

1,4-Phenylene diisocyanate

sc-223060

Material Safety Data Sheet



The Power is Question

Hazard Alert Code Key:

EXTREME

HIGH

MODERATE

LOW

Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME

1,4-Phenylene diisocyanate

STATEMENT OF HAZARDOUS NATURE

CONSIDERED A HAZARDOUS SUBSTANCE ACCORDING TO OSHA 29 CFR 1910.1200.

NFPA



SUPPLIER

Company: Santa Cruz Biotechnology, Inc.

2145 Delaware Ave
Santa Cruz, CA 95060

Telephone: 800.457.3801 or 831.457.3800

Emergency Tel: **CHEMWATCH: From within the US and Canada:**
877-715-9305

Emergency Tel: **From outside the US and Canada: +800 2436 2255**
(1-800-CHEMCALL) or call +613 9573 3112

PRODUCT USE

■ Intermediate. Speciality isocyanate for cast and thermoplastic elastomers. Due to its small size and symmetry PPDI provides a compact hard segment and phase separation in polyurethane formulations. PPDI has a slightly lower vapor pressure than TDI. Nevertheless, it is high enough to exceed the upper exposure limit (STEL) at room temperature, and thus care must be taken to avoid personnel exposure during handling and processing. PPDI also has a tendency to sublime

SYNONYMS

C₆H₄(NCO)₂, "benzene, 1, 4-diisocyanato-", PPDI, "p-phenylene diisocyanate"

Section 2 - HAZARDS IDENTIFICATION

CHEMWATCH HAZARD RATINGS

		Min	Max	
Flammability:	1			
Toxicity:	2			
Body Contact:	3			
Reactivity:	1			
Chronic:	2			
				Min/Nil=0 Low=1 Moderate=2 High=3 Extreme=4



CANADIAN WHMIS SYMBOLS



EMERGENCY OVERVIEW

RISK

Risk of serious damage to eyes.
May cause SENSITIZATION by inhalation and skin contact.
Harmful by inhalation, in contact with skin and if swallowed.
Irritating to respiratory system and skin.

POTENTIAL HEALTH EFFECTS

ACUTE HEALTH EFFECTS

SWALLOWED

- Accidental ingestion of the material may be harmful; animal experiments indicate that ingestion of less than 150 gram may be fatal or may produce serious damage to the health of the individual.
- Swallowing of the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis; serious consequences may result. (ICSC13733).

EYE

- If applied to the eyes, this material causes severe eye damage.
- This material can cause eye irritation and damage in some persons.

SKIN

- Skin contact with the material may be harmful; systemic effects may result following absorption.
- This material can cause inflammation of the skin on contact in some persons.
- The material may accentuate any pre-existing dermatitis condition.
- Open cuts, abraded or irritated skin should not be exposed to this material.
- Entry into the blood-stream, through, for example, cuts, abrasions or lesions, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

INHALED

- Inhalation of dusts, generated by the material, during the course of normal handling, may be harmful.
- The material can cause respiratory irritation in some persons. The body's response to such irritation can cause further lung damage.
- Persons with impaired respiratory function, airway diseases and conditions such as emphysema or chronic bronchitis, may incur further disability if excessive concentrations of particulate are inhaled.
- The vapor/mist may be highly irritating to the upper respiratory tract and lungs; the response may be severe enough to produce bronchitis and pulmonary edema. Possible neurological symptoms arising from isocyanate exposure include headache, insomnia, euphoria, ataxia, anxiety neurosis, depression and paranoia. Gastrointestinal disturbances are characterized by nausea and vomiting. Pulmonary sensitization may produce asthmatic reactions ranging from minor breathing difficulties to severe allergic attacks; this may occur following a single acute exposure or may develop without warning for several hours after exposure. Sensitized people can react to very low doses, and should not be allowed to work in situations allowing exposure to this material. Continued exposure of sensitized persons may lead to possible long term respiratory impairment. Inhalation hazard is increased at higher temperatures.

CHRONIC HEALTH EFFECTS

- Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems. Inhaling this product is more likely to cause a sensitization reaction in some persons compared to the general population.
- Skin contact with the material is more likely to cause a sensitization reaction in some persons compared to the general population.
- Limited evidence suggests that repeated or long-term occupational exposure may produce cumulative health effects involving organs or biochemical systems.
- Long term exposure to high dust concentrations may cause changes in lung function i.e. pneumoconiosis; caused by particles less than 0.5 micron penetrating and remaining in the lung. Prime symptom is breathlessness; lung shadows show on X-ray.
- Persons with a history of asthma or other respiratory problems or are known to be sensitised, should not be engaged in any work involving the handling of isocyanates. [CCTRADE-Bayer, APMF].

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
1,4-phenylene diisocyanate	104-49-4	>98

Section 4 - FIRST AID MEASURES

SWALLOWED

-
- IF SWALLOWED, REFER FOR MEDICAL ATTENTION, WHERE POSSIBLE, WITHOUT DELAY.
- Where Medical attention is not immediately available or where the patient is more than 15 minutes from a hospital or unless instructed otherwise:

- For advice, contact a Poisons Information Center or a doctor.
- Urgent hospital treatment is likely to be needed.
- If conscious, give water to drink.
- INDUCE vomiting with fingers down the back of the throat, ONLY IF CONSCIOUS. Lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration.

NOTE: Wear a protective glove when inducing vomiting by mechanical means.

- In the mean time, qualified first-aid personnel should treat the patient following observation and employing supportive measures as indicated by the patient's condition.
- If the services of a medical officer or medical doctor are readily available, the patient should be placed in his/her care and a copy of the MSDS should be provided. Further action will be the responsibility of the medical specialist.
- If medical attention is not available on the worksite or surroundings send the patient to a hospital together with a copy of the MSDS.
- If spontaneous vomiting appears imminent or occurs, hold patient's head down, lower than their hips to help avoid possible aspiration of vomitus.

EYE

■ If this product comes in contact with the eyes:

- Wash out immediately with fresh running water.
- Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids.
- If pain persists or recurs seek medical attention.
- Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

SKIN

■ If skin contact occurs:

- Immediately remove all contaminated clothing, including footwear
- Flush skin and hair with running water (and soap if available).
- Seek medical attention in event of irritation.

INHALED

■

- If fumes or combustion products are inhaled remove from contaminated area.
- Lay patient down. Keep warm and rested.
- Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures.
- Apply artificial respiration if not breathing, preferably with a demand valve resuscitator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary.
- Transport to hospital, or doctor, without delay.

NOTES TO PHYSICIAN

■ for poisons (where specific treatment regime is absent):

BASIC TREATMENT

- Establish a patent airway with suction where necessary.
- Watch for signs of respiratory insufficiency and assist ventilation as necessary.
- Administer oxygen by non-rebreather mask at 10 to 15 l/min.
- Monitor and treat, where necessary, for pulmonary edema .
- Monitor and treat, where necessary, for shock.
- Anticipate seizures .
- DO NOT use emetics. Where ingestion is suspected rinse mouth and give up to 200 ml water (5 ml/kg recommended) for dilution where patient is able to swallow, has a strong gag reflex and does not drool.

ADVANCED TREATMENT

- Consider orotracheal or nasotracheal intubation for airway control in unconscious patient or where respiratory arrest has occurred.
- Positive-pressure ventilation using a bag-valve mask might be of use.
- Monitor and treat, where necessary, for arrhythmias.
- Start an IV D5W TKO. If signs of hypovolemia are present use lactated Ringers solution. Fluid overload might create complications.
- Drug therapy should be considered for pulmonary edema.
- Hypotension with signs of hypovolemia requires the cautious administration of fluids. Fluid overload might create complications.
- Treat seizures with diazepam.
- Proparacaine hydrochloride should be used to assist eye irrigation.

BRONSTEIN, A.C. and CURRANCE, P.L.

EMERGENCY CARE FOR HAZARDOUS MATERIALS EXPOSURE: 2nd Ed. 1994.

Section 5 - FIRE FIGHTING MEASURES

Vapour Pressure (mmHG):	<1 hPa, 20 C
Upper Explosive Limit (%):	Not Available
Specific Gravity (water=1):	1.17
Lower Explosive Limit (%):	Not Available

EXTINGUISHING MEDIA

-
- Small quantities of water in contact with hot liquid may react violently with generation of a large volume of rapidly expanding hot sticky semi-solid foam.
- Presents additional hazard when fire fighting in a confined space.
- Cooling with flooding quantities of water reduces this risk.
- Water spray or fog may cause frothing and should be used in large quantities.
- Foam.
- Dry chemical powder.
- BCF (where regulations permit).
- Carbon dioxide.
- Water spray or fog - Large fires only.

FIRE FIGHTING

-
- Alert Emergency Responders and tell them location and nature of hazard.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by any means available, spillage from entering drains or water course.
- Use fire fighting procedures suitable for surrounding area.
- DO NOT approach containers suspected to be hot.
- Cool fire exposed containers with water spray from a protected location.
- If safe to do so, remove containers from path of fire.
- Equipment should be thoroughly decontaminated after use.

GENERAL FIRE HAZARDS/HAZARDOUS COMBUSTIBLE PRODUCTS

- Combustion products include: carbon monoxide (CO), carbon dioxide (CO₂), isocyanates, and minor amounts of, hydrogen cyanide, nitrogen oxides (NO_x), other pyrolysis products typical of burning organic material.
- Combustible.
- Moderate fire hazard when exposed to heat or flame.
- When heated to high temperatures decomposes rapidly generating vapor which pressures and may then rupture containers with release of flammable and highly toxic isocyanate vapor.
- Burns with acrid black smoke and poisonous fumes.
- Combustion yields traces of highly toxic hydrogen cyanide HCN, plus toxic nitrogen oxides NO_x and carbon monoxide.

FIRE INCOMPATIBILITY

- Avoid contamination with oxidizing agents i.e. nitrates, oxidizing acids, chlorine bleaches, pool chlorine etc. as ignition may result.

PERSONAL PROTECTION

Glasses:

Chemical goggles.

Gloves:

Respirator:

Particulate

Section 6 - ACCIDENTAL RELEASE MEASURES

MINOR SPILLS

-
- Remove all ignition sources.
- Clean up all spills immediately.
- Avoid contact with skin and eyes.
- Control personal contact by using protective equipment.
- Use dry clean up procedures and avoid generating dust.
- Place in a suitable, labelled container for waste disposal.

Spill cleanup and waste disposal procedures are similar to those for other isocyanates, except a unique characteristic must be considered and addressed. In contrast to some other isocyanates, only fine particles of PPDl can be readily deactivated with water or ammonia/water systems. In the case of larger particles or lumps, a crust or skin of urea compound forms on the outer surface, leaving an inner core of PPDl. Any deactivation procedure must provide breakup into smaller particles or exposure to deactivation agent for extended periods of time.

Spills of PPDl should be handled as follows:

Evacuate and barricade the area.

Employees entering a barricaded spill area must wear proper protective equipment, including a full-face air-supplied respirator.

Decontaminate the spill and surrounding floor area with a deactivating agent, such as one of the following:

? 8% concentrated ammonia solution, 2% detergent, and balance water

? Hot water or steam

? 50/50 mixture of isopropyl alcohol and triethanol amine

Monitor the spill area for active PPDl with portable monitor or personnel badges.

Place the spill cleanup material in an appropriate container, and dispose of solids as outlined in the Waste Disposal

For PPDl solutions that remain a liquid at room temperature, add the following steps to the procedure for handling solid PPDl spills:

Dike the spill area with an absorbent material (sand, absorbent clay, etc.).

Cover the spill with an absorbent/neutralising mixture such as:

? 60 wt% absorbent material (sawdust, fuller's earth, etc.)

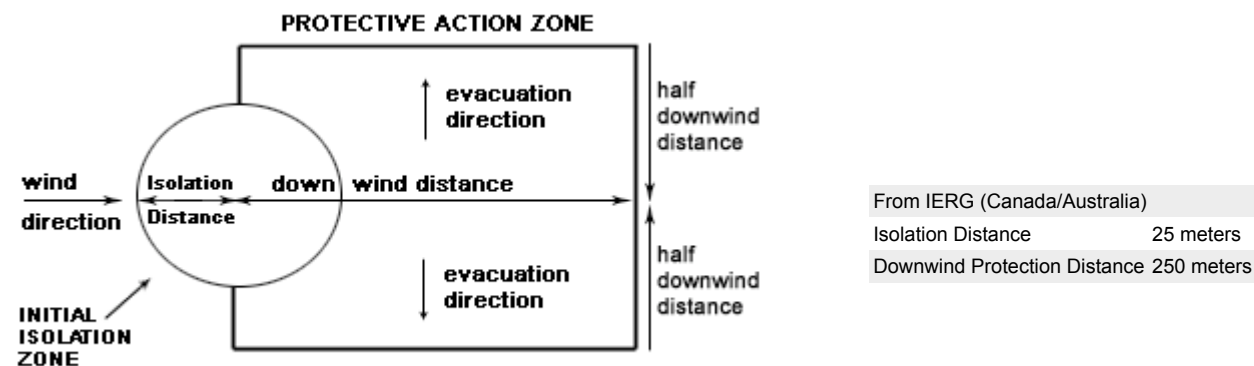
? 40 wt% ammonia aqueous solution

Shovel contaminated absorbent into open-top steel drums and store in a ventilated area with lids loosely sealed for several days to allow any residual carbon dioxide gas to escape.

MAJOR SPILLS

- Treat isocyanate spills with sufficient amounts of isocyanate decontaminant preparation.
- Typically, such a preparation may consist of: sawdust: 20 parts by weight Kieselguhr 40 parts by weight plus a mixture of {ammonia (s.g. 0.880) 8% v/v non-ionic surfactant 2% v/v water 90% v/v}.
- Let stand for 24 hours.
- Clear area of personnel and move upwind.
- Alert Emergency Responders and tell them location and nature of hazard.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by any means available, spillage from entering drains or water course.
- Stop leak if safe to do so.
- Contain spill with sand, earth or vermiculite.
- Collect recoverable product into labeled containers for recycling.
- Neutralize/decontaminate residue.
- Collect solid residues and seal in labeled drums for disposal.
- Wash area and prevent runoff into drains.
- After clean up operations, decontaminate and launder all protective clothing and equipment before storing and re-using.
- If contamination of drains or waterways occurs, advise emergency services.

PROTECTIVE ACTIONS FOR SPILL



From US Emergency Response Guide 2000 Guide 155

FOOTNOTES

1 PROTECTIVE ACTION ZONE is defined as the area in which people are at risk of harmful exposure. This zone assumes that random changes in wind direction confines the vapour plume to an area within 30 degrees on either side of the predominant wind direction, resulting in a crosswind protective action distance equal to the downwind protective action distance.

2 PROTECTIVE ACTIONS should be initiated to the extent possible, beginning with those closest to the spill and working away from the site in the downwind direction. Within the protective action zone a level of vapour concentration may exist resulting in nearly all unprotected persons becoming incapacitated and unable to take protective action and/or incurring serious or irreversible health effects.

3 INITIAL ISOLATION ZONE is determined as an area, including upwind of the incident, within which a high probability of localised wind reversal may expose nearly all persons without appropriate protection to life-threatening concentrations of the material.

4 SMALL SPILLS involve a leaking package of 200 litres (55 US gallons) or less, such as a drum (jerrican or box with inner containers). Larger packages leaking less than 200 litres and compressed gas leaking from a small cylinder are also considered "small spills". LARGE SPILLS involve many small leaking packages or a leaking package of greater than 200 litres, such as a cargo tank, portable tank or a "one-tonne" compressed gas cylinder.

5 Guide 155 is taken from the US DOT emergency response guide book.

6 IERG information is derived from CANUTEC - Transport Canada.

ACUTE EXPOSURE GUIDELINE LEVELS (AEGL) (in ppm)

AEGL 1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL 2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Section 7 - HANDLING AND STORAGE

PROCEDURE FOR HANDLING

- Avoid all personal contact, including inhalation.
- Wear protective clothing when risk of exposure occurs.
- Use in a well-ventilated area.
- Prevent concentration in hollows and sumps.
- DO NOT enter confined spaces until atmosphere has been checked.
- DO NOT allow material to contact humans, exposed food or food utensils.
- Avoid contact with incompatible materials.
- When handling, DO NOT eat, drink or smoke.
- Keep containers securely sealed when not in use.
- Avoid physical damage to containers.
- Always wash hands with soap and water after handling.
- Work clothes should be laundered separately.
- Launder contaminated clothing before re-use.
- Use good occupational work practice.
- Observe manufacturer's storing and handling recommendations.
- Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions are maintained.

Empty containers may contain residual dust which has the potential to accumulate following settling. Such dusts may explode in the presence of an appropriate ignition source.

- Do NOT cut, drill, grind or weld such containers.
- In addition ensure such activity is not performed near full, partially empty or empty containers without appropriate workplace safety authorisation or permit.

RECOMMENDED STORAGE METHODS

- Lined metal can, Lined metal pail/drum
- Plastic pail
- Polyliner drum
- Packing as recommended by manufacturer.
- Check all containers are clearly labeled and free from leaks.

For low viscosity materials

- Drums and jerricans must be of the non-removable head type.
- Where a can is to be used as an inner package, the can must have a screwed enclosure.

For materials with a viscosity of at least 2680 cSt. (23 deg. C) and solids (between 15 C deg. and 40 deg C.):

- Removable head packaging;
- Cans with friction closures and
- low pressure tubes and cartridges may be used.

- Where combination packages are used, and the inner packages are of glass, there must be sufficient inert cushioning material in contact with inner and outer packages *. - In addition, where inner packagings are glass and contain liquids of packing group I and II there must be sufficient inert absorbent to absorb any spillage *. - * unless the outer packaging is a close fitting molded plastic box and the substances are not incompatible with the plastic.

STORAGE REQUIREMENTS

- Store in original containers.
- Keep containers securely sealed.
- Store in a cool, dry, well-ventilated area.
- Store away from incompatible materials and foodstuff containers.
- Protect containers against physical damage and check regularly for leaks.
- Observe manufacturer's storing and handling recommendations.

SAFE STORAGE WITH OTHER CLASSIFIED CHEMICALS



X: Must not be stored together

O: May be stored together with specific preventions

+: May be stored together

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

The following materials had no OELs on our records

- 1,4-phenylene diisocyanate: CAS:104-49-4

MATERIAL DATA

1,4-PHENYLENE DIISOCYANATE:

- Some jurisdictions require that health surveillance be conducted on occupationally exposed workers.
 - demography, occupational and medical history and health advice
 - completion of a standardized respiratory questionnaire
 - physical examination of the respiratory system and skin
 - standardized respiratory function tests such as FEV1, FVC and FEV1/FVC

CEL TWA: 0.03 mg/m³ (aerosol/ vapour); 0.005 ppm (vapour/ vapour), 8- and 12- hour TWA for particulate and vapour combined (cf DuPont AEL)

PERSONAL PROTECTION



Consult your EHS staff for recommendations

EYE

- - Safety glasses with side shields.
 - Chemical goggles.
 - Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses.

HANDS/FEET

- NOTE: The material may produce skin sensitization in predisposed individuals. Care must be taken, when removing gloves and other protective equipment, to avoid all possible skin contact.

Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include: such as:

- frequency and duration of contact,
- chemical resistance of glove material,
- glove thickness and
- dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).

- When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.
- When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.
- Contaminated gloves should be replaced.

Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturiser is recommended.

- Isocyanate resistant materials include Teflon, Viton, nitrile rubber and some PVA gloves.
- Protective gloves and overalls should be worn as specified in the appropriate national standard.
- Contaminated garments should be removed promptly and should not be re-used until they have been decontaminated.
- NOTE: Natural rubber, neoprene, PVC can be affected by isocyanates

OTHER

- - Overalls.
 - Eyewash unit.
 - Barrier cream.
 - Skin cleansing cream.
- - Respirators may be necessary when engineering and administrative controls do not adequately prevent exposures.
 - The decision to use respiratory protection should be based on professional judgment that takes into account toxicity information, exposure measurement data, and frequency and likelihood of the worker's exposure - ensure users are not subject to high thermal loads which may result in heat stress or distress due to personal protective equipment (powered, positive flow, full face apparatus may be an option).
 - Published occupational exposure limits, where they exist, will assist in determining the adequacy of the selected respiratory . These may be government mandated or vendor recommended.
 - Certified respirators will be useful for protecting workers from inhalation of particulates when properly selected and fit tested as part of a complete respiratory protection program.
 - Use approved positive flow mask if significant quantities of dust becomes airborne.
 - Try to avoid creating dust conditions.

RESPIRATOR

■			
Protection Factor	Half-Face Respirator	Full-Face Respirator	Powered Air Respirator

10 x PEL	P1	-	PAPR-P1
	Air-line*	-	-
50 x PEL	Air-line**	P2	PAPR-P2
100 x PEL	-	P3	-
		Air-line*	-
100+ x PEL	-	Air-line**	PAPR-P3

* - Negative pressure demand ** - Continuous flow

Explanation of Respirator Codes:

Class 1 low to medium absorption capacity filters.

Class 2 medium absorption capacity filters.

Class 3 high absorption capacity filters.

PAPR Powered Air Purifying Respirator (positive pressure) cartridge.

Type A for use against certain organic gases and vapors.

Type AX for use against low boiling point organic compounds (less than 65°C).

Type B for use against certain inorganic gases and other acid gases and vapors.

Type E for use against sulfur dioxide and other acid gases and vapors.

Type K for use against ammonia and organic ammonia derivatives

Class P1 intended for use against mechanically generated particulates of sizes most commonly encountered in industry, e.g. asbestos, silica.

Class P2 intended for use against both mechanically and thermally generated particulates, e.g. metal fume.

Class P3 intended for use against all particulates containing highly toxic materials, e.g. beryllium.

The local concentration of material, quantity and conditions of use determine the type of personal protective equipment required.

Use appropriate NIOSH-certified respirator based on informed professional judgement. In conditions where no reasonable estimate of exposure can be made, assume the exposure is in a concentration IDLH and use NIOSH-certified full face pressure demand SCBA with a minimum service life of 30 minutes, or a combination full facepiece pressure demand SAR with auxiliary self-contained air supply. Respirators provided only for escape from IDLH atmospheres shall be NIOSH-certified for escape from the atmosphere in which they will be used.

ENGINEERING CONTROLS

■ Spraying of material or material in admixture with other components must be carried out in conditions conforming to local state regulations. Local exhaust ventilation with full face air supplied breathing apparatus (hood or helmet type) is normally required. Unprotected personnel must vacate spraying area.

NOTE: Isocyanate vapors will not be adequately absorbed by organic vapor respirators. Air contaminants generated in the workplace possess varying "escape" velocities which, in turn, determine the "capture velocities" of fresh circulating air required to effectively remove the contaminant.

Type of Contaminant:	Air Speed:
direct spray, spray painting in shallow booths, drum filling, conveyer loading, crusher dusts, gas discharge (active generation into zone of rapid air motion)	1-2.5 m/s (200-500 f/min.)

Within each range the appropriate value depends on:

Lower end of the range	Upper end of the range
1: Room air currents minimal or favourable to capture	1: Disturbing room air currents
2: Contaminants of low toxicity or of nuisance value only	2: Contaminants of high toxicity
3: Intermittent, low production.	3: High production, heavy use
4: Large hood or large air mass in motion	4: Small hood-local control only

Simple theory shows that air velocity falls rapidly with distance away from the opening of a simple extraction pipe. Velocity generally decreases with the square of distance from the extraction point should be adjusted, accordingly, after reference to distance from the contaminating source. The air velocity at the extraction fan, for example, should be a minimum of 4-10 m/s (800-2000 f/min.) for extraction of solvents generated by spraying at a point 2 meters distant from the extraction point. Other mechanical considerations, producing performance deficits within the extraction apparatus, make it essential that theoretical air velocities are multiplied by factors of 10 or more when extraction systems are installed or used.

- Local exhaust ventilation is required where solids are handled as powders or crystals; even when particulates are relatively large, a certain proportion will be powdered by mutual friction.
- Exhaust ventilation should be designed to prevent accumulation and recirculation of particulates in the workplace.
- If in spite of local exhaust an adverse concentration of the substance in air could occur, respiratory protection should be considered. Such protection might consist of:

(a): particle dust respirators, if necessary, combined with an absorption cartridge;

(b): filter respirators with absorption cartridge or canister of the right type;

(c): fresh-air hoods or masks

- Build-up of electrostatic charge on the dust particle, may be prevented by bonding and grounding.
- Powder handling equipment such as dust collectors, dryers and mills may require additional protection measures such as explosion venting.

Air contaminants generated in the workplace possess varying "escape" velocities which, in turn, determine the "capture velocities" of fresh circulating air required to efficiently remove the contaminant.

Type of Contaminant:	Air Speed:
direct spray, spray painting in shallow booths, drum filling, conveyer loading, crusher dusts, gas discharge (active generation into zone of rapid air motion)	1-2.5 m/s (200-500 f/min.)

grinding, abrasive blasting, tumbling, high speed wheel generated dusts (released at high initial velocity into zone of very high rapid air motion). 2.5-10 m/s (500-2000 f/min.)

Within each range the appropriate value depends on:

Lower end of the range	Upper end of the range
1: Room air currents minimal or favorable to capture	1: Disturbing room air currents
2: Contaminants of low toxicity or of nuisance value only	2: Contaminants of high toxicity
3: Intermittent, low production.	3: High production, heavy use
4: Large hood or large air mass in motion	4: Small hood-local control only

Simple theory shows that air velocity falls rapidly with distance away from the opening of a simple extraction pipe. Velocity generally decreases with the square of distance from the extraction point (in simple cases). Therefore the air speed at the extraction point should be adjusted, accordingly, after reference to distance from the contaminating source. The air velocity at the extraction fan, for example, should be a minimum of 4-10 m/s (800-2000 f/min) for extraction of crusher dusts generated 2 meters distant from the extraction point. Other mechanical considerations, producing performance deficits within the extraction apparatus, make it essential that theoretical air velocities are multiplied by factors of 10 or more when extraction systems are installed or used.

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

State	Divided Solid	Molecular Weight	160.13
Melting Range (°F)	204.8- 210.2	Viscosity	1.32 cSt@40°C
Boiling Range (°F)	500	Solubility in water (g/L)	Partly Miscible
Flash Point (°F)	248	pH (1% solution)	Not Applicable
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not Applicable
Autoignition Temp (°F)	Not Available	Vapour Pressure (mmHG)	<1 hPa, 20 C
Upper Explosive Limit (%)	Not Available	Specific Gravity (water=1)	1.17
Lower Explosive Limit (%)	Not Available	Relative Vapor Density (air=1)	Not Applicable
Volatile Component (%vol)	Negligible	Evaporation Rate	Not Applicable

APPEARANCE

White crystalline solid; does not mix well water.

Section 10 - CHEMICAL STABILITY

CONDITIONS CONTRIBUTING TO INSTABILITY

- Presence of incompatible materials.
- Product is considered stable.
- Hazardous polymerization will not occur.

STORAGE INCOMPATIBILITY

- Avoid reaction with water, alcohols and detergent solutions.
- Isocyanates and thioisocyanates are incompatible with many classes of compounds, reacting exothermically to release toxic gases. Reactions with amines, strong bases, aldehydes, alcohols, alkali metals, ketones, mercaptans, strong oxidisers, hydrides, phenols, and peroxides can cause vigorous releases of heat. Acids and bases initiate polymerisation reactions in these materials.
- Isocyanates easily form adducts with carbodiimides, isothiocyanates, ketenes, or with substrates containing activated CC or CN bonds.
- Some isocyanates react with water to form amines and liberate carbon dioxide. This reaction may also generate large volumes of foam and heat. Foaming in confined spaces may produce pressure in confined spaces or containers. Gas generation may pressurise drums to the point of rupture.
- Do NOT reseal container if contamination is expected
- Open all containers with care
- Base-catalysed reactions of isocyanates with alcohols should be carried out in inert solvents. Such reactions in the absence of solvents often occur with explosive violence,
- Isocyanates will attack and embrittle some plastics and rubbers.
- A range of exothermic decomposition energies for isocyanates is given as 20-30 kJ/mol.
- The relationship between energy of decomposition and processing hazards has been the subject of discussion; it is suggested that values of energy released per unit of mass, rather than on a molar basis (J/g) be used in the assessment.
- For example, in "open vessel processes" (with man-hole size openings, in an industrial setting), substances with exothermic decomposition energies below 500 J/g are unlikely to present a danger, whilst those in "closed vessel processes" (opening is a safety valve or bursting disk) present some danger where the decomposition energy exceeds 150 J/g.

BRETHERRICK: Handbook of Reactive Chemical Hazards, 4th Edition.

Section 11 - TOXICOLOGICAL INFORMATION

1,4-phenylene diisocyanate

TOXICITY AND IRRITATION

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

■ Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's edema. The pathogenesis of contact eczema involves a cell-mediated (T lymphocytes) immune reaction of the delayed type. Other allergic skin reactions, e.g. contact urticaria, involve antibody-mediated immune reactions. The significance of the contact allergen is not simply determined by its sensitization potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitizing substance which is widely distributed can be a more important allergen than one with stronger sensitizing potential with which few individuals come into contact. From a clinical point of view, substances are noteworthy if they produce an allergic test reaction in more than 1% of the persons tested.

Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.

Allergic reactions involving the respiratory tract are usually due to interactions between IgE antibodies and allergens and occur rapidly. Allergic potential of the allergen and period of exposure often determine the severity of symptoms. Some people may be genetically more prone than others, and exposure to other irritants may aggravate symptoms. Allergy causing activity is due to interactions with proteins.

Attention should be paid to atopic diathesis, characterized by increased susceptibility to nasal inflammation, asthma and eczema.

Exogenous allergic alveolitis is induced essentially by allergen specific immune-complexes of the IgG type; cell-mediated reactions (T lymphocytes) may be involved. Such allergy is of the delayed type with onset up to four hours following exposure.

for diisocyanates:

In general, there appears to be little or no difference between aromatic and aliphatic diisocyanates as toxicants. In addition, there are insufficient data available to make any major distinctions between polymeric (<1000 MW) and monomeric diisocyanates. 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.

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 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/m³) 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. Two case reports of human exposure to IPDI by inhalation 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. 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.

Isocyanate vapors are irritating to the airways and can cause their inflammation, with wheezing, gasping, severe distress, even loss of consciousness and fluid in the lungs. Nervous system symptoms that may occur include headache, sleep disturbance, euphoria, inco-ordination, anxiety, depression and paranoia. Digestive effects include nausea and vomiting. Breathing difficulties may occur unpredictably after a period of tolerance and after skin contact. Allergic inflammation of the skin can occur, with rash, itching, blistering, and swelling of the hands and feet. Sensitive people can react to very low levels and should not be exposed to this material.

Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

1,4-PHENYLENE DIISOCYANATE:

■ Hydrolysis would represent the primary fate mechanism for the majority of the commercial isocyanate monomers, 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 volatilisation is negligible. Atmospheric degradation is not expected with removal from air occurring by washout or dry deposition. Volatilisation from surface waters (e.g., lakes and rivers) is expected to take years. In wastewater treatment this process is not expected to be significant.

Review of the estimated properties of the isocyanates suggest that sorption 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 of the $N=C=O$ will occur in less than hours in most instances and within minutes for more than 90% of the commercial isocyanates. 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.

Aerobic and/or anaerobic biodegradation of the isocyanates is not expected to occur at significant levels. Most of the substances take several months to degrade.

Degradation of the hydrolysis products will occur at varying rates depending on the moiety formed.

■ DO NOT discharge into sewer or waterways.

Ecotoxicity

Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
1,4-phenylene diisocyanate	HIGH		LOW	MED

Section 13 - DISPOSAL CONSIDERATIONS

Disposal Instructions

All waste must be handled in accordance with local, state and federal regulations.

! Puncture containers to prevent re-use and bury at an authorized landfill.

Legislation addressing waste disposal requirements may differ by country, state and/ or territory. Each user must refer to laws operating in their area. In some areas, certain wastes must be tracked.

A Hierarchy of Controls seems to be common - the user should investigate:

- Reduction
- Reuse
- Recycling
- Disposal (if all else fails)

This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. Shelf life considerations should also be applied in making decisions of this type. Note that properties of a material may change in use, and recycling or reuse may not always be appropriate.

DO NOT allow wash water from cleaning equipment to enter drains. Collect all wash water for treatment before disposal.

- Recycle wherever possible.
- Consult manufacturer for recycling options or consult Waste Management Authority for disposal if no suitable treatment or disposal facility can be identified.
- Dispose of by: Burial in a licensed land-fill or Incineration in a licensed apparatus (after admixture with suitable combustible material)
- Decontaminate empty containers. Observe all label safeguards until containers are cleaned and destroyed.

Waste PPDI should be neutralized prior to disposal. The exact method used depends on quantities of waste on hand.

The preferred method is to react the PPDI with excess polyol to make a low-quality polymer or foam that can be incinerated. PPDI can be incinerated, but this should be done only in properly supervised equipment specifically designed and licen

Section 14 - TRANSPORTATION INFORMATION



DOT:

Symbols:	None	Hazard class or Division:	6.1
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Identification Numbers:	UN2206	PG:	III
Label Codes:	6.1	Special provisions:	IB3, T7, TP1, TP13, TP28
Packaging: Exceptions:	153	Packaging: Non-bulk:	203
Packaging: Exceptions:	153	Quantity limitations: Passenger aircraft/rail:	60 L
Quantity Limitations: Cargo aircraft only:	220 L	Vessel stowage: Location:	E
Vessel stowage: Other:	25, 40, 48		
Hazardous materials descriptions and proper shipping names: Isocyanates, toxic, n.o.s. or Isocyanate solutions, toxic, n.o.s., flash point more than 61 degrees C and boiling point less than 300 degrees C			
Air Transport IATA:			
ICAO/IATA Class:	6.1	ICAO/IATA Subrisk:	None
UN/ID Number:	2206	Packing Group:	III
Special provisions:	A3		

Shipping Name: ISOCYANATE SOLUTION, TOXIC, N.O.S. * †(CONTAINS 1,4-PHENYLENE DIISOCYANATE)

Maritime Transport IMDG:

IMDG Class:	6.1	IMDG Subrisk:	None
UN Number:	2206	Packing Group:	III
EMS Number:	F-A , S-A	Special provisions:	223 274
Limited Quantities:	5 L		

Shipping Name: ISOCYANATES, TOXIC, N.O.S. or ISOCYANATE SOLUTION, TOXIC, N.O.S.(contains 1,4-phenylene diisocyanate)

Section 15 - REGULATORY INFORMATION



REGULATIONS

1,4-phenylene diisocyanate (CAS: 104-49-4) is found on the following regulatory lists;

"Canada Non-Domestic Substances List (NDSL)", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US List of Lists - Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act", "US Toxic Substances Control Act (TSCA) - Inventory", "US TSCA Section 8 (a) - Preliminary Assessment Information Rules (PAIR) - Reporting List", "US TSCA Section 8 (d) - Health and Safety Data Reporting"

Section 16 - OTHER INFORMATION

LIMITED EVIDENCE

■ Cumulative effects may result following exposure*.

* (limited evidence).

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■ Classification of the mixture and its individual components has drawn on official and authoritative sources as well as independent review by the Chemwatch Classification committee using available literature references.

A list of reference resources used to assist the committee may be found at:
www.chemwatch.net/references.

■ The (M)SDS is a Hazard Communication tool and should be used to assist in the Risk Assessment. Many factors determine whether the reported Hazards are Risks in the workplace or other settings. Risks may be determined by reference to Exposures Scenarios. Scale of use, frequency of use and current or available engineering controls must be considered.

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