethane coating.

Type III: One package heat curable coating with blocked polyisocyanate groups.

Type IV: Two packages catalyzed urethane coatings: one package contains the polyisocyanate while the other contains the catalyst.

Type V: Two packages polyol-urethane coating: one package contains the polyisocyanate while the other contains polyols, with or without a catalyst.

Type VI: One package urethane coating in which the polyisocyanate has already reacted.

Various characteristics of these ASTM types are summarized in the Exhibit 1. Of these six categories, only one (Type V) is considered to be the major type of coating used for automotive refinishing (based on information from Bayer Corporation).

Exhibit 2 lists industrially important diisocyanates, with their CAS numbers, chemical synonyms, and selected physical property data. Exhibit 2 also identifies whether a particular diisocyanate is known to be used in the manufacture of polyurethane coatings and, if so, identifies its use in one or more of the ASTM classifications for polyurethane coatings. The diisocyanates in Exhibit 2 are listed according to whether the diisocyanate is an aliphatic diisocyanate, aromatic diisocyanate, or aliphatic aromatic diisocyanate.

## EXHIBIT 1

### Notable Characteristics of the Primary Polyurethane ASTM Designations

ASTM TYPE	I	II	III	IV	V	VI
Description	Urethane oil modified	Moisture cure	Blocked	Polyol cured	Catalyzed	Urethane lacquer
Cure	O <sub>2</sub>	NCO + H <sub>2</sub> O	NCO + -OH	Polyol +NCO	NCO + H <sub>2</sub> O +various	Solvent evaporation
Reactivity	Nonreactive	Reactive	Reactive	Reactive	Reactive	Nonreactive
Polymer Characteristic	Prereacted isocyanate	Prepolymer	Capped prepolymer and polyol	Prepolymer and polyol	Prepolymer and catalyst	Prereacted isocyanate
Pot Life	Unlimited	Extended	Unlimited	Limited	Limited	Extended
Pigmentation	Standard	Very difficult	Standard	Standard with additives	Difficult	Difficult
Principal Use	Interior wood Marine Exterior Topcoats	Marine Leather Concrete Maintenance	Wire coatings	Maintenance Wood-furniture Marine Exterior	Leather Wood	Wood paneling Furniture Paper Decorative

Source: Paul 1986.

## EXHIBIT 2

### Commercially Important Diisocyanates

	CAS Number	Chemical Name and Synonyms	Boiling Point °C (kPa)	Melting Point °C	Used in Coating	I	II	III	IV	V	VI	References
<b>Aliphatic Diisocyanates</b>												
HDI	822-06-0	Hexamethylene diisocyanate Synonyms: 1,6-Diisocyanatohexane	127° (1.33)	?	Yes	?	Y	?	Y	Y	?	(1) (2, p. 512) (4, p. 686) (7, p. 665) (13, p. 621)
IPDI	4098-71-9	Isophorone diisocyanate Synonyms: 5-Isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane	158° (1.33)	?	Yes	Y	Y	?	Y	Y	Y	(2, p. 512) (4, p. 686) (7, p. 666) (13, pp. 615, 621)
TMXDI or m-TMXDI	58067-42-8	Tetramethylxylidene diisocyanate Synonym: Tetramethyl-m-xylylene diisocyanate	150° (0.4)	-10°		?	?	?	?	?	?	(4, p. 686) (13, p. 615)
<b>Aromatic Diisocyanates</b>												

	CAS Number	Chemical Name and Synonyms	Boiling Point °C (kPa)	Melting Point °C	Used in Coating	I	II	III	IV	V	VI	References
4,4'-MDI	101-68-8	Diphenylmethane-4,4'-diisocyanate  Synonyms: Methylene di-p-phenylene isocyanate; Methylene (bisphenyl isocyanate); Methyl diphenyl diisocyanate; 4,4'-Diaminodiphenylmethane diisocyanate	208° (1.33)	39.5°	Yes	?	Y	Y	Y	Y	Y	(1) (2, p. 512) (13, pp. 614, 621)
TDI, 80/20 isomeric	26471-62-5	80/20 mixture of 2,4- and 2,6-isomers of toluene diisocyanate	121° (1.33)	13.6°	Yes	Y	Y	?	Y	Y	?	(1) (2, p. 512) (7, p. 665) (9) (13, p. 614)
<b>Derivatives of Diisocyanates</b>												
HDI-Biuret	28182-81-2		> 127° (1.33)	?	Yes	?	?	?	Y	Y	?	(7, p. 665) (13, p. 616)
HDI-Isocyanurate	28182-81-2		> 127° (1.33)	?	Yes	?	?	?	Y	Y	Y	(7, p. 665) (13, p. 616)

For Note ? = Information is not ready. Available data will be collected over time.

## **TOXICOLOGY**

The Agency's assessment of diisocyanate toxicity supports the need for exposure reductions. Diisocyanates are extremely reactive. Although they may affect other organ systems, the primary target of toxicity is the upper and lower respiratory tract. In addition, diisocyanates are known dermal sensitizers and, some are respiratory sensitizers. The following is a summary of the data derived from animal and epidemiological studies or case reports in humans.

For repeated dose studies, only information from inhalation studies has been included. Studies conducted by the oral route are not considered to be relevant because the oral route is not expected to be an occupational route of exposure nor are releases to water expected to result in exposures to diisocyanates because the diisocyanate moiety will hydrolyze in water.

Developmental and reproductive toxicity studies are not included in this profile because they are not the most sensitive endpoints for this class of compounds.

### **Repeated Dose Respiratory Tract Toxicity**

Based on repeated dose studies in animals by the inhalation route, the monomeric diisocyanates, both aromatic and aliphatic, appear to be of high concern for pulmonary toxicity at low exposure levels. For monomers, effects on the respiratory tract (lungs and nasal cavities) were observed in animal studies at exposure concentrations of less than 0.005 mg/L. The experimental animal data available to the Agency on prepolymeric diisocyanates show similar adverse effects at levels that range from 0.002 mg/L to 0.026 mg/L.

There is also evidence that both aromatic and aliphatic diisocyanates are acutely toxic via the inhalation route.

### **Oncogenicity**

Most members of the diisocyanate category have not been tested for carcinogenic potential. Commercially available Poly-MDI was tested in a 2-year inhalation study in rats. The tested material contained 47% aromatic 4,4'-methylenediphenyl diisocyanate (MDI) and 53% higher molecular weight oligomers. Interim sacrifices at one year showed that males and females in the highest dose group (6 mg/m<sup>3</sup>) had treatment related histological changes in the nasal cavity, lungs and mediastinal lymph nodes. The incidence and severity of degeneration and basal cell hyperplasia of the olfactory epithelium and Bowman's gland hyperplasia were increased in males at the mid and high doses and in females at the high dose following the two year exposure period. Pulmonary adenomas were found in 6 males and 2 females, and pulmonary adenocarcinoma in one male in the high dose group. However, aliphatic hexamethylene diisocyanate (HDI) was found not to be

carcinogenic in a two year repeated dose study in rats by the inhalation route. HDI has not been tested in mice by the inhalation route.

Though the oral route is not an expected route of exposure to humans, it should be noted that in two year repeated dose studies by the oral route, aromatic toluene diisocyanate (TDI) and 3,3'-dimethoxy-benzidine-4,4'-diisocyanate (dianisidine diisocyanate, DADI) were found to be carcinogenic in rodents. TDI induced a statistically significant increase in the incidence of liver tumors in rats and mice as well as dose-related hemangiosarcomas of the circulatory system and has been classified by the Agency as a B2 carcinogen. DADI was found to be carcinogenic in rats, but not in mice, with a statistically increase in the incidence of pancreatic tumors observed.

### **Respiratory and Dermal Sensitization**

Based on the available toxicity data in animals and epidemiologic studies of humans, aromatic diisocyanates such as TDI and MDI are strong respiratory sensitizers. Aliphatic diisocyanates are generally not active in animal models for respiratory sensitization. However, HDI and possibly isophorone diisocyanate (IPDI), are reported to be associated with respiratory sensitization in humans. Symptoms resulting from occupational exposure to HDI include shortness of breath, increased bronchoconstriction reaction to histamine challenges, asthmatic reactions, wheezing and coughing. Hazardous Substance Database (HSDB, 1995) cites two case reports of human exposure to IPDI by inhalation that suggest IPDI is a respiratory sensitizer in humans. In view of the information from case reports in humans, it would be prudent at this time to assume that both aromatic and aliphatic diisocyanates are respiratory sensitizers. Studies in both human and mice using TDI, HDI, MDI and dicyclohexylmethane-4,4'-diisocyanate (HMDI) suggest cross-reactivity with the other diisocyanates, irrespective of whether the challenge compound was an aliphatic or aromatic diisocyanate.

At present, there appears to be no reliable animal model for testing for respiratory sensitization that gives an adequate correlation with human respiratory sensitization. In the absence of such a model, and in light of the conflicting animal and human data, it is prudent to assume that all diisocyanates have the potential to be human respiratory sensitizers.

Diisocyanates are moderate to strong dermal sensitizers in animal studies. There seems to be little or no difference in the level of reactivity between aromatic and aliphatic diisocyanates.

### **Dermal Irritation**

Skin irritation studies performed on rabbits and guinea pigs indicate no difference in the effects of aromatic versus aliphatic diisocyanates. The level of irritation ranged from slightly to severely irritating to the skin. One chemical, hydrogenated MDI (1,1'-methylenebis-4-isocyanatocyclohexane), was found to be corrosive to the skin in guinea pigs.

## **Conclusions**

In general, there appears to be little or no difference between aromatic and aliphatic diisocyanates for the above listed end-points. Based on repeated dose studies in animals by the inhalation route, both aromatic and aliphatic diisocyanates appear to be of high concern for pulmonary toxicity at low exposure levels. Based upon a very limited data set, it appears that diisocyanate prepolymers exhibit the same respiratory tract effects as the monomers in repeated dose studies. There is also evidence that both aromatic and aliphatic diisocyanates are acutely toxic via the inhalation route. Most members of the diisocyanate category have not been tested for carcinogenic potential. Though the aromatic diisocyanates tested positive and the one aliphatic diisocyanate tested negative in one species, it is premature to make any generalizations about the carcinogenic potential of aromatic versus aliphatic diisocyanates. In the absence of more human data, it would be prudent at this time to assume that both aromatic and aliphatic diisocyanates are respiratory sensitizers. Diisocyanates are moderate to strong dermal sensitizers in animal studies. Skin irritation studies performed on rabbits and guinea pigs indicate no difference in the effects of aromatic versus aliphatic diisocyanates.

See the New Chemicals Program's Category description for Isocyanate Compounds in Appendix A. Definitions of the terms "monomer," "prepolymer," and "polymer," and "polyisocyanates," are provided in Appendix A-1. A clarification of monomer content in prepolymers and polymers is provided in Appendix A-2.

May 1990; revised June 2005 (See Editor's Note)

## **OCCUPATIONAL EXPOSURE**

### **Worker Activities**

Worker activities at automobile refinishing shops include wet sanding, car washing, stripping (paint removal), machine sanding, blowing, buffing, polishing, paint spraying, paint and primer mixing, and inspection (Pfanstiehl, 1992). In contrast, worker at or near automobile OEM painting operations operate robotics painting equipment, perform mixing, clean paint booths, inspect vehicles, and perform manual "touch-up" painting. It is expected that manual touch-up painting operations would be conducted in spray booths, allowing minimal or no overspray to other sections of the plant.

## Number of Workers/Site

EPA found that a typical automobile refinishing shop employs 4 employees in production (BSB, 1995)<sup>1</sup>. The number of production employees ranges from 1.9 to 10.1, on average depending on shop size, with an overall average for all shops of 3.88. EPA estimated that at new automobile manufacturing facilities, 17 workers are involved in manual “touch-up” painting.

EPA found no information indicating that other workers in painting operations would be potentially exposed to polyisocyanates (USEPA, 1994b).

## Inhalation Exposure

EPA found exposure data specific to the automobile refinishing industry for both total mist levels during spray painting, and isocyanate levels during spray painting. The data, presented in Appendix B represents a variety of engineering controls and spray gun types. The data show a lowering of worker exposure to isocyanate in downdraft paint booths compared with crossdraft booths. The data also show a lowering of isocyanate exposure when using HVLP spray guns as compared to conventional spray guns. The data are summarized as follows:

Scenario 1. *Crossdraft booth and conventional spray gun* (Crossdraft hood with paint spray filters or waterfall and air atomization paint-spray gun) Estimated 8-hr time weighted average (TWA) concentration range 0.1-18.4 mg/m<sup>3</sup> (Janko, 1992 and Lesage, 1992).

Scenario 2. *Downdraft booth and conventional spray gun* Estimated 8-hr TWA concentration range 0.1-5.7 mg/m<sup>3</sup> (Goyer 1995 and Lesage, 1992).

Scenario 3. *Crossdraft booth and HVLP spray gun* Estimated 8-hr TWA concentration range 1.0-5.2 mg/m<sup>3</sup> (Rudzinski 1995).

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<sup>1</sup>The BSB data was compiled from the results of a voluntary survey sent to 4,000 body shops in early 1995, of which 1,662 were returned. Not every shop answered every question, so the actual number of respondents to a particular question is unknown, but much less than 1,662. The distribution of 1994 sales from the BSB survey is comparable to 1992 Department of Commerce data for SIC 7532 (top, body, and upholstery repair shops and paint shops). Due to different presentation methods between the two sources, more exact comparisons are not possible:

<u>Annual Sales, thousands</u>	<u>BSB</u>	<u>DOC (Dept. of Commerce)</u>
< \$125		} 29%
\$125-250	21%	} 52%
\$250-350	13%	} 41%
\$350-750	21%	
750-1,000	7%	
> 1,000	9%	7%

Scenario 4. *Downdraft booth and HVLP spray gun* Estimated 8-hr TWA range 0.5-1.5 mg/m<sup>3</sup> based on paint mist data (Heitbrink, 1995). This is based on the assumption that approximately 30% of particulate overspray is from a polyisocyanate for a typical HDI based paint system (Rudzinski, 1995).

The percentage of refinishing shops using crossdraft booths is 30%, using downdraft booths is 50%, and those using HVLP guns is 64% (BSB, 1995). In comparison, more than 90% of the spray booths in 15 OEM plants surveyed were downdraft (USEPA, 1994b).

## **Dermal Exposure**

EPA did not find any data specific to dermal exposure in the automotive industry. EPA uses data developed from other activities to estimate dermal exposures during mixing, painting, etc.

## **PRODUCTION VOLUMES/DISTRIBUTION**

Within the Paint and Allied Products Industry (SIC 2851) group, automotive refinishes are aggregated under the transportation and machinery refinishes subset (SIC 2851313) of the special purpose coatings category (SIC 28513) and covers not only automotive refinishes but also other transportation (e.g., light- and/or heavy-duty vehicles such as trucks, vans, sport utility and recreational vehicles, buses, aircraft, railroad cars, and automotive parts) and machinery and equipment refinish paints and enamels, including primers.

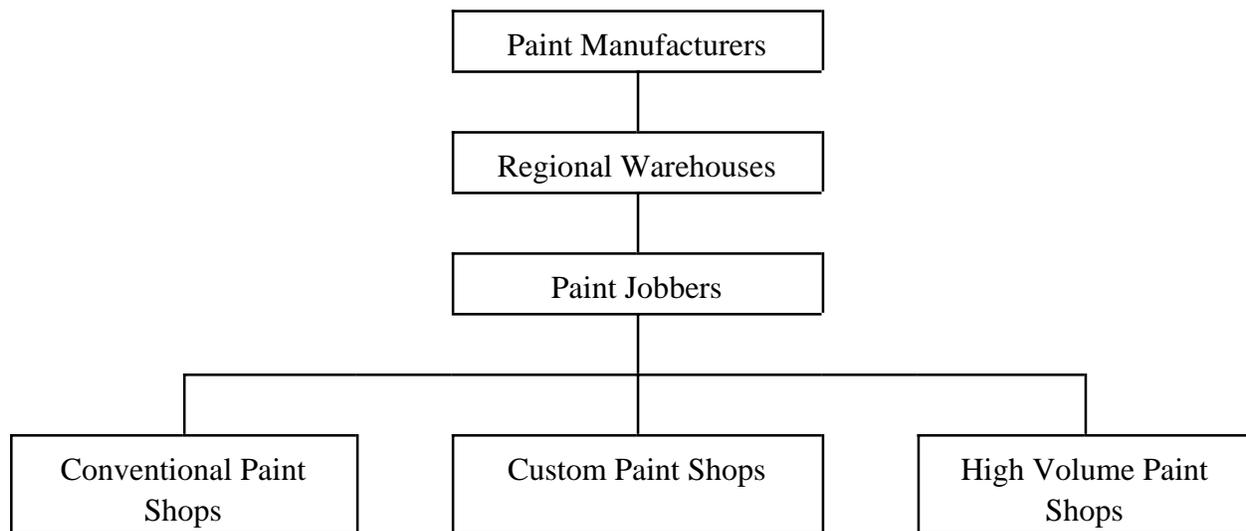
Time series data extracted from the Bureau of the Census' Current Industrial Reports for 1990 - 1994 are presented in Appendix C for the transportation and machinery subset. One industry source has indicated that in 1990, consumption of auto refinishes comprised approximately 75% of this category with the balance allocated between other transportation (17%; trucks, buses, vans, etc.) and machinery refinishing (8%) (Rauch 1991).

In the late 1980s, transportation and machinery refinishes included: specially designed acrylic enamels (36%); lacquers, mainly acrylic (33%); base coat/top coat (17%), acrylic urethane (9%); and, synthetic enamels (5%) (Rauch 1991).

Channels of distribution vary significantly between the refinish and OEM markets. The first market is characterized by thousands of end-users, often operating independently; thus, developing strong distribution channels is more of a challenge in refinishing products. In the OEM market, distribution is a less complex issue due to the limited number of light vehicle manufacturers operating in North America. However, as each vehicle production/assembly plant varies in terms of equipment for the application of finishes, OEM distribution channels are geared toward addressing plants rather than light vehicle companies (Freedonia 1991).

The automotive refinishing trade is so widespread across the nation that an individual in any state, in any type of motor vehicle, can have paint repairs done which will be acceptable in quality and color to the OEM finishes used. This is due, in part, to the huge volume of motor vehicles on the road and the need for convenient automotive service and repair shops (Chudy 1982). A basic flowchart depicting the distribution channels making this possible is presented in Figure 1.

**Figure 1. Automotive Refinishing Trade Channels of Distribution** (Chudy 1982).



Paint manufacturers produce paints for the OEM and/or refinishing markets. OEM paints are formulated primarily to undergo "high-baked" curing; whereas, refinishing paints are composed of slightly different compounds to allow for air-dry or slightly elevated ambient temperature curing (Chudy 1982). Large paint manufacturers may service several regions; whereas, small manufacturers may only serve a particular region.

In each of its regions, the paint manufacturer has a refinish warehouse which is stocked with complete lines of refinishing products for fast distribution to all paint jobbers. Refinish warehouses are wholesale distributors of paint products and do not sell to the general public (Chudy 1982). Distributors usually offer services other than just selling. They can be helpful in ensuring fast service, technical support, credit extension, inventory management and personal attention. In a world becoming more attuned to just-in-time delivery, zero-defect manufacturing, and strict quality control, the role of the distributor is growing in importance (Freedonia 1991).

Paint jobbers supply a complete line of refinishing products (e.g., paints, fillers, sandpaper, masking tape, striping tape, paint mixing equipment, etc.) to all paint shops in the automotive

refinishing market. Refinished products can also be sold to vocational schools but are not intended for sale to the general public (Chudy 1982).

Paint shops can be divided into many categories, depending on the type of painting performed. However, the three most common categories of paint shops include: conventional; high-volume, low-cost; and, custom (Chudy 1982). Appendix D presents 1992 Economic Census data on the number of companies, number of establishments, number of employees, and sales (receipts) for the selected SIC Codes that relate to the automotive coating industry. The number of establishments presented represents those establishments whose primary business activity is covered by the appropriate SIC code. Based on the information presented in Appendix D, there are up to 60,000 facilities that conduct automobile painting. This includes all facilities conducting auto body repair and all new and used car dealerships because Bayer Corporation has indicated that a significant amount of these facilities conduct painting operations, although some may not.

- *Conventional paint shops* do most of the paint work in the aftermarket since they greatly outnumber all other paint shops. They use refinishing materials in accordance with factory recommendations and work in close cooperation with insurance companies and collision repair shops (Chudy 1982).
- *High-volume, low-cost paint shops* do a good share of the refinishing business nationally but offer a limited set of colors. These shops are set up like a small assembly line employing production-line-type specialists to do surface preparation and masking (Chudy 1982).
- *Custom paint shops* have the ability to do the best quality work but are the most expensive. Their artistic and refinishing skills are the most advanced in the trade. Custom painting involves the use of exotic color materials and systems not used on OEM vehicles (Chudy 1982).

Another source estimates that based on survey data there are 50,000 auto body shops and are employing 75,000 painters. (BASF, 1996)

## **PROCESS DESCRIPTION**

In automobile refinishing, almost all spray coating operations are expected to involve a worker spraying the vehicle, typically in a ventilated spray booth with dry filters to collect overspray. The car can dry at atmospheric conditions, or at elevated temperatures through the use of heated paint booth air or portable heat sources (USEPA, 1994a). The curing temperature is likely to be comparable to that used in OEM "touch-up" activities (i.e., up to 180°F). In contrast, the automobile original equipment manufacturing (OEM) involves applying several layers of paint alternated with heating to cure the paint often at temperatures as high as 450°F, although lower

temperatures are used to simply remove water (Pfanstiehl, 1992). Painting is conducted by robots and overspray is collected in waterwash booths of downdraft or crossdraft design. Water is used almost exclusively to collect overspray in new automobile manufacturing plants (USEPA, 1994b). Individual sites may add additional painting steps to achieve protection in certain areas, may modify the drying/curing steps, and may conduct "touch-up" repairs. In these cases, the paint is applied manually and cured at temperatures up to 180°F.

## **CONTROL TECHNOLOGY**

A range of control methods and technologies have been developed and are being widely used to control occupational exposures for spray painting in this industry. The most effective controls are engineering controls, particularly high volume low pressure spray guns and downdraft spray paint booths. New paint formulations have been developed to meet regulatory requirements in reducing solvent emissions in the industry. Other controls such as personal protective equipment including respiratory protection are also used to reduce employee exposures.

### **Paint Spray Equipment**

Spray painting in auto body shops is a manual process where automotive painters use spray guns to apply successive coats of paint until the finish of the repaired sections of the vehicle matches that of the original undamaged portions. To speed drying between coats or for coatings which must be heated to cure, the painted vehicle surface is heated with heat lamps, in special infrared ovens, or in heated spray paint booths. After each coat of primer dries, the surface is sanded to remove any irregularities and to improve the adhesion of the next coat. Final sanding of primers may be done with a fine grade of sandpaper. A sealer is then applied and allowed to dry, followed by the final topcoat. When lacquer is used, the finished surface is usually polished after the final coat has dried, whereas enamel dries to a high gloss and is usually not polished.

Spray guns used in refinishing automobiles atomize paint with compressed air and project a paint mist onto the vehicle surface. The mechanism used in atomization and delivery of the paint directly affects the efficiency of the painting process. Transfer efficiency is the ratio of the amount of coating solids deposited onto the surface of the coated part to the total amount of coating solids that exit the spray gun nozzle. The waste paint directed outside the main spray pattern and not deposited onto the vehicle surface is referred to as overspray. In addition, atomized paint can be pulled away from the car surface by compressed air currents deflected by the car surface and the painting technician, and appears to "bounce back". The bounce back can account for 20% of the 60% of the paint which does not reach the car surface when conventional spray guns are used (Fettis, 1995).

## Conventional Air Spray Guns

Conventional air spray guns have been the standard spray equipment used to apply coatings in the automotive refinishing industry. With this type of spray gun, a low volume (2 to 10 cubic feet per meter (cfm)) of air is pressurized and forced through a nozzle; the paint or coating is atomized in the air at the nozzle throat. Conventional spray guns are usually operated with air pressures of 30 to 90 pounds per square inch (psi) at a fluid pressure of 10 to 20 psi. Air is supplied by an air compressor during spraying operations. There are two basic types of conventional spray guns: syphon-feed and gravity feed. In syphon-feed guns, the paint cup is attached below the spray gun, and the rapid flow of air through the gun creates a vacuum that syphons the coating out of the cup. Three syphon-feed guns are used when large areas need to be painted. In contrast, gravity-feed guns have the paint cup above the gun and require less air pressure to move the coating through the gun (USEPA, 1994; Schrantz, 1992). Gravity-feed guns are used primarily for touch-up when small amounts of paint are required. Their use results in less waste and clear-up residue. The advantage of conventional spray guns is their capability to achieve very fine atomization. The disadvantages of this equipment are the development of excessive spray mist and overspray fog. Conventional spray gun equipment has a transfer efficiency in the range of 20% to 40%, and therefore most of the paint becomes an overspray that may contaminate the air in the worker's breathing zone (Heitbrink, 1996).

## High Volume Low Pressure Spray Guns

High Volume Low Pressure (HVLP) spray guns are systems which use a high volume (30 cfm to 200 cfm) of low pressure (pressure at the gun of between 0.1 and 10.0 psi) and at a fluid pressure of 50.0 psi. The lower velocity of the atomizing air stream results in a more controlled spray pattern, less bounce back, and enhanced transfer efficiency. HVLP guns are estimated to have a transfer efficiency of at least 65% (Heitbrink, 1996). Some disadvantages to this equipment include: higher initial cost; inability to atomize coatings as finely as can be achieved with conventional spray guns; slower application speed; and the need for operator training. HVLP technology has become commonplace in auto body shops because of reduced paint usage and the acceptable finish quality provided by the guns on the market (BAAQMD, 1995). In 1995, approximately 64% of U.S. auto body shops reported owning HVLP equipment. Approximately 49% of small auto body shops (<\$124,999 annual sales) and approximately 68% of very large (>\$1 million annual sales) owned HVLP spray painting equipment. Also in 1995, approximately 12% of auto body shops surveyed planned to purchase HVLP spray equipment (BSB, 1995).

Testing conducted by the National Institute for Occupational Safety and Health (NIOSH) in an equipment manufacturer's test facility, demonstrated that particulate overspray concentration was reduced by a factor of 2, and that there was a 30% increase in the ratio of paint film thickness to mass of paint applied when a HVLP spray gun was used. These results indicate that using an HVLP spray-painting gun can reduce paint usage and overspray production, resulting in noticeably lower worker exposures (Heitbrink, 1996).

Discussions with a refinisher indicated that the establishment had 6 different models of HVLP spray guns. The manager confirmed that paint spray efficiency had increased to almost a 70% transfer rate, although some of the new low VOC paint formulations would not spray as well as some of the older lacquer paints. The high solid, low VOC paints often required more than 10 PSI nozzle pressure to atomize. A paint manufacturer's vendor indicated that HVLP technology has come a long way in the last three years. He said that he could line up 6 HVLP guns, all with similar ratings and supply 40 PSI into each gun, but the nozzle spray would not be uniform. Often the output would range from 6 - 10 PSI. The representative indicated that true atomization of low VOC paint formulations often occurs at nozzle pressures higher than 10 PSI (CCC, 1996).

A closed container HVLP gun cleaner was seen on site. Both the shop manager and the paint vendor indicated that this equipment was purchased in response to a new regulation in Maryland.

### Low Volume Low Pressure Spray Guns

Other guns used in the industry include low volume, low pressure (LVLP) guns. LVLP spray guns, like HVLP guns atomize coatings at lower velocity (9.5 to 10 psi) and at a lower velocity than conventional spray guns but use approximately 45 to 60 percent smaller volume of air than HVLP guns. Energy costs for air compression are reported to be less than with HVLP guns (USEPA, 1994).

### Electrostatic Spray Guns and Powder Coating Systems

Electrostatic spraying systems, which have deposition efficiencies of between 60 and 90 percent, are widely used in U.S. automotive assembly plants. Air-powered, electrostatic spray guns function in essentially the same way as electrostatic spray guns. Although transfer efficiencies for powder spray guns are similar to wet spray guns, the powder can be reused and these systems can operate with powder utilization rates of up to 98 percent. Neither of these systems are practical for refinishing systems, however, for the following reasons: (1) prohibitively high cost of electrostatic spray guns, (2) large amount of coating contained in the hose connecting electrostatic spray gun to pot, which must be removed when changing colors, (3) high curing temperatures required for powder systems (i.e., resulting in damage to other vehicle components), and (4) grounding methods required for electrostatic systems in an OEM environment cannot be duplicated for automobile refinishing.

Appendix E is a comparison of the characteristics of paint spray equipment for automotive refinishers.

### Spray Booths

Automobile spray painting operations produce aerosols containing droplets and solvent vapors where workers may be exposed. Spray booths, which are power-ventilated structures

enclosing a spraying operation, can confine and limit the escape of spray, vapor, and residue, and safely conduct or direct overspray and vapors to an exhaust system. Automobile painting activities are usually performed inside a spray booth to ensure a good finish, to reduce employee exposures to inhalation of solvent vapors and paint solids, and to reduce the hazards of fire and explosion arising from components used in paints and varnishes (Goyer, 1995). After painting, spray booths are used for ambient air drying or for drying at elevated temperatures. Evaluations of controls in the auto body refinishing industry, conducted by NIOSH, indicate that currently available spray-painting booths do not completely control worker exposure to paint overspray (Heitbrink, 1995).

Dry-type booths use filters to intercept and trap particles of overspray while water-wash booths use a flow of water over a solid surface to accomplish the same thing. Dry filters are commonly used for low to intermediate volume spray operations (NFPA, 1981). Waterwash booths are spray booths equipped with a water-washing system designed to minimize concentrations of dusts or residues entering exhaust ducts and to permit the collection of dusts or residues. Where high volume spray coating operations are conducted for several hours a day, waterfall or cascade scrubbers are commonly used (NFPA, 1981). Either type can be used successfully in almost all applications, however; in general dry-type booths are most often used in automotive refinishing shops. Water-wash booths are rarely used in auto body refinishing shops (Garcia, 1996).

Typical automobile refinishing industry spray-painting booths have a painting cycle and a curing cycle. These booths are equipped with supply air fans and exhaust air fans. The supply air fan moves air from outside the shop through a heat exchanger or natural gas burners, through a bank of filters, and into the spray painting booth. The exhaust air moves out of the booth through filters and out of the building (Heitbrink, 1995). To cure paint and polyisocyanate hardeners, the booths are operated at temperatures as high as 79° C (175° F), although curing temperatures are typically 49° C to 60° C (120° to 140° F). Purchase costs of small basic spray paint booths range from \$5,400 to \$23,000 (Spray Systems, 1996). For example, at a medium-size repair shop in Maryland the cost to install two booths in 1992 was approximately \$400,000. The purchase cost of each booth was approximately \$60,000 but the installation required extensive foundation modifications to accommodate the ventilation system (CCC, 1996).

Three types of commercially available spray-painting booths found in auto body shops include downdraft, semi-downdraft, and crossdraft spray painting booths. The characteristics of these booths are summarized below and presented in Appendix E.

### Crossdraft Spray Booths

In a crossdraft booth, the air enters through filters in the front of the booth and is exhausted through filters in the back of the booth (Heitbrink, 1995). Approximately 50% of U.S. auto body shops have crossdraft booths. An industry profile study, which provides data for 1995, indicates that approximately 42% of small (<\$124,999 annual sales) auto body shops had downdraft spray booths and approximately 25% of very large firms (>\$1 million annual sales) owned crossdraft spray booths

(BSB, 1995). The cost for crossdraft spray booths are in the \$5,500 to \$23,000 range plus installation and modifications to the physical plant.

### Downdraft Spray Booths

Downdraft spray-painting booths are designed to let air enter through filters in the ceiling of the booth and leave through a metal grate in the floor of the booth. In most U.S. automotive assembly plants, painting is done in a downdraft paint spray booth. During the painting process, conditioned ambient air is introduced to the paint spray booth through the roof. The air and paint pass downward over the parts to be painted. The paint overspray and solvent fumes exit with the exhaust air from the painting area through grates on the floor (Eklund, 1995).

Approximately 30% of U.S. auto body shops in 1995 reported having downdraft spray-painting booths, including approximately 8% of very small firms and 83% of very large shops. Approximately 19% of auto body shops planned to purchase downdraft booths (BSB, 1995). The cost for downdraft spray booths are in the \$12,000 to \$60,000 range plus installation and modifications to the physical plant.

### Semi-Downdraft Spray Booths

In a semi-downdraft booth, air enters through filters in the ceiling of the booth and is exhausted through filters in the back of the booth. During the painting process, conditioned ambient air is introduced to the paint spray booth through the roof. The air and paint pass down and across the parts to be painted. The paint overspray and solvent fumes exit with the exhaust air from the painting area through openings usually on one side of the booth (EPA, 1994).

Approximately 30% of U.S. auto body shops in 1995 reported having downdraft spray-painting booths, including approximately 8% of very small firms and 83% of very large shops. Approximately 19% of auto body shops planned to purchase downdraft booths (BSB, 1995). The BSB industry profile did not specify if the downdraft spray paint booth data represented semi-downdraft models. The cost for semi-downdraft spray booths are in the \$10,000 to \$23,000 range plus installation and modifications to the physical plant.

## **RESPIRATORY PROTECTION**

Because potential occupational exposures can exceed OSHA PELs during spray painting operations, respiratory protection is normally required for spray operations. Many types of respirators are available for such operations such as half-face air purifying, full-face air purifying, and airline (supplied air). If properly selected and used, respirators can help reduce worker exposure when other means of control are not feasible. The selection of a respirator is usually based on several factors such as the type of chemical exposure, duration of exposure, the physical state of

the chemical, and the regulatory standards or recommended exposure guidelines. OSHA standard 1910.134 details specific requirements for respiratory programs that employers must develop if respirators are needed to reduce occupational exposures. Data from a NIOSH study indicates that respirator usage at five of six auto body repair shops evaluated was inappropriate; respirators were in poor shape and not maintained properly, and the shops lacked formal, written respiratory program (Heitbrink, 1996). A second NIOSH study found that in the three auto body shops surveyed, workers used full face air and half face air purifying respirators with organic vapor cartridges and pre-filters designed for paint mists. This study also found that the respiratory protection programs in these three shops were not effective, and were not providing adequate protection to the employees (Heitbrink, 1995). A study of Australian auto body shops indicated that only 32% of the auto body repair workers had half-face piece air purifying respirators that did not leak (Heitbrink, 1996). As expected, surveys have found that breathing resistance and physical discomfort, such as pressure on the face and head, sweat on the face, and tightness of harness are often cited as the main reasons workers do not use respirators or use them improperly. A trend toward increased use of airline respirators in the auto body repair shops has been reported (Janko, 1992). This type of respirators typically causes less physical discomfort and should offer better protection.

NIOSH considers TDI as a potential occupational carcinogen and recommends that employees reduce worker exposure to the lowest feasible concentration. The use of respirators is the least preferred method of controlling worker exposure. Even as such, NIOSH recommends that only the most protective respirators should be used. These respirators include self contained breathing apparatus with full face pieces that are operated in a pressure demand or other positive-pressure mode or any supplied air respirator with a full face piece operated in pressure demand (NIOSH, 1989).

A respirator manufacturer's representative stated that in his opinion, it is likely that most auto body refinishing shops will have some sort of respirator on-site for refinishing operations. He also believes that the majority of the automotive refinishing shops have no written respirator program, and have not provided respirator training or fit testing for the workers. The larger shops, with annual sales of over one million probably have written respirator programs and more than one type of respirator available for the employees. He stated that his company and its regional distributors do not focus sales on this market segment so specific use data is not available. (Schmidt, 1996)

## **OPPORTUNITY FOR RISK REDUCTION AND INNOVATION**

### **Engineering Opportunities**

Occupational exposures are currently being managed through the use of various control technologies. The most effective means are engineering controls, particularly high volume low

pressure spray guns and downdraft spray paint booths. Other controls such as personal protective equipment including respiratory protection are also being used.

High Volume Low Pressure (HVLP) spray guns are the most effective spray guns at controlling occupational exposures. This is because they are better at atomizing the air stream resulting in a more controlled spray pattern, less bounce back, and enhanced transfer efficiency. In addition, they have a higher transfer rate than other types of spray guns (Heitbrink, 1995). As a result, HVLP technology has become commonplace in the industry (BAAWMD, 1995). As stated earlier, in 1995, approximately 64% of U.S. auto body shops reported owning HVLP equipment (approximately 49% of small auto body shops (<\$124,999 annual sales) and approximately 68% of very large (>\$1 million annual sales). Also in 1995, approximately 12% of auto body shops surveyed planned to purchase HVLP spray equipment (BSB, 1995). This provides an opportunity to encourage the wider use of HVLP spray guns and in providing product stewardship information to help counter some of the perceived disadvantages.

The wider adoption of spray booths provide the opportunity to reduce general worker exposure. The types of booths include both downdraft with either dry-type when painting is limited or waterfall or cascade scrubbers when high volume spray coating operations are conducted for several hours a day. For example, NIOSH recommends in their Hazard Control documents that “properly used and maintained HVLP spray painting guns and downdraft booths will greatly reduce paint overspray concentrations, but they will not completely eliminate overspray from the air that workers breathe. Therefore, Personal Protective Equipment is also recommended with a Respiratory Protection Program that contains all of the elements currently required by the OSHA standard (such as worker evaluation, selection of appropriate air purifying or supplied air respirators, fit testing, training, and maintenance needed to fully protect workers from this hazard.” (NIOSH, 1996)

### **Green Chemistry Opportunities**

The Pollution Prevention Act of 1990 (PPA) establishes a national pollution prevention ethic in dealing with environmental problems in the United States. The PPA states that:

“The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner.”

During the past several years, the chemical industry has put a lot of efforts toward pollution prevention issues associated with the manufacture and use of various chemicals. Particularly, in the PPA’s mandate on source reduction. Source reduction in the PPA is defined, in part, as

“any practice which (I) reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and (ii) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants.”

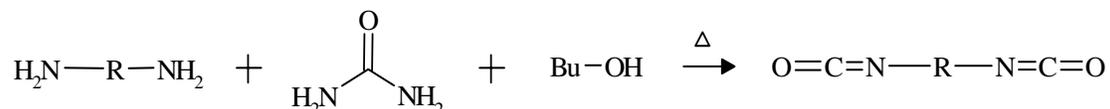
A great number of innovative chemistries (e.g., Green Chemistry practices) have been developed under this mandate.

### Practices in Isocyanates Manufacture

Isocyanates monomers are commonly produced by the phosgenation processes as mentioned before. In the present day climate of moving toward greater protection of health, safety, and the environment, efforts to replace phosgene with safer substitutes that by design are benign chemical processes are gaining ground. Some examples of new phosgene-free synthetic pathways have been identified. They show potential for replacement of conventional phosgenation processes long used by the isocyanates chemical industry.

#### Huls A.-G.’s Urea Adduct-based, Phosgene-free Diisocyanate Process

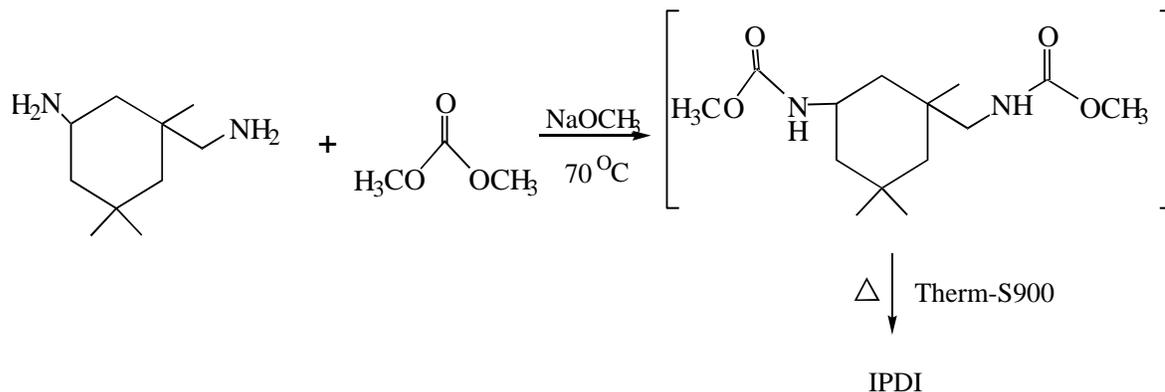
During the past ten years, Huls in Germany has developed a novel, pilot-scale process for the production of diisocyanates from diamines. The new route accomplishes the conversion of isophorone diamine (IPDA) to IPDI using a urea adduct-based process. Huls has announced this will be the large scale manufacturing process used in the \$40 million diisocyanate plant to be operational in Theodore, Alabama, by 1996. According to Hunter and Rotman, it is said to be a highly versatile technology by which "any diamine can be converted [into a diisocyanate]" (1994). Hul also manufactures other aliphatic diisocyanate raw materials for the coatings industry that are said to include the saturated compounds, dimethyl diisocyanate and hexamethylene diisocyanate. BASF A.-G. (Germany) has a similar process developed to produce various diisocyanates (Hellbach *et al*, 1984; Merger *et al*, 1984). The overall reaction is:



#### Daicel’s Phosgene-free Process to Produce Diisocyanates via Diurethanes

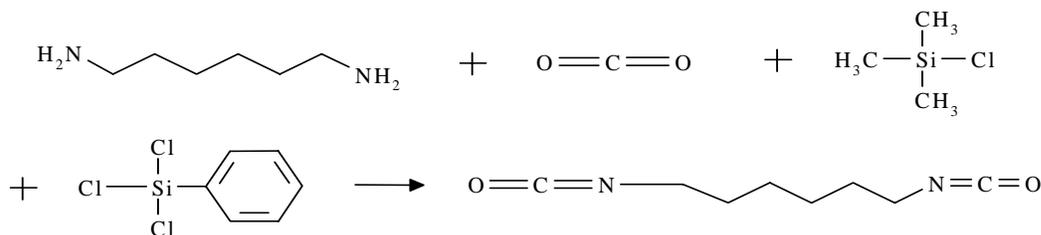
Daicel Chemical Industries, Ltd., has patented a process for reacting diamines such as isophorone diamine (IPDA) with dimethyl carbonate (Yagii *et al.*, 1988). The condensation is accomplished in the presence of an alkaline catalyst such as methanolic sodium methylate at 70° C to produce the diurethane. Treatment of the diurethane with hydrogenated terphenyl containing

manganese acetate at 230°C in vacuo produces isophorone diisocyanate by thermal decomposition. This non-phosgene process has a reported product yield of 93% of IPDI containing 1% isophorone monoisocyanate. The overall reaction is:



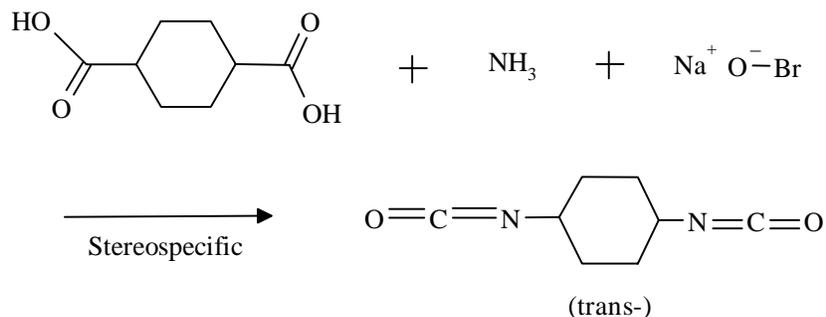
#### Union Carbide Corp. - CO<sub>2</sub>- based Process to Produce Diisocyanates

This process offers an alternative for isocyanates from amine and dry ice via halosilyl carbamates intermediate without using phosgene. The silylcarbamate was trans-silylated with trichlorophenylsilane and then heated to give hexamethylene diisocyanate (Hedaya et al., 1981). The reaction is:



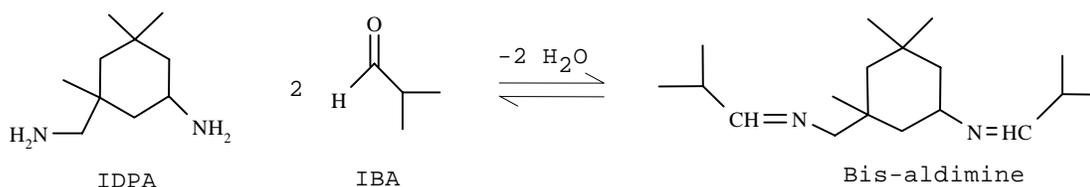
#### Akzo Corp., Obernburg (Germany) - Phosgene-free Process to Produce Diisocyanate

This is a new phosgene-free process for isocyanates/diisocyanates from acids or esters (Zengel et al, 1980). Terephthalic acid or 1,4-cyclohexanedicarboxylic acid (obtained from hydrogenation of terephthalic acid) were converted to diisocyanate by a 4-step process consisting of ammonolysis, amide chlorination (or bromination), Hofmann rearrangement, followed by urethane cleavage (if Br<sub>2</sub>/NaOCH<sub>3</sub>/CH<sub>3</sub>OH were used in Hofmann rearrangement). The reaction is as follows:

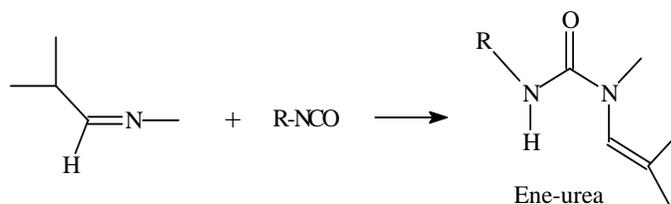


### Practice in Other Area

Under the President's Green Chemistry Challenge Awards Program for 1995-1996, Bayer Corporation submitted a nomination, titled "A Foundation for Environmentally-Friendly High Solids Coatings" (Bayer Corp., 1995). The technology presented is a reactive coating system comprised of an aliphatic polyisocyanate and a low viscosity, bis-aldimine functional resin. The bis-aldimine resin is formed by the reaction:



The bis-aldimine resin has viscosity of less than 100 mPa. Therefore, it also functions as solvent in the coatings/paints application to reduce the VOC content. When this bis-aldimine reacts with isocyanate, it gives an Ene-urea without releasing aldehyde (scheme below). Water is the catalyst for isocyanate rxn.



## **Environmental Benefits of the Technology**

### VOC Reduction in Polyurethane Paints

The aldimine coreactants were developed with the intention of reducing the VOC content of 2-component polyurethane coatings. Due to the lower viscosity of the aldimines as compared to traditional products, a smaller amount of solvent is required to get the coating material to the desired application viscosity.

### Waste Reduction

When aldimines are mixed with polyisocyanates, the formulations increase very slowly in viscosity as long as they are stored in a closed container. The paint therefore has a long pot life, thus minimizing the amount of unused paint which must be disposed. In addition, in contrast to typical high-solids coreactants, the paint dries quickly at ambient temperatures after its application, and thus avoids the time and energy requirements for thermal baking of the coating.

### Control of Release into Aqueous Environments

The parent amines used for the aldimines are water soluble but the aldimine products themselves are characterized by very low solubility. According to Bayer's document, there is no hydrolysis of aldimines (detectable by IR) when they were exposed to a large molar excess of water, even when the reaction is run homogeneously in a polar organic solvent. This insolubility provides two major benefits. First, it aids in the physical isolation of the product in the case of release. Second, it keeps the product available for reaction with the polyisocyanate which is also insoluble in water.

## **ENVIRONMENTAL RELEASES**

In automotive refinishing, the potential release points of a nonvolatile PMN are as follows:

- Air filter waste from overspray.
- PMN-containing mist entrained in the stack air.

EPA estimates that up to 10% of the solids may be released to the facility's waste water treatment plant, based on a pilot plant operation of paint solids removal in a non-automotive industry (Sokolovic, 1996). This assumption is uncertain due to the absence of industry specific data and may be conservative.

Water releases are not expected. EPA's information from the literature and from a spray booth manufacturer (Garcia, 1996) indicates that water controls in spray booths are seldom, if ever, used.

Air releases can result from the dry filter control if this air is not recycled to the spray booth. EPA estimates this release as 10 percent of the daily overspray generation quantity, based on a midpoint paint booth removal efficiency of 90 percent for various types of paint with dry filters (Rodriguez, 1987).

Solid waste releases (to landfill or incineration) will also result from overspray, equipment cleanup, and container residue. EPA estimates the quantity from overspray as 75 percent of the use volume (based on Heitbrink, 1996, for conventional guns). EPA did not find information for equipment cleanup and container residue specific to the automobile industry, but estimates these quantities as totaling 5 percent of the use volume based on similar operations in other industries.

## **ENVIRONMENTAL FATE**

The assessment that follows is a general characterization of the environmental fate and wastewater treatment pathways for the isocyanate substances based on PMNs containing isocyanate data. The isocyanates subject to this fate assessment comprise a diverse group of compounds whose fate in the environment varies little. Hydrolysis would represent the primary fate mechanism for the majority of the compounds reviewed, but, is tempered somewhat by the lack of water solubility. In the absence of hydrolysis, sorption to solids (e.g., sludge and sediments) will be the primary mechanism of removal. Biodegradation is minimal for most compounds and volatilization is negligible. Atmospheric degradation is not expected with removal from air occurring by washout or dry deposition.

### **Volatilization**

The volatility of most compounds reviewed ranged from  $10^{-4}$  to  $10^{-7}$ . Volatilization from surface waters (e.g., lakes and rivers) is expected to take years. In wastewater treatment this process is not expected to be significant.

### **Sorption**

Review of the estimated properties suggest that this mechanism is the primary removal mechanism in the ambient environment and in wastewater treatment in the absence of significant hydrolysis. Sorption to solids in wastewater treatment is considered strong to very strong for most compounds. Sorption to sediments and soils in the ambient environment is very strong in most instances. Migration to groundwater and surface waters is not expected due to sorption or hydrolysis.

## Hydrolysis

Hydrolysis of the N=C=O will occur in less than hours in most instances and within minutes for more than 90% of the substances reviewed. However, the low to very low solubility of these substances will generally lessen the effectiveness of hydrolysis as a fate pathway. But hydrolysis should be considered one of the two major fate processes for the isocyanates.

## Biodegradation

Aerobic and/or anaerobic biodegradation of the isocyanates is not expected to occur at significant levels. Most of the substances reviewed indicate greater than months for degradation. Degradation of the hydrolysis products will occur at varying rates depending on the moiety formed.

## REGULATORY HISTORY

The regulations cited in this report, especially the testing and reporting rules, have a direct impact on the chemical manufacturers of these isocyanates. However, the impact of these regulations goes beyond manufacturers and extends to wholesale distributors of paint products, paint jobbers, and operators of auto body shops. At each of these operations (manufacture, distribution, and use) it is important to evaluate how regulatory activity affects the transport of these chemicals, the disposal of hazardous wastes resulting from the use of these chemicals, and the releases of VOCs. Regulatory activity was investigated for 18 isocyanate chemicals in the following areas:

- Federal Environmental Regulations (to include TSCA, SARA, CAA, SDWA, and CWA)
- Dept. of Transportation Regulations
- OSHA Regulations
- State Regulations (CA, CO, NJ, OR, TX, and WA)
- International Regulations
- TSCA PMN Actions

Some regulatory activity was found for almost all the chemicals in this group. In fact, of the 18 chemicals examined, only three had absolutely no regulatory activity (058067-42-8, 083748-30-5, and 028679-16-5). The regulatory activity was focused primarily in TSCA and EPCRA. Specifically within TSCA the regulations were either 8(a) reporting rules under CAIR and PAIR, 8(d) Health and Safety Reporting, and ITC actions were the most prevalent. Within the SARA regulatory area, the regulations, dealt primarily with adding chemicals to the Toxic Release Reporting Inventory or to the Extremely Hazardous Substances list.

In the occupational exposure regulation area, OSHA has promulgated a set of PELs on some of the diisocyanates that each employer must comply with. Individual states can also establish a more stringent exposure limits. Outside of regulatory activity, NIOSH and ACGIH have

recommended their respective exposure limits for some of the diisocyanates. NIOSH's recommended limits are called the Recommended Exposure Limit (REL) while the ACGIH calls their exposure limits as the Threshold Limit Value (TLV). Both these recommended exposure limits are not legally enforceable. The PEL, REL, and TLV can be established for a daily TWA (either as 8-hour or 10-hour TWA), a Short Term Exposure Limit (STEL), or as a ceiling limit. The following is a summary of these values.

CAS #	Name	OSHA PEL (ppm) 8-hr TWA	OSHA PEL (ppm) 15-min Ceiling	NIOSH REL (ppm) 10-hr TWA	NIOSH REL (ppm) 10-min Ceiling	ACGIH TLV (ppm) 8-hr TWA	ACGIH TLV (ppm) STEL	California PEL (ppm) 8-hr TWA	California PEL (ppm) 15-min Ceiling
000101-68-8	MDI	--	0.02	0.005	0.02	0.005	--	0.005	--
000504-84-9	TDI	--	0.02	0.005	0.02	0.005	--	0.005	--
000822-06-0	HDI	--	--	0.005	0.02	0.005	--	0.005	--
004098-71-9	IPDI	--	--	0.005	0.02	0.005	--	0.005	--
005124-30-1	Methylenebis (4-cyclohexylisocyanate)	--	--	0.005	0.02	0.005	--	0.005	--
028679-16-5	Trimethylhexamethylene diisocyanate	--	--	--	--	--	--	0.005	--

Of the states investigated, California, Colorado, and New Jersey had the more extensive regulations on these chemicals. The regulatory actions for isocyanates identified in these six states can be organized into four broad categories: 1) those that identify and list the chemical as a hazardous air pollutant or substance; 2) those setting emission standards; 3) those subjecting the chemical to reduction goals; 4) those that establish worker safety standards (similar to or more stringent than OSHA/NIOSH standards).

Summary of findings by type of regulation is presented below:

1. There was more regulatory activity under TSCA than any other regulatory area. Most of the activity involved listing a chemical under section 8(a) or 8(d) or deleting a chemical from the requirements under these sections. In total, there were 10 chemicals with 8(a) information gathering activity and 13 chemicals with 8(d) health and safety reporting activity.
2. SARA had the second most regulatory activity. Within the SARA regulatory area, the regulations dealt primarily with adding chemicals to the Toxic Release Inventory (TRI) or to the Extremely Hazardous Substances list. Of the chemicals under investigation, 12 are listed under the TRI and three are listed as Extremely Hazardous Substances.
3. No CWA or SDWA regulations exist on these chemicals, according to EPA sources including the Safe Drinking Water Hotline, and the Wastewater Treatment Information Exchange.
4. There were only three chemicals that were regulated under the Clean Air Act's Hazardous Air Pollutant regulations. These chemicals are MDI (101-68-8), TDI (584-84-9), and HDI (822-06-0). However, general CAA VOC regulations significantly affect the automotive refinishing industry in spurring the development of lower VOC isocyanates in paint formulations.
5. DOT regulatory activity was uncovered for four chemicals. These regulations require special shipping and handling requirements for these chemicals.

Appendix G summarizes the type of regulatory activity for each of the isocyanate CAS Numbers.

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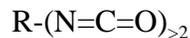
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## APPENDIX A

### ISOCYANATE CHEMICAL CATEGORY

**Definition.** Any molecular structure containing two or more isocyanate groups is considered to be a member of the category for new chemical purposes:



Members of the class include new isocyanate monomers as well as new oligomers, polymers, prepolymers, or reaction products of existing isocyanate monomers. Most new chemical isocyanates of concern are polymers or oligomers containing well-known diisocyanate monomers such as toluene diisocyanate (TDI) or methylenebis (p-phenylisocyanate) (MDI).

**Hazard Concerns.** Isocyanates are of concern for potential dermal and pulmonary sensitization, and other lung effects. Aromatic isocyanates may be potential carcinogens based on analogy to TDI or 3,3'-dimethoxybenzidine-4,4'-diisocyanate (dianisidine diisocyanate, DADI).

**Boundaries.** Structures with an isocyanate equivalent weight  $\geq 5,000$  are presumed not to pose a hazard under any conditions. Typically, concerns are confined to those species with molecular weights  $< 1,000$ . Based on submitted test data, the Agency does not have pulmonary sensitization concerns for polymers derived from m-tetramethylxylene diisocyanate (CAS# 2778-42-9) or a,a-dimethyl-m-isopropenyl benzyl isocyanate (CAS # 2094-99-7).

The new chemical program has thus far been concerned only with those isocyanates having potentially significant inhalation exposure.

Frequently, new chemical isocyanates are manufactured with a significant excess of isocyanate monomer. Under these circumstances, the excess monomer is usually regarded as more hazardous than the “new” chemical component, and these PMN substances are ordinarily not regulated under section 5 TSCA. A PMN substance is considered “existing” if more than 50% of the free isocyanate groups in the PMN substance (new chemical component + existing chemical monomer) reside on unreacted monomer(s).

#### General Testing Strategy

The following three tests are usually prescribed for isocyanates found to pose a potentially unreasonable risk:

- Dermal sensitization (40 CFR 798.4100)

- 90-day subchronic inhalation toxicity (40 CFR 798.2450)
- Pulmonary sensitization be either the Karol method (Toxicol. Appl. Pharmacol. 68:229-241, 1983) or the Sarlo and Clark method, level 3 & 4 (Fundamental & Applied Toxicology 18:107-114, 1982) or an equivalent method.

May 1990; revised 1993; revised February 1995.

## APPENDIX A-1

### DEFINITIONS

*Editor's Note:* EPA has added Appendix A-1 to reference definitions of terms provided by the American Chemistry Council<sup>2</sup> on September 8, 2004.

<<http://www.epa.gov/quality/informationguidelines/iqg-list.html>>

This Appendix also contains definitions used by the National Institute for Occupational Safety and Health (NIOSH) in its summary of diisocyanate health hazard evaluations<sup>3</sup> and the definition of “polymer” in the TSCA polymer exemption rule, 40 CFR 723.250(b)).

Definitions of Monomer, Prepolymer, Polymer, and Polyisocyanates and related terms:

1.) Nomenclature provided by the American Chemistry Council’s Diisocyanates Panel.

A “polymer” is a substance where each molecule is made of many repeating structural units, and the various molecules are of varying molecular weights (that is, the number of repeating units varies). Fully-reacted diisocyanate-based polymers are primarily substances known as polyurethanes – two component polymers made by reacting diisocyanate monomers or prepolymers with polyols. There are also fully-reacted single-component diisocyanate-based polymers known as polyisocyanurates. There are no reactive isocyanate groups in a fully-reacted diisocyanate-based polymer – all isocyanate groups were reacted during the formation of the polymer.

A “monomer” is the starting unit from which the polymer is formed. An aliphatic diisocyanate monomer consists of an aliphatic hydrocarbon chain (straight-chained or cyclic) with two isocyanate groups.

“Oligomer” is used to refer to a substance in which each molecule is made up of several repeating structural units. It can be thought of as a start on a polymer, but it does not have enough repeating units to qualify as a polymer. Unlike the fully-reacted diisocyanate-based polymer, the oligomer molecules may still have reactive isocyanate units.

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<sup>2</sup> Letter from the American Chemistry Council Aliphatic Diisocyanates Panel to EPA’s Information Quality Guidelines Staff, September 8, 2004, p. 3.

<<http://www.epa.gov/quality/informationguidelines/iqg-list.html>> [RFC 04025](#) (PDF 100 KB) **Subject:** Information on health effects of diisocyanates on the Design for the Environment Web page.

<sup>3</sup>A Summary of Health Hazard Evaluations: Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002, Department of Health and Human Services, January 2004, NIOSH Publication No. 2004-116 <<http://www.cdc.gov/niosh/docs/2004-116/pdfs/2004-116.pdf>> or 1-800-356-4674.

The term “prepolymer” is usually used to refer to short chain oligomers made from at least two different monomers, e.g., HDI with glycols. For aliphatic diisocyanates, the term “prepolymer” is also sometimes used to refer to what is technically a homopolymer, or polyisocyanate.

A “homopolymer” is a short chain oligomer made from a single monomer (versus a prepolymer made from two or more monomers). Diisocyanate homopolymers are known as “polyisocyanates.”

2.) Definitions provided by National Institute for Occupational Safety and Health (NIOSH).

**Diisocyanates (Monomers):** The difunctional isocyanate species from which polyisocyanates and polyurethanes are derived. Common examples of monomeric isocyanates include 1,6-hexamethylene diisocyanate (HDI), 2,4- and/or 2,6-toluene diisocyanate (TDI), 4,4' diphenylmethane diisocyanate (MDI), methylene bis (4-cyclohexylisocyanate) (HMDI), isophorone diisocyanate (IPDI), and 1,5-naphthalene diisocyanate (NDI). Commercial-grade TDI is an 80:20 or 65:35 mixture of the 2,4- and 2,6-isomers of TDI, respectively.

**Polyisocyanates:** Species possessing free isocyanate groups and derived from monomeric isocyanates either by directly linking these monomeric units (a homopolymer) or by reacting these monomers with di- or poly-functional alcohols or amines (a copolymer).

**Prepolymers:** Species possessing free isocyanate groups, prepared from the reaction of a polyol with an excess of di- or polyisocyanate. Commercially available isocyanate products frequently contain prepolymers in lieu of more volatile isocyanate monomers.

**Oligomeric Isocyanates (Oligomers):** Relatively low molecular weight polyisocyanates.

**Intermediates:** Species possessing free isocyanate groups, formed during use of an isocyanate product by partial reaction of the isocyanate species with a polyol.

3.) Polymer definition: TSCA Polymer Exemption Rule, 40 CFR 723.250(b)

**Polymer** - a chemical substance consisting of molecules characterized by the sequence of one or more types of monomer units and comprising a simple weight majority of molecules containing at least 3 monomer units which are covalently bound to at least one other monomer unit or other reactant and which consists of less than a simple weight majority of molecules of the same molecular weight. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units. In the context of this definition, sequence means that the monomer units under consideration are covalently bound to one another and form a continuous string within the molecule, uninterrupted by units other than monomer units.”

## APPENDIX A-2

### CLARIFICATION OF MONOMER CONTENT IN PREPOLYMERS AND POLYMERS

*Editor's Note:* EPA has added Appendix A-2 to include information on the monomer content in prepolymers and polymers provided by the American Chemistry Council<sup>4</sup> on September 8, 2004. <<http://www.epa.gov/quality/informationguidelines/iqg-list.html>>.

HDI prepolymers (or polyisocyanates) contain only a small residual amount of monomer – usually less than 1%. The trimer (isocyanurate trimer) form of HDI polyisocyanate contains less than 0.2% of residual monomer, and this amount is stable over time. The biuret form contains approximately 0.5% when first manufactured; during storage this amount may rise to as much as 1.6% if temperatures are high (>120 F). Thus, in any circumstance, residual monomer in an HDI prepolymer (polyisocyanate) is less than 2%. HDI prepolymers are isocyanate-terminated, leaving functional isocyanate groups that can react with polyols or other substances.

IPDI-based polyisocyanates are typically isocyanurate trimer homopolymers of IPDI. They usually contain less than 0.5% monomeric IPDI at the time of manufacture, and, like the HDI isocyanurate polyisocyanates, their monomer content is stable over time.

A fully-cured polymer (polyurethane or polyisocyanurate) contains no residual monomer. It also has no functional isocyanate groups – all such groups are reacted in the formation of the polymer.

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<sup>4</sup> Letter from the American Chemistry Council Aliphatic Diisocyanates Panel to EPA's Information Quality Guidelines Staff, September 8, 2004, p. 4. <<http://www.epa.gov/quality/informationguidelines/iqg-list.html>> [RFC 04025](#) (PDF 100 KB) **Subject:** Information on health effects of diisocyanates on the Design for the Environment Web page.

## APPENDIX B

### SPRAY PAINT EXPOSURE SUMMARIES FOR ISOCYANATES

Industry	Isocyanate Sampled	Eng controls/ gun type	Activity Description	Airborne Concentration (mg/m <sup>3</sup> )	Reference
Automobile painting (crash repair workshop)	Active isocyanate	none/NA	Paint mixing & Spray gun washing	0.001 (P) (# of samples not provided)	Pisaniello & Muriale, 1989 (#10)
Automobile painting (crash repair workshop)	Active isocyanate	none/NA	Dry rubbing with mechanical sander (when new coat is few hours old)	0.006- 0.02 (P) (#=2) sample periods were approx 18 min duration	Pisaniello & Muriale, 1989 (#10)
USAF Automobile & Miscellaneous parts	HDI	crossdraft/ HVLP	Spray painting of large vehicles and objects	0.017-0.22 (P) (#=2) 0.004-0.14 (A) (#=4) sample period not reported	Rudzinski et. al., 1995 (#12)
Keesler AFB	N-75 (aliphatic polyisocyanates)	crossdraft/ HVLP	Spray painting trucks	1.0-1.9 (P) (#=2) 1.6-4.1 (A) (#=4) sample period not reported	Rudzinski et. al., 1995 (#12)
Langley AFB	N-75 (aliphatic polyisocyanates)	crossdraft/ HVLP	Spray painting aircraft ground equipment	4.7-5.2 (P) (#=2) 4.9-13.9 (A) (#=4) sample period not reported	Rudzinski et. al., 1995 (#12)
Car Paint Shops	Oligomer HDI	downdraft/ conventional	Spray paint operations (measured at various heights above floor)	5 in. - 2.6 (A) 32 in. - 2.9 (A) 43 in. - 1.9 (A) 55 in. - 1.4 (A)	Lesage et al, 1992 (#53)
USAF vehicle painting	TDI	crossdraft/ conventional	Spray painting operations	3.0 (P) (#=3) sample period not reported	Dept. of the Army Medical Command, 1996 (#69)

Industry	Isocyanate Sampled	Eng controls/ gun type	Activity Description	Airborne Concentration (mg/m <sup>3</sup> )	Reference
Paint Manufacturing & Application Operations using PUR coatings	HDI and HDI-based polyisocyanates	no information	Transportation Aftermarket	0.0006-0.015 (P) (geometric mean = 0.03) (#=35) sample period not reported	H.E. Myer et al, 1993 (#70)
Car Spray painting	HDI polyisocyanate	Downdraft/ no info	Spray painting	0.25 - 3.0 (P) (#=12) sample period not reported	Maitre et al, 1996 (#54)
Paint Manufacturing & Application Operations using PUR coatings	HDI	no information	Heavy Equipment/Military	0.04 (geom mean) (#=25)(P)	H.E. Myer et al, 1993 (#70)
Paint Manufacturing & Application Operations using PUR coatings	HDI	no information	Maintenance/Construction	0.05 (geom mean) (#=16) (P)	H.E. Myer et al, 1993 (#70)
Paint Manufacturing & Application Operations using PUR coatings	HDI	no information	Wood/Furniture	0.02 (geom mean) (#=11) (P)	H.E. Myer et al, 1993 (#70)
Industrial Spray Operations	HDI monomers & HDI polyisocyanates	crossdraft/ conventional	Spray Painting & Related Operations	HDI monomer 0.007 (P) (geom mean) (#=24) HDI polyisocyanates 0.70-12.2 (P) (geom mean =3.87) (#=24)	M. Janko et al, 1992 (#76)
Auto Body Shops	HDI monomers & HDI polyisocyanates	crossdraft/ conventional	Spray Painting & Related Operations	HDI monomer 0.014 (P) (geom mean) (#=55) HDI polyisocyanates ND-18.4 (P) (geom mean =1.60) (#=55)	M. Janko et al, 1992 (#76)
Spray Finishing of Large Objects	HDI monomers & HDI polyisocyanates	crossdraft/ conventional	Spray Painting & Related Operations	HDI monomer 0.007-0.11(P) (#=31) HDI polyisocyanates 2.09-15.9 (P) (#=31)	M. Janko et al, 1992 (#76)
Auto Refinishing	HDI Oligomer	downdraft/ no info		0.1-2.16 mg/m <sup>3</sup> sample period twa	(#91)

P = personal sample

A = area sample

# = No. Samples collected

**APPENDIX C**

**PAINT AND ALLIED PRODUCTS: QUANTITY (000 GALLONS) AND VALUE (\$000) FOR SELECTED SIC CODES, 1990 - 1994**

Year	Item	Total Paints & Allied Products (2851)	Total Architectural Coatings (28511)	Total OEM Product Finishes (28512)	Special Purpose Coatings		Total Miscellaneous Products (28515)
					Total (28513)	Refinishes <sup>1</sup> (2851313)	
1990	Quantity	1,231,759	558,438	325,566	<b>184,542</b>	<b>63,385</b>	163,213
	% Quantity	100.00%	45.34%	26.43%	<b>14.98%</b>	NA	13.25%
				100.00%	<b>37.06%</b>		
1990	Value	12,424,316	4,913,598	3,877,474	<b>2,624,041</b>	<b>1,272,607</b>	1,990,203
	% Value	100.00%	39.55%	31.21%	<b>21.12%</b>	NA	8.12%
				100.00%	<b>48.50%</b>		
	\$/Gal	\$10.09	\$8.80	\$11.91	<b>\$14.22</b>	<b>\$18.61</b>	\$6.18
1991	Quantity	1,178,366	537,939	308,123	<b>169,367</b>	<b>47,536</b>	162,937
	% Quantity	100.00%	45.65%	26.15%	<b>14.37%</b>	NA	13.83%
				100.00%	<b>28.07%</b>		
1991	Value	12,536,222	4,900,736	3,851,364	<b>2,746,074</b>	<b>1,230,006</b>	1,028,048
	% Value	100.00%	39.12%	30.75%	<b>21.92%</b>	NA	8.21%
				100.00%	<b>44.79%</b>		
	\$/Gal	\$10.63	\$9.11	\$12.50	<b>\$16.21</b>	<b>\$25.88</b>	\$6.31
1992	Quantity	1,228,531	571,022	315,148	<b>170,815</b>	<b>45,187</b>	171,546
	% Quantity	100.00%	46.48%	25.65%	<b>13.90%</b>	NA	13.96%
				100.00%	<b>26.45%</b>		

Year	Item	Total Paints & Allied Products (2851)	Total Architectural Coatings (28511)	Total OEM Product Finishes (28512)	Special Purpose Coatings		Total Miscellaneous Products (28515)
					Total (28513)	Refinishes <sup>1</sup> (2851313)	
	Value % Value	13,538,654 100.00%	5,252,250 38.79%	4,260,334 31.47% 100.00%	<b>2,901,840</b> <b>21.43%</b> <b>46.41%</b>	<b>1,346,777</b> NA	1,124,230 8.30%
	\$/Gal	\$11.02	\$9.20	\$13.52	<b>\$16.99</b>	<b>\$29.80</b>	\$6.55
1993	Quantity % Quantity	1,328,755 100.00%	603,326 45.41%	360,530 27.13% 100.00%	<b>177,013</b> <b>13.32%</b> <b>22.16%</b>	<b>39,222</b> NA	187,886 14.14%
	Value % Value	14,574,244 100.00%	5,570,784 38.22%	4,841,594 33.22% 100.00%	<b>2,905,703</b> <b>19.94%</b> <b>42.14%</b>	<b>1,224,395</b> NA	1,256,163 8.62%
	\$/Gal	\$10.97	\$9.23	\$13.43	<b>\$16.42</b>	<b>\$31.22</b>	\$6.69
1994	Quantity % Quantity	1,420,240 100.00%	640,054 45.07%	386,315 27.20% 100.00%	<b>191,490</b> <b>13.48%</b> <b>20.45%</b>	<b>39,161</b> NA	202,381 14.25%
	Value % Value	15,415,397 100.00%	5,865,814 38.05%	5,139,166 33.34% 100.00%	<b>3,041,246</b> <b>19.73%</b> <b>38.48%</b>	<b>1,170,158</b> NA	1,369,171 8.88%
	\$/Gal	\$10.85	\$9.16	\$13.30	<b>\$15.88</b>	<b>\$29.88</b>	\$6.77

<sup>1</sup> SIC 2851313 consists of automotive, other transportation and machinery refinish paints and enamels, including primers.  
Source: BOC-CIR 1992, 1993, 1994, 1995.

## APPENDIX D

### 1992 ECONOMIC CENSUS DATA FOR SELECTED AUTOMOTIVE AND PAINT-RELATED SIC CODES

SIC Code	SIC Description	Number of Companies	Number of Establishments	Number of Employees	Number of Sales (\$000)	Sales per Employee per Establishment (\$000)	Establishment (\$000)
<i>CENSUS OF MANUFACTURERS (BOC-COM 1992)</i>							
2851	Paints and Allied Products	1,130	1,418	51,200	14,973,700	36.1	10,559.7
28512	OEM Product Finishes		286	17,000	3,884,800	59.4	13,583.2
28513	Special Purpose Coatings		179	10,100	3,280,500	56.4	18,326.8
<i>CENSUS OF SERVICE INDUSTRIES (BOC-CSI 1992)</i>							
7532 (part)	Automotive Repair Shops	N/A	2,762	12,008	772,842	4.3	279.8
7532 (part)	Top, Body and Upholstery Repair Shops	N/A	32,281	153,886	11,489,644	4.8	355.9
551	New and Used Car Dealers	N/A	24,380	860,139	333,801,369	35.3	13,691.6

## APPENDIX E

### COMPARISON OF CHARACTERISTICS OF PAINT SPRAY EQUIPMENT FOR AUTOMOTIVE REFINISHERS

Type of Painting System	Performance Characteristics		System Transfer Efficiency (%)	Cost Range (\$)	Population of Shops Using Equipment
	Advantages	Disadvantages			
<b>Conventional</b>	<p>Low cost                      Low maintenance                      Excellent material atomization                      Excellent operator control                      Quick color change capabilities                      Coating can be applied by syphon or under pressure</p>	<p>Uses high volume of air                      Develops excessive spray dust and overspray fog                      Does not adapt to high volume material output (economies of scale)                      Low transfer efficiency                      Pressure fed systems require high volumes of coatings</p>	20 to 40	up to 350	Specific population data is unknown. Some states have mandated the use of HVLP systems by automotive refinishers.
<b>High Volume Low Pressure</b>	<p>Low blowback and spray fog                      Will apply high-viscosity high solid coatings (low VOC coatings)                      Relatively easy to clean                      Can be used for intricate parts                      Good operator controls</p>	<p>High initial cost                      Slower application speed with some coatings                      Does not fully atomize some coatings                      Higher maintenance costs                      Requires operator training                      Still relatively new to the market</p>	at least 65	500-1000	64% of all shops
<b>Low Volume Low Pressure</b>	<p>Low blowback and spray fog                      Will apply high-viscosity high solid coatings                      Easy to clean                      Can be used for intricate parts                      Good operator controls                      Needs less air compression than HVLP                      Lower energy requirements</p>	<p>High initial cost                      Slower application speed than HVLP                      Does not fully atomize some coatings                      Higher maintenance costs                      Requires operator training                      Still relatively new to the market</p>	at least 65	500-1000	Population data is unknown
<b>Powder Coating</b>	<p>Almost zero VOC emissions                      Excess or waste powder can often be melted                      Powder can be applied to hot or cold parts                      Ideal for robotic application                      Applied in single coat system                      Economical for long runs of a few colors</p>	<p>Generally, capital equipment outlay is greater than for conventional coatings                      High energy usage due to high temperature ovens                      Some powders require temperatures as high as 500°F for curing                      Not suited for every application (parts that can not tolerate high temperature plastics, rubber, upholstery)</p>	Up to 95	5000-100000	Population data is unknown Powder coating systems are used primarily in OEM operations.

Sources: EPA, 1994 and BSB, 1995

## APPENDIX F

### COMPARISON OF CHARACTERISTICS OF PAINT SPRAY BOOTHS

Paint Booth System	Performance Characteristics <sup>1</sup>		Cost Range <sup>2</sup>	Population of Shops Using Equipment <sup>3</sup>
	Functional Advantages	Disadvantages		
<b>Downdraft</b>	State of the Art worker protection Air movement - enters the booth through the ceiling and passes out the floor of the unit Lowest air turbulence of the three systems available Best system for preventing paint deformities	May cost more than other systems May require extensive renovation at existing facilities Operator training necessary Extra energy needed for heated systems	\$12,000-\$60,000	30% of all body shops use downdraft or semi-downdraft paint booth systems Most common paint booth system in shops with sales greater than \$750,000 annually
<b>Semi-Downdraft</b>	Low air turbulence Air movement - enters the booth through the ceiling and passes out the back of the unit Installation may not require as much site renovation as downdraft	More air turbulence than downdraft May require extensive construction at existing facilities Operator training necessary Extra energy needed for heated systems	\$10,000-\$23,000	30% of all body shops use downdraft or semi-downdraft paint booth systems Most common paint booth system in shops with sales greater than \$750,000 annually
<b>Crossdraft</b>	Most affordable system Air movement - enters the booth through one side and passes out the other Installation may not require as much site renovation as semi-downdraft or downdraft	Highest air turbulence of three available models Least effective model for preventing paint deformities Operator safety Extra energy needed for heated systems	\$5,500-\$23,000	50% of all body shops have a cross draft paint booth system Most common paint booth in body shops with sales less than \$750,000 annually

Sources: 1 - EPA, 1994, 2 - Spray Systems and CCC, 1996, 3 - BSB, 1995)

## APPENDIX G

### SUMMARY OF REGULATORY ACTIVITY FOR EACH OF THE ISOCYANATE CAS NUMBERS

CAS Number and Chemical Name	Summary
000091-97-4 3,3'-dimethyl-4,4'-biphenylene diisocyanate	This chemical is regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. In addition, releases of this chemical must be reported under the TRI. Lastly, while NIOSH has Recommended Exposure Limits there are no OSHA regulations for worker protection.
000101-68-8 Methylylene bisphenyl isocyanate (MDI)	This chemical has been regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, the ITC, in its 37th Report (2/2/96) recommended that this isocyanate be removed from its Priority Testing List. In addition, releases of this chemical must be reported under the TRI. Air emissions are also listed as a Hazardous Air Pollutant under the CAA. The DOT also identifies this chemical as a both a hazardous chemical and poisonous. In the area of worker safety, OSHA has issued Permissible Exposure Limits and the ACGIH has made recommendations for Threshold Limit Values.
000104-49-4 1,4-Phenylene diisocyanate	This chemical was regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, in 1993 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI.
000584-84-9 Toluene-2,4-diisocyanate (TDI)	This chemical has been regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. This chemical was also subject to the 8(a) CAIR rule. However, the ITC, in its 37th Report (2/2/96) recommended that this isocyanate be removed from its Priority Testing List. In addition, releases of this chemical must be reported under the TRI. Further regulatory action under SARA has also been taken -- since 1989 this chemical has been listed as an Extremely Hazardous Substance. The CAA also identifies this chemical as a Hazardous Air Pollutant. In the area of worker safety, OSHA has issued Permissible Exposure Limits and the ACGIH has made recommendations for Threshold Limit Values.
000822-06-0 Hexamethylene diisocyanate (HDI)	<p>This chemical was regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, in 1995 the EPA terminated reporting requirements under section 8(d) for this chemical. In 1989 the ITC recommended that EPA remove this chemical (HDI) from the priority list because the EPA proposed a Notice of Proposed Rulemaking. In addition, in 1992 the EPA put HDI on its Master Testing List (negotiations are currently underway between EPA and industry to develop an enforceable testing agreement for HDI under TSCA section 4).</p> <p>Releases of this chemical must be reported under the TRI. Air emissions are also listed as a Hazardous Air Pollutant under the CAA. The DOT also identifies this chemical as a both a hazardous chemical and poisonous. In the area of worker safety, both NIOSH and the ACGIH have made recommendations for exposure.</p>

**APPENDIX G (cont.)**

**SUMMARY OF REGULATORY ACTIVITY FOR EACH OF THE ISOCYANATE CAS NUMBERS**

<b>CAS Number and Chemical Name</b>	<b>Summary</b>
001321-38-6 Diisocyanatomethylbenzene	This chemical was regulated under the 8(a) CAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, in 1993 the EPA terminated reporting requirements under section 8(d) for this chemical.
002556-36-7 1,4-Cyclohexane diisocyanate	This chemical was regulated under the 8(a) CAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, in 1993 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI.
003173-72-6 1,5-naphthalene diisocyanate	This chemical was regulated under the 8(d) Health and Safety Data Reporting Rule. However, in 1995 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI.
004098-71-9 Isophorone diisocyanate (IPDI)	This chemical has been regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. This chemical was also subject to the 8(a) CAIR rule. However, the ITC, in its 37th Report (2/2/96) recommended that this isocyanate be removed from its Priority Testing List. In addition, releases of this chemical must be reported under the TRI. Further regulatory action under SARA has also been taken -- since 1989 this chemical has been listed as an Extremely Hazardous Substance. The DOT also identifies this chemical as a both a hazardous chemical and poisonous. In the area of worker safety, the ACGIH has made recommendations for Threshold Limit Values.
005124-30-1 Methylene bis (4-cyclohexylisocyanate)	This chemical has been regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. This chemical was also subject to the 8(a) CAIR rule. However, the ITC, in its 37th Report (2/2/96) recommended that this isocyanate be removed from its Priority Testing List. In addition, releases of this chemical must be reported under the TRI. The DOT also identifies this chemical as hazardous, poisonous, and flammable. In the area of worker safety, the ACGIH has made recommendations for Threshold Limit Values.
009016-87-9 Polymeric diphenylmethane diisocyanate	This chemical was regulated under the 8(d) Health and Safety Data Reporting Rule. However, in 1995 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI. The DOT lists this chemical as a bulk hazardous material and noxious liquid.

**APPENDIX G (cont.)**

**SUMMARY OF REGULATORY ACTIVITY FOR EACH OF THE ISOCYANATE CAS NUMBERS**

<b>CAS Number and Chemical Name</b>	<b>Summary</b>
015646-96-5 2,4,4-Trimethylhexamethylene diisocyanate	This chemical was regulated under the 8(a) PAIR rule and the 8(d) Health and Safety Data Reporting Rule. However, in 1993 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI.
038661-72-2 1,3-Bis(methylisocyanate) cyclohexane	This chemical was regulated under the 8(d) Health and Safety Data Reporting Rule. However, in 1993 the EPA terminated reporting requirements under section 8(d) for this chemical. In addition, releases of this chemical must be reported under the TRI.
002094-99-7 $\alpha,\alpha$ -dimethyl-m-isopropenyl benzyl isocyanate	There are several international regulations on this chemical but no national regulations exist.
003634-83-1 m-xylene- $\alpha,\alpha'$ -diisocyanate	In 1990 the ITC revised its Priority List and added this chemical to the list. In the area of worker safety, NIOSH has made a recommendation for exposure limits.