OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TOLUENE DIISOCYANATE

INTRODUCTION

This guideline summarizes pertinent information about toluene diisocyanate (TDI) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• Formula: C₉H₆N₂O₂

• Structure:

• Synonyms: 2,4-Diisocyanato-l-methyl benzene; TDI; toluene-2, 4-diisocyanate; 2,4-toluene diisocyanate

• Identifiers: CAS 584-84-9; RTECS CZ6300000; DOT 2078, label required: "Poison"

• **Appearance and odor:** Colorless to pale yellow liquid with a sharp, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 174.16

2. Boiling point (at 760 mmHg): 251°C (484°F)

3. Specific gravity (water = 1): 1.22

4. Vapor density (air = 1 at boiling point of TDI): 6.0

5. Melting point: 21°C (69.8°F)

6. Vapor pressure at 25 °C (77 °F): 0.05 mmHg

7. Insoluble in water (reacts exothermically)

8. Evaporation rate (butyl acetate = 1): Much less than 1

9. Saturation concentration in air (approximate) at 25°C (77°F): 0.00657% (65.7 ppm)

Reactivity

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water, acids, bases, and amines may cause reactions that liberate heat and cause violent foaming and spattering.

2. Hazardous decomposition products: Toxic gases and vapors (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving TDI.

3. Caution: TDI will attack some forms of plastic, rubber, and coatings.

• Flammability

1. Flash point: 132 °C (270 °F) (open cup)

2. Flammable limits in air, % by volume: Lower, 0.9; upper, 9.5

3. Extinguishant: Carbon dioxide, dry chemical powder, or foam

4. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

Warning properties

1. Odor threshold: 0.17 ppm

2. Eye irritation levels: 0.05-0.1 ppm

3. Evaluation of warning properties for respirator selection: Because of the lack of odor and irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), TDI can only be detected above the NIOSH REL; thus TDI is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TDI is 0.02 parts of TDI per million parts of air (ppm) [0.14 milligrams of TDI per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.005 ppm (0.135 mg/m³) as a time-weighted average (TWA) concentration for up to a 10-hour workshift, 40-hour workweek, and the ceiling concentration is 0.02 ppm (0.14 mg/m³) as determined in any 10-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.005 ppm (0.04 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek, and the short-term exposure limit (STEL) is 0.02 ppm (0.15 mg/m³) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

Public Health Service Centers for Disease Control National Institute for Occupational Safety and Health Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for toluene diisocyanate

	Exposure limits	
	ppm	mg/m³
OSHA PEL ceiling	0.02	0.14
NIOSH REL TWA	0.005	0.035
Ceiling (10 min)	0.02	0.14
ACGIH TLV® TWA	0.005	0.04
STEL	0.02	0.15

HEALTH HAZARD INFORMATION

• Routes of exposure

TDI may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

Summary of toxicology

- 1. Effects on animals: Chronic administration of TDI by gavage to rats and mice produced cancer of the skin, pancreas, liver, mammary glands, and blood vessels. Chronic inhalation of TDI by rats caused increased fibrous tissue in the lung bronchioles, inflammation of the lungs and trachea, and death due to hemorrhage in the lungs. NIOSH will continue to monitor the research regarding TDI to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.
- 2. Effects on humans: Exposure to TDI has caused severe bronchospasm, lung inflammation, fluid in the lungs, and decreased breathing capacity. It has also caused sensitization of the respiratory tract, as manifested by acute asthmatic reaction upon return to work after a period of time away from exposure.

• Signs and symptoms of exposure

- 1. Short-term (acute): Exposure to TDI can cause coughing, tightness of the chest, chest pain, nausea, vomiting, abdominal pain, headache, and insomnia. TDI can also cause severe skin irritation with redness, swelling, and blistering, and eye irritation with permanent damage if untreated.
- 2. Long-term (chronic): Exposure to TDI can cause respiratory sensitization; initial symptoms include coughing during the night, with difficult or labored breathing. Skin sensitization can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to TDI, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, eyes, and skin. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TDI at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to preexisting chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. The physician should note that a bronchial challenge test for nonspecific airway hyperreactivity (e.g., to cold air, exercise, methacholine, or histamine) may not be sufficiently sensitive or specific for identifying workers who are susceptible or sensitized to the effects of TDI.

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to TDI. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system, eyes, and skin as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: stan-

dardized questionnaires, pre- and post-shift tests of lung func-

tion, and chest X-rays. At the current state of knowledge, tests

Periodic medical screening and/or biologic monitoring

for tolyl-specific serum IgE antibodies are not sufficiently sensitive or specific for use in medical screening or diagnosis of bronchial hypersensitivity in workers exposed to TDI.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to TDI may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

· Sentinel health events

- 1. Acute SHE's include: Extrinsic asthma (acute).
- 2. Delayed-onset SHE's include: Extrinsic asthma (chronic).

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to TDI should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TDI. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the Occupational Exposure Sampling Strategy Manual.

Method

Sampling and analysis may be performed by collecting TDI vapors using midget impingers filled with a solution of I-(2-methoxy phenyl)-piperazine in toluene and analyzing by liquid chromatography with UV detection. Detector tubes or other direct-reading devices calibrated to measure TDI may also be used if available. A detailed sampling and analytical method for TDI may be found in the NIOSH Manual for Analytical Methods (method number 2535).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with TDI.

Workers should be provided with and required to use splashproof safety goggles where TDI may come in contact with the eyes.

SANITATION

Clothing which is contaminated with TDI should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of TDI from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TDI's hazardous properties. Before being laundered, contaminated clothing shall be placed in a decontaminating solution of water containing 10% ammonia in a container that is impervious to TDI. Caution: Do not tightly close containers used for decontamination because of a possible increase in gas pressure.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with TDI should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle TDI should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to TDI may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for toluene diisocyanate

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Operations	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment	
During use in the manufac- ture of diisocyanatepolyol surface coatings and and fin- ishes, polyurethane paints, and electrical and thermal insulation		
During use in the manufac- ture and curing of flexible polyurethane foams and elastoplastics, adhesives, and sealants	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment	

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to TDI, an eye-wash fountain should be provided within the immediate work area for emergency use.

If TDI gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to TDI, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If TDI gets on the skin, wash it immediately with soap and water. If TDI penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If TDI is spilled or leaked, the following steps should be taken:

- 1. Remove all ignition sources.
- 2. Ventilate area of spill or leak.
- 3. For small quantities of liquids containing TDI, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from TDI vapors. Burn the paper in a suitable location away from combustible materials.
- 4. Large quantities of liquids containing TDI may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. TDI should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
- 5. Liquids containing TDI may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed

to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.

For each level of respirator protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for toluene diisocyanate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.05 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 0.125 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 10 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10	Any self-contained breathing apparatus with a full facepiece and operated in a pressure- demand or other positive pressure mode
ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure- demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

Only NIOSH/MSHA-approved equipment should be used.

[†] The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.005 ppm (0.035 mg/m³) (TWA) and 0.02 ppm (0.14 mg/m³) (ceiling).