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.

$$R\text{-}\ (N{=}C{=}O)_{\geq 2}$$

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

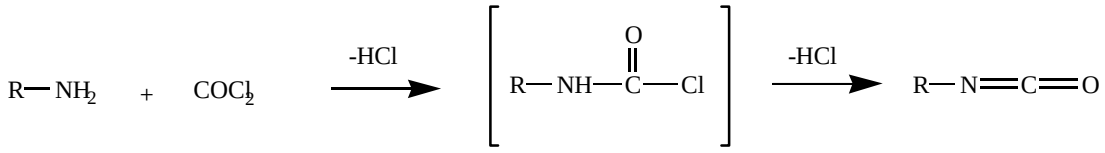
Isocyanates are of concern for potential dermal and pulmonary sensitization, and other lung effects. The aromatic isocyanates may be potential carcinogens based on analogy to TDI or 3,3'-dimethoxybenzidine-4,4'-diisocyanate (dianisidine diisocyanate, DADI).

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 monomers 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 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 versatility 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 types 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_2	NCO + H_2O	NCO + -OH	Polyol +NCO	NCO + H_2O +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
Aliphatic Diisocyanates												
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)

	CAS Number	Chemical Name and Synonyms	Boiling Point °C (kPa)	Melting Point °C	Used in Coating	I	II	III	IV	V	VI	References
Aromatic Diisocyanates												
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)
Derivatives of Diisocyanates												
HDI-Biuret	28182-81-2		> 127° (1.33)	?	Yes	?	?	?	Y	Y	?	(7, p. 665) (13, p. 616)
HDI-Isocyan-urate	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.