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Document Title	INITIAL SUBMISSION: LETTER FROM INTL ISOCYANATE INST INC TO SUBMITTING INFO ON 2,4 AND 2,6 TOLYLENE (OR TOLUENE) (TDI) AND THE ISOMER MIXTURE, DATED 3/31/81		
Chemical Category	2,4 TOLYLENE DIISOCYANATE; 2,5 TOLYLENE		

FYI-0794-1028

INTERNATIONAL ISOCYANATE INSTITUTE, INC.
P.O. Box 1288
71 ELM STREET
NEW CANAAN, CONN. 06840

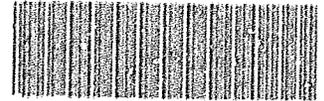


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CABLE ADDRESS:
ISOCYANATE-NEW CANAAN, CONN.

(203) 866-7555

March 31, 1981



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Martin Greif, Executive Secretary
TSCA Interagency Testing Committee
Environmental Protection Agency (TS-732)
401 M Street, S.W.
Washington, D. C. 20460

Dear Mr. Greif:

The following comments are submitted by the International Isocyanate Institute for consideration relative to the list of candidates for possible recommendations to the U. S. Environmental Protection Agency to be given priority for testing for adverse health and environmental effects pursuant to section 4 of TSCA published in the Federal Register, Vol. 45, No. 196, Tuesday, October 7, 1980.

The International Isocyanate Institute was founded on August 18, 1972 as a non-profit corporation. It is organized under the laws of the United States and is registered in the State of New York. It is an association of 22 Isocyanate producers located in Europe, Japan and the Americas. The purpose of the Institute is to promote the proper use of Isocyanates and products made from these most versatile chemicals. To qualify for membership a company must be engaged in the manufacture of Isocyanates. III Brochure #2 enclosed, describes our purpose, organization and safety research activities. A list of the present member companies will be found on the last page.

As you know the list of candidates includes CAS 91087, Benzene, 1,3-diisocyanato-2-methyl-; 584849, Benzene, 2,4-diisocyanato-1-methyl; and 26471-62-5 Benzene, 1,3-diisocyanatomethyl-. These are commonly referred to as 2,4 and 2,6 tolylene (or toluene) diisocyanate, or TDI. An 80/20 mixture of the two isomers makes up the largest part of TDI used. Most of the attached data is for this isomer mixture.

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March 31, 1981

We estimate the total national TDI airborne emissions to be less than 50,000 lbs/yr or 0.008% of the U. S. annual production. Published data show TDI has a 1/3 life of 8 seconds in air at 75 F, 50% RH and a 0.5 second to 3 day half life in water depending upon pH and agitation. Without agitation TDI will sink to the bottom of the water source and react slowly at the interface.

We also estimate the number of people exposed or potentially exposed to TDI to be in the range of 20,000 to 30,000 people. OSHA has an established standard of a 20 ppb, 8 hour TWA and a 20 ppb ceiling for TDI. Local exhaust ventilation and protective clothing is used to meet these guidelines.

Because TDI reacts with water there is almost no chance for bioaccumulation to occur. Previous tests determine a 96 hour LC₅₀ of 164 mg/l for fathead minnows and no significant mortality in grass shrimp exposed to 508 mg/l.

*Long-term
Tox*
There has been a five year prospective respiratory and immunologic evaluation of isocyanate exposure conducted under NIOSH Contract No. 210-75-0006(1) in a new manufacturing plant. A copy of the final report of this study is enclosed.

Study of Progress
A two year rat and mouse inhalation study with TDI is now being concluded under the sponsorship of the International Isocyanate Institute, Inc. A copy of the final report of this study will be made available to EPA.

Study of Progress
The National Cancer Institute has a carcinogenicity study of TDI underway using dosing by intubation. We are sure that the National Cancer Institute members of ITC can provide details of these tests.

The International Isocyanate Institute, Inc. continues to sponsor studies at Tulane University on the mechanism of the bronchial asthmatic reaction to TDI that a small fraction of persons having occupational exposures may develop. Incidentally, a paper is in preparation describing a case of bronchial asthmatic reactivity that lost reactivity after being away from exposure for approximately one year. A reprint of this paper, when available, will be provided to the ITC.

The International Isocyanate Institute, Inc. also continues to sponsor studies on the effects and fate of TDI released into the environment from accidental spills or from other sources. As the results of these studies become available, III, Inc. will make copies available to ITC.

March 31, 1981

In view of the studies that have been completed and other studies already in progress, we respectfully recommend that TDI (CAS 91087, 5848-9 and 264 -62-5) not be included in TSCA Section 4(e) Priority List.

Very truly yours,



Arthur E. Chivvis
Managing Director

ABC:vor
Attach,

cc with enclosures to the Honorable David A. Stockman

- Enclosures:
- ✓ III Brochure #1
 - ✓ III Brochure #2
 - ✓ III Brochure #3
 - ✓ Dyson and Hermann
Fetsch and Dun Tu
 - ✓ NIOSH Contract #210-75-0006 (1) (Tulane-Olin Study)
 - ✓ DuPont Decontamination Report
 - ✓ TDI Bibliographies: ✓ 1973 NIOSH Report, ✓ 1978 NIOSH Report,
General Summary
 - ✓ III Transportation & Handling Committee Summary Reports
#1, 2, 3, 4 & 5
 - ✓ Curtis, Copeland & Ward
 - ✓ Carney
 - ✓ Sangha & Alarie
 - ✓ Kane, Barrow & Alarie
 - ✓ Henck, Kociba, Keyes and McKenna
 - ✓ Kociba, Keys and Wolfe
 - ✓ III - EE-12 - Report on "Reaction of TDI with Water and
with Wet Sand."
 - ✓ Copy of letter to Honorable David A. Stockman

✓ sent to Dr. Gregory CDSC April 9, 1982

Interagency Test Committee - Response for
Toluene Diisocyanate

Identification

CAS Numbers: 91087, 584849 and 26471-62-5
Name: Toluene Diisocyanate
Synonyms: Benzene, 1, 3 diisocyanate-2-methyl
Benzene, 2, 4 diisocyanate-1-methyl
Benzene, 1, 3 diisocyanatomethyl

Physical Properties

Description: Water White to Pale Yellow Liquid
Boiling Point: 251° C at 760 mm Hg
Vapor Pressure: 0.01 mm Hg at 20° C
Specific Gravity: 1.22 @ 25/15.5° C
Auto Ignition Temperature: 277° C for mixture of 80% 2,4 isomer;
20% 2,6 isomer
Flash Point: 135° C Tag Open Cup
Freezing Point: 14° C for mixture of 80% 2,4 isomer; 20% 2,6 isomer
Freezing Point: 22° C for 100% 2,4 isomer (CAS 584849)
Concentration of Saturated Vapor: 19.62 ppm at 20° C
Solubility in Water: Insoluble, reacts slowly and non violently
with water at ambient conditions to form
insoluble polyureas
Solubility in Organic Solvents: Soluble in aromatic hydrocarbons,
chlorinated aromatic hydrocarbons,
nitro benzene, acetone, ethers
and esters
Partition Coefficient (octanol/water): Can't be measured since
TDI reacts with water

Exposure - Released to Environment

TDI Production Residues: See Health and Environmental Effects of TDI - background document. This document states approximately 13,000,000 lbs/yr of production residues are produced. Industry estimates less than 100,000,000 lbs of TDI residue are produced and disposed of via acceptable RCRA disposal criteria

Production Plant Airborne Emissions: See NIOSH Contract #210-75-0006 (1). Personnel monitoring was less than 0.05 ppm. This calculates to approximately 1/2 lb/day of air emissions or 4 1/2 lbs/day from the 9 manufacturing plants in the U.S. operating under normal operating conditions of a closed, continuous process of manufacture

Foam Plant Airborne Emissions: See Fetsch & Tu Dung report. Shows 50 grams emitted/ton of TDI consumed or approximately 30,000 lbs/yr emitted from user sites

Total TDI airborne emissions in the U.S. are less than 50,000 lbs/yr or 0.008% of the annual production.

Exposure - Persistence

Air: See Dyson & Hermann, 1971, page 744

Water: See EPA TDI Bulletin PS: 33-01 page 162.5
Half life is reported as 0.5 seconds to 3 days depending upon pH and agitation.

Atmosphere: Because of the rapid reaction with water and only having a 1/3 life of 8 seconds in air (Dyson & Herman), we strongly refute the suggestion (EPA Document p.162.5) of an atmosphere half life of 3981 days

Number of People Exposed

A June 1980 OSHA report - An Interim Report to Congress on Occupational Diseases - claims 130,000 people are exposed to TDI each year in the U.S. We challenge this number. We estimate 20-30,000 people are exposed. Unpublished data on industry surveys of user sites and the Tulane University NIOSH survey of the Olin plant indicate less than 4500 people/yr are exposed in the manufacture of TDI and foam on a long term occupational exposure basis, not on an incidental basis (non-continuing routine exposure). Our less than 4500 exposure number was derived as follows:

Manufacturing Sites (NIOSH - Tulane study) - 150 people x 9 plants = 1350 people

Slab stock foam producers - 100 plants x 15 people/plant = 1500 people

Molded foam producers - 10 plants x 100 people/plant = 1000 people

Approximately 80% of TDI used is in the manufacture of polyurethane foam.

In the manufacture and use of paint, coatings and adhesives, we estimate 15-25,000 people are exposed or potentially exposed to TDI or TDI containing products. This could be on a routine or intermitten basis.

Frequency of Exposure

OSHA has established standards of a 20 ppb ceiling, 8 hour TWA for TDI. Local exhaust ventilation & the use of respirators for accidental spills protects the workers and keeps them within the OSHA guidelines. In the manufacture of TDI a closed, continuous chemical process is used thus minimizing exposure.

Protective Clothing

See International Isocyanate Institute Brochure #1 on the Recommendations for the Handling of Aromatic Isocyanates.

Also see various labels & bulletins from U.S. TDI producers.

Environmental Fate

Chemical: See International Isocyanate Institute Research Report EE-12 on the reaction of TDI with water in wet sand.

See DuPont Decontamination Report

The International Isocyanate Institute is now funding a project to study the liquid phase after decontamination of TDI residues to develop information on the disposal or treatment of these liquids in accordance with local regulations

Bioaccumulation: Almost no chance for this to occur due to TDI's reaction with water

Aquatic: See TDI background bulletin PS:33-01 page 162-12. Reports 96 hour LC₅₀ of 164.5 mg/l in fathead minnows and no significant mortality in grass shrimp exposed to 508.3 mg/l.

Data believed to be from Curtis, Copeland & Ward,
Rice University, Houston, TX (1978) - Acute Toxicity
of 12 Industrial Chemicals to Freshwater & Saltwater
Organisms.

Toxicology

Mutagenic Activity:

The NIOSH Criteria for a Recommended Standard. . . . Occupational Exposure to Diisocyanates (p.65) state that TDI did not show mutagenic activity to *Salmonella typhimurium*. Anderson and Styles (copy attached) also report that 2, 4-TDI was negative by the Ames test; the paper does not specify whether or not the TDI was tested in a DMSO solution.

Anderson et al. (copy attached) reported mutagenic activity when TDI dissolved in DMSO is tested by the Ames test. When TDI reacts with water by mixing TDI and water, insoluble polyureas are formed. However, when TDI dissolved in DMSO is treated with an aqueous solution for metabolic activation and then tested by the Ames test, there is the possibility that TDA as well as polyureas may be formed and TDA is mutagenic by the Ames test. Thus, the actual mutagenic action reported by Anderson et al. may have been due to a metabolite such as TDA that may be formed in a DMSO-water system.

Carcinogenic activity

The NIOSH Criteria Document cited above reports no evidence of carcinogenic activity for TDI.

The EPA listing Background Document, Toluene Diisocyanate Production, p. 162-3 (copy attached) states that TDI tested by the National Cancer Institute for carcinogenicity was found not to be carcinogenic.

A lifetime inhalation study of TDI at concentrations of 0.05 and 0.15 PPM with rats has been conducted. No evidence of carcinogenicity has been seen. The data are undergoing audit by the contracting laboratory. This study was funded by the International Isocyanate Institute, Inc. A copy of the Final Report will be provided as soon as the Report is cleared for release.

Teratogenic activity

The NIOSH Criteria Document cited above states that there are no reports of teratogenicity of TDI. The EPA Listing Background Document also states no references on teratology of TDI were found. Considering the reactivity of TDI with compounds containing active hydrogens that are plentiful in animal tissues, it is unlikely that TDI could be absorbed, circulated, and pass through the placental barrier.

Reproductive effects

The comments in 3 above apply to reproductive effects.

Acute toxicity

The acute toxicity of TDI is reported in the NIOSH Criteria Document.

The acute toxicity of TDI also has been reported by Carney in a paper presented at the International Conference on Cellular and Noncellular Polyurethanes, Strasbourg, France, June 9-10, 1980 (copy attached).

The acute inhalation toxicity of TDI also was determined in tests performed by Dow Chemical Co. under sponsorship of the International Isocyanate Institute, Inc. These tests were done preliminary to conducting subchronic tests. A copy of the report is attached.

Subchronic toxicity

Subchronic inhalation toxicity of TDI has been reported by Carney (Copy attached). Subchronic inhalation toxicity tests were conducted by Dow Chemical Co. under sponsorship of the International Isocyanate Institute, Inc.; a copy of the report on these tests is attached.

Other toxic effects

A small fraction of the population occupationally exposed to TDI may develop a bronchial asthmatic hyperreactivity. Excessive exposure to TDI vapor can cause respiratory irritation.

The most extensive prospective study of the effects of occupational exposure to TDI was conducted by Tulane University personnel under sponsorship of NIOSH. A copy of the final report to NIOSH on this study is attached.

The International Isocyanate Institute, Inc. is continuing to sponsor studies at Tulane University on the mechanism of the bronchial asthmatic hyperreactivity that some persons develop from occupational exposure to TDI. In the course of these studies, one person who had developed hyperreactivity and was kept from exposure to TDI has lost his sensitivity; a case report is being prepared for publication and will be supplied when published. Two other cases that appear to be losing sensitivity are being followed.

Chemical Properties

- Stability:** Reacts with water, acid, base, alcohols and amines. Reaction is catalyzed by tertiary amines, strong bases, some organic metallic compounds
- Reactivity:** Considered a stable compound but reacts with compounds containing active hydrogens. Reaction with water results in the evolution of carbon dioxide.
- Photodegradation:** See Dyson and Hermann, 1971, page 744. Shows 1/3 life of 8 seconds at 50% R.H., 75° F.
Also see Fetsch and Tu Dung, University of Stuttgart, March 1980.
- Thermal Degradation:** Discolors and dimerization may occur above 40° C
Above 100-120° C TDI trimerizes
Above 175° C Carbodiimides and CO₂ form

Sources

Production Method: Phosgenation of Toluene Diamine

Annual U. S. Production: Approximately 600,000,000 lbs in 1979

Uses

Main uses are in the manufacture of polyurethane foams, elastomers, coatings and adhesives. Approximately 80% of TDI use is in the manufacture of foam.

Storage & Distribution

See the following III Brochures for the handling of TDI - Brochures #1 and the Transportation and Handling Committee Summary Reports #'s 1, 2, 3, 4 and 5 covering the safe handling and shipping of TDI plus emergency procedures.

Sangha and Alarie and Kane, Barrows and Alarie have reported the results of short term animal tests for sensory irritation of TDI; copies of these papers are attached.

The International Isocyanate Institute, Inc. continues to participate in sponsoring studies on respiratory effects of occupational exposure to Isocyanates being conducted by personnel of the Tokyo Women's Medical College and by the United Kingdom Medical Research Council-British Rubber Manufacturers Association. The latter study will cover a seven year period of exposure measurements and health evaluations. As reports of results from these studies become available, copies will be provided to EPA.

In summary, there has been extensive toxicologic tests of TDI and there continues to be a significant amount of research on possible health effects of exposure to TDI. It does not appear that additional meaningful research would be likely to be initiated by putting TDI on a priority list of chemicals for additional tests.

Summary and Recommendation

Toluene diisocyanate has undergone extensive toxicological testing. It is well characterized from a physical and chemical point of view and its high reactivity with water precludes significant environmental effects. Both the environmental and occupational exposure have been determined and appropriate exposure limits have been set and there exist adequate recommendations for handling the substance. The International Isocyanate Institute continues to review the health and environmental aspects of this chemical and is continuing to sponsor appropriate studies.

There is sufficient data on the effects of TDI on health and the environment to permit an assessment of the risk the substance presents, therefore, any recommendations to the EPA for priority testing are unnecessary.

Arthur B. Chivvis

Arthur B. Chivvis
Managing Director
International Isocyanate Institute, Inc.