

Guidance for Selection of Personal Protective Equipment for TDI Users

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Purpose

The purpose of this document is to provide guidance for selecting the appropriate personal protective equipment (PPE) for working with toluene diisocyanate (TDI)^[1] and to analyze the performance characteristics of gloves, coveralls, splash suits, and other protective garments commonly used when working with TDI.

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Health and Safety Information

During the handling, processing, and application of TDI, contact with vapor, liquid, or aerosols may cause adverse health effects to the skin, eyes, and respiratory system. Inhalation of TDI vapors or aerosols at concentrations above occupational exposure limits (e.g., ACGIH-Threshold Limit Value (TLV) or OSHA-Permissible Exposure Limit (PEL)) can irritate the respiratory system (nose, throat, lungs) causing runny nose, sore throat, coughing, chest discomfort, shortness of breath or reduced lung function. The odor threshold of TDI is above the established exposure limits. Therefore, odor should never be used to indicate the presence of TDI. As a result of previous overexposures (above the TLV or PEL), certain individuals may develop respiratory sensitization to diisocyanates (asthma or asthma-like symptoms) that may cause them to experience asthma-like symptoms with a later exposure to diisocyanates at levels well below the TLV or PEL. Persons with a pre-existing respiratory condition, such as asthma, or respiratory sensitization, can respond to airborne concentrations below the TLV or PEL.

Understand and adhere to safe handling practices for TDI and other chemicals that pose potential health hazards. Direct skin contact with TDI may cause irritation with symptoms of reddening, itching, and rash and, in some cases, skin sensitization. Animal tests and other research indicate that skin contact with TDI may play a role in developing respiratory sensitization.

Engineering controls (e.g., local exhaust ventilation) and sound workplace practices may be the first line of defense against potential exposure to TDI, and guidelines have been established by OSHA to help individuals avoid overexposure and adverse health effects. It is important that employees wear PPE recommended for their specific job functions to prevent direct skin/eye contact with liquid TDI or inhalation of TDI vapors or aerosols.

Eye Protection and Respiratory Protection

In addition to the gloves and garments analyzed later in this bulletin, individuals working with TDI products need to consider the use of appropriate eye, face, and respiratory protection.

Eye Protection

TDI may irritate the eyes and can be difficult to remove, so eye protection is very important. Eye irritation may result in redness, but tissue injury is not expected if TDI is immediately and thoroughly rinsed from the eye.

In situations where there is splash potential (e.g., when directly handling liquid product), workers should wear goggles and, depending upon the extent of potential contact, a face shield. These situations may include line-breaking (transfer



hose disconnect) and transfer of material using a drum pump, etc. In situations where splash potential is low, safety glasses with side shields may be worn.

Respiratory Protection

At normal room temperatures (i.e., 70 °F), airborne concentrations of TDI can quickly exceed the TLV or PEL. Therefore, wear respiratory protection in work situations with inadequate ventilation. The type of respiratory protection selected must comply with OSHA's Respiratory Protection Standard (29 CFR 1910.134). The use of air purifying (cartridge) respirators (APRs) is acceptable in certain situations as part of a comprehensive respiratory protection program². An organic vapor (OV) cartridge may be used with the APR where the concentration of TDI in air can



be documented, it is verified that the sorbent capacity will prevent breakthrough, and where the protection factor will not be exceeded. OSHA requires a cartridge change out schedule to be part of the respiratory protection program by OSHA. When concentrations of TDI exceed or are likely to exceed the

protection afforded by the cartridge respirator (e.g., emergency situations or identified high exposure potential activities), a supplied air respirator (SAR) is required under OSHA's standard.

Selecting Gloves and Protective Clothing

For individuals who work with TDI, appropriate gloves and protective clothing are essential for the prevention of skin exposures.

When selecting gloves and protective clothing consider the following factors:

- **Chemical Resistance of Glove or Clothing:** To be effective, the protective clothing should resist permeation by the chemical or chemicals being handled. Protective gloves and garments should also be resistant to permeation by solvents used in combination with TDI.
- **Use Characteristics of Specific Job Functions:** The nature of the job tasks being performed will greatly influence what aspects of protection are most important. For example, analyzing foam samples in a laboratory may require light-duty gloves (<10 mils in thickness) that are flexible and preserve manual dexterity. On the other hand, a maintenance project such as repairing a pump line may require thicker gloves that are rugged and durable offering abrasion, cut, and thermal protection.
- **Disposable versus Reusable Protective Clothing:** Consider which type of protective clothing is best for the work situation. The use of disposable gloves and clothing is often preferred because proper decontamination of reusable items can be difficult.
- **Potential for Chemical Exposure:** The variation of chemicals being handled as well as the duration of potential exposure will determine which type of protective clothing material is most suitable for the job function. Depending on the properties of the chemicals, a higher chemical resistant protective clothing may be necessary. See Appendix B, Table 1 for a list of attributes for various protected clothing materials.
 - Different barrier materials used in chemical protective clothing will have different holdout and

degradation characteristics for different chemicals. These characteristics are evaluated by permeation and degradation testing, which are described in more detail in the 'Background Information' in Appendix A.

- Considering all chemicals to which one may be exposed is important. Often, the chemical presenting the primary hazard under consideration is not the most important one for selecting the best barrier material: solvents are frequently the driving force for permeation and degradation of chemical protective clothing barrier materials even though other chemicals dissolved in the solvent may present more severe hazardous properties.
- **Protective Clothing Selection is an Informed Judgment:** Matching the protective clothing attributes with the relative importance of the protection requirements of the job necessitates a judgment based on the available information. It is likely that there is no one glove or suit that offers the perfect combination of the required attributes for a given situation. For example, providing mechanical attributes such as manual dexterity, cut and abrasion resistance, or protection from heat or cold may be more important than the need for superior chemical barrier properties if the potential for chemical contact is low or incidental.

In addition to these factors, individual work habits, industrial hygiene practices and pre-existing workplace procedures and controls will influence decisions made when selecting protective clothing.

Research on Protective Gloves and Clothing

The International Isocyanate Institute (III) conducted studies in the 1990s at the Texas Research Institute which evaluated materials from more than 50 items of chemical protective clothing—35 gloves of 10 different materials and 17 suits of 14 different materials—to determine the degree of resistance to permeation of TDI in its most common commercial form (i.e., 80% 2,4-TDI / 20% 2,6-TDI) offered by each. Also included were permeation studies of solutions of TDI in chlorobenzene (MCB) and ortho-dichlorobenzene (o-DCB), two process solvents used in the production of TDI. The results of the studies are shown in Tables 1 and 2 in Appendix B. (Note: While some of the manufacturers and model numbers of the items tested are no longer available, most of the barrier materials are still used in currently available chemical protective clothing.)

The III research measured the length of time it took TDI to penetrate the protective clothing material under conditions of continuous contact and complete surface coverage with TDI.

The tables from this III-sponsored study are organized by glove or garment type, and within each category, are arranged in descending order according to the breakthrough time provided³. Research included the model name, manufacturer, thickness, and durability of each item.

The key points from the testing are summarized below:

- Effects of degradation (swelling, softening, and tearing) were not seen with undiluted TDI for any of the glove materials tested. With the 10% TDI in MCB or o-DCB, several materials exhibited degradation after the test.
 - This result emphasizes that chemical protective clothing materials should be selected based on the chemicals present at the highest concentration – often these are solvents. Clothing manufacturers often have permeation and degradation test data for many commonly used solvents.

Glove Materials:

- Materials that provided long-term permeation protection in heavy contact with undiluted TDI and in MCB or o-DCB solutions: laminated PE/EVAL, fluoroelastomer.
- Other materials that provided good permeation protection per unit of thickness: neoprene, butyl rubber, nitrile.
- Useful practical concept: for heavy contact situations: double-gloving
 - Concept:
 - > inner glove selected for permeation resistance
 - > outer glove chosen for other characteristic (manual dexterity, thermal protection, abrasion / cut resistance, etc.)

Light duty example:

Polyethylene inner glove

+

nitrile outer glove



Heavy duty example:

PE/EVAL inner glove

+

nitrile outer glove



Suit Materials:

- Materials that provided long-term permeation protection in heavy contact with TDI: laminates, neoprene.
- Non-woven materials offer limited protection, but may be useful in one-time use for protection if only slight incidental contact is anticipated

The TDI breakthrough times presented in the tables are the times required for TDI to penetrate the chemical protective glove or garment material and can conservatively be considered the maximum suggested use times. A cautious approach is to change gloves and garments with sufficient frequency to avoid exceeding the listed breakthrough times. For example, if a job requires the use of thin, flexible gloves with a 30- minute breakthrough time, then the wearer could change gloves within 30 minutes of initial contact with TDI.

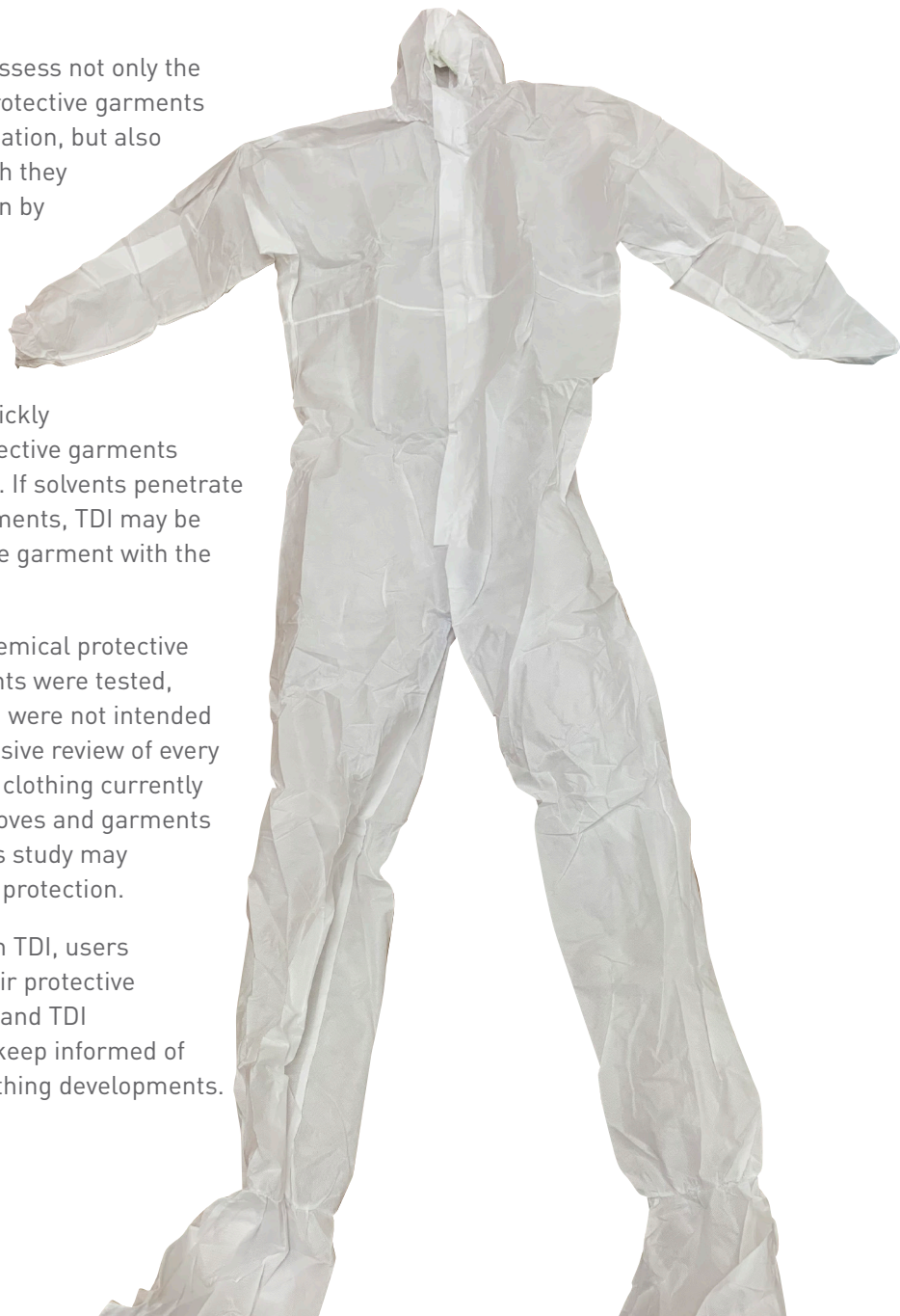
It is important to assess not only the degree to which protective garments prevent TDI permeation, but also the degree to which they prevent permeation by any solvents used.

MCB and o-DCB are just two examples.

Some solvents are expected to quickly penetrate the protective garments listed in the tables. If solvents penetrate the protective garments, TDI may be carried through the garment with the solvent.

Although many chemical protective gloves and garments were tested, these studies by III were not intended to be a comprehensive review of every piece of protective clothing currently available. Other gloves and garments not included in this study may provide equivalent protection.

When working with TDI, users should consult their protective clothing suppliers and TDI manufacturers to keep informed of new protective clothing developments.



Footnotes

- 1 For more details on the use of air purifying respirators under the OSHA Standard, please refer to CPI Guidance Document AX 501 Guidance for Developing a Written Respiratory Protection Standard, available at www.polyurethane.org.
- 2 For more details on the use of air purifying respirators under the OSHA Standard, please refer to CPI Guidance Document AX 5001, CPI Guidance for Developing a Written Respiratory Protection Program. With the Occupational Safety and Health Administration Respiratory Protection Standard 29 CFR §1910.134 available at www.polyurethane.org.
- 3 Breakthrough times refer only to the time required for TDI to penetrate the garment and do not address permeation by solvents or TDI solvent combinations.

Additional Information

For additional information on TDI protective clothing, safe handling, and disposal, consult the following sources:

Guidelines for the Selection of Chemical Protective Clothing, American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-7, Cincinnati, Ohio 45211-4438.

Technical Data Sheets (TDS) and current Safety Data Sheets (SDS) for toluene diisocyanate (TDI) available from the supplier.

Working With TDI: Things You Should Know (AX202), Center for the Polyurethanes Industry.

Health Effects of Diisocyanates: Guidelines for Medical Personnel (AX150), Center for the Polyurethanes Industry.

Guidelines for the Responsible Disposal of Containers and Wastes from Polyurethane Raw Materials Processing (AX151), Center for the Polyurethanes Industry.

Guidance for Developing a Written Respiratory Protection Program (AX501)

Legal

This guidance document was prepared by the American Chemistry Council's Center for the Polyurethanes Industry. It is intended to provide general information on selecting protective clothing for TDI users. It is not intended to serve as a substitute for in-depth training or specific protective clothing, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons involved in safe handling and use of TDI have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. The guidance is necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions and economic and technological feasibility. Neither the American Chemistry Council, nor the individual member companies of the Center for the Polyurethanes Industry of the American Chemistry Council, nor any of their respective directors, officers, employees, subcontractors, consultants, or other assigns, makes any warranty or representation, either express or implied, with respect to the accuracy or completeness of the information contained in this guidance document; nor do the American Chemistry Council or any member companies assume any liability or responsibility for any use or misuse, or the results of such use or misuse, of any information, procedure, conclusion, opinion, product, or process disclosed in this guidance document. **NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.**

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APPENDIX A BACKGROUND INFORMATION ON PROTECTIVE CLOTHING

Evaluating the Chemical Barrier Properties of Protective Clothing

Protective clothing that is intended to offer protection from contact with chemicals includes a liquid proof barrier layer, usually made of some type of polymer coating or film. Common chemical protective clothing barrier materials include neoprene, butyl rubber, natural rubber ('latex'), acrylonitrile – butadiene rubber (NBR or 'nitrile rubber'), polyvinyl chloride (PVC), and polyethylene. As mentioned earlier, the barrier properties of a material are evaluated by permeation and degradation testing with the chemical or mixture in question.

Permeation testing involves simulating the extreme case of continuous complete surface contact of the outside surface of the protective clothing material with the liquid chemical for an 8-hour period. During the test, an air or water collection medium on the inside surface of the protective clothing material is monitored for the concentration of the test chemical. The elapsed time when the chemical is first detected in the collection medium is called the **breakthrough time (BT; minutes)**. After breakthrough, the rate of chemical transfer through the material increases, usually reaching a steady 'dose rate' value; this is reported as the **permeation rate (PR; $\mu\text{g}/\text{cm}^2/\text{min}$)**.

Degradation testing is usually done concurrently with permeation testing. It involves observations of the effects on the protective clothing sample from contact with the chemical. Typical degradation effects include swelling, discoloration, or even mechanical failure (i.e., tearing) or dissolution.

Interpretation of Chemical Barrier Property Testing

It is important to note that degradation and permeation test results are simply additional information to be factored into a protective clothing selection judgement. Note that considering BT as a maximum use time, is a very conservative approach since (1) gloves and suits are not usually used under the conditions of the test (continuous liquid contact with the chemical over the entire surface of the glove or suit), and (2) having the low level of permeated vapor inside the glove or suit as occurs at breakthrough is not an immediate exposure hazard for most chemicals. Permeation data can be considered as informative for ranking the relative holdout properties of various materials and material combinations to the test chemical. Likewise, the degradation rate gives a qualitative indication of the degree to which the barrier material will be weakened or broken down by the test chemical

APPENDIX B SUMMARIZED PERMEATION TESTING RESULTS

Table 1—Permeation Testing Results for Protective Gloves with Toluene Diisocyanate (TDI): Undiluted and as 10% Solutions in Monochlorobenzene (MCB) or ortho-Dichlorobenzene (o-DCB)

Glove Type*	Barrier Material	Manufacturer	Model Name/#	Thick-ness (mil)	Mechanical Durability*	Dexterity*	Breakthrough Time (hours)	
							TDI	10% TDI in 90% MCB or o-DCB
Heavy Duty	Neoprene	Ansell Edmont	Neox 9-924	72.0	High	Low	6.0	0.75
Heavy Duty	Neoprene	Ansell Edmont	Scorpio 8-352	38.5	Medium	Medium	4.7	0.5a
Heavy Duty	PVC	Jomac	8122	57.0	High	Low	1.5	--
Heavy Duty	PVC	Best	Black Night 7712R	51.0	High	Low	1.5	--
Heavy Duty	PVC	Jomac	7112	39.0	High	Low	1.3	--
Heavy Duty	Nitrile	Best	Ultraflex 21R	42.0	High	Medium	0.75	--
Medium Duty	Butyl	North	B-161	7.5	Medium	Medium	>8.0	--
Medium Duty	Laminated PE/EVAL	North	Silver Shield 7094	4.0	Medium	Medium	>8.0	>8.0
Medium Duty	Fluoroelastomer	North	Viton F-101	15	Medium	High	--	>8.0
Medium Duty	Nitrile	Perfect Fit	Stansolve AF-18	18.5	Medium	Medium	>8.0	1.0a
Medium Duty	Butyl	North	B-131	11.5	Medium	High	>8.0	--
Medium Duty	Laminated PE/EVAL	Safety 4 (Ansell Edmont)	4H 87400	2.0	Medium	Medium	>8.0	>8.0
Medium Duty	Nitrile	Ansell Edmont	Solvex 37-155	12.5	Medium	Medium	>8.0	0.5
Medium Duty	Natural Rubber	Ansell Edmont	Canners & Handlers 392	20.0	Medium	Medium	0.5	--
Medium Duty	Natural Rubber	Marigold	326Y	18.0	Low	High	0.33	--
Medium Duty	Natural Rubber	Perfect Fit	L118	11.0	Low	High	<0.25	--
Light Duty	Nitrile	Best	N-Dex 7005	4.0	Low	High	0.5	<0.25a
Light Duty	Natural Rubber	Best	Dermathin 1005	7.0	Low	High	<0.25	--
Light Duty	PVC	Perfect Fit	Pylox 212 (V-10)	9.0	Low	High	<0.25	--
Light Duty	Natural Rubber	Johnson & Johnson	Microtouch (1)	5.0	Low	High	<0.25	--
Light Duty	Nitrile	Best	N-Dex 9005	6.0	Low	High	<0.25	--
Light Duty	Polyethylene	Ansell Edmont	Poly-D 35-112	1.5	Low	High	<0.25	--

*Qualitative descriptions;

'Glove Type': Heavy Duty – heavy mechanical tasks with expected chemical contact (e.g., pump or filter replacement)

Medium Duty – general plant tasks where incidental contact might be expected (e.g., process sampling)

Light Duty – low expected contact where dexterity is needed (e.g., lab sample handling)

'Mechanical Durability': resistance to cuts and abrasion

'Dexterity': ability to conduct manual tasks requiring detailed control

a Material degraded after the test

**Table 2—
Permeation Testing Results for Protective Suits with Toluene Diisocyanate (TDI)**

Suit Type	Material ¹	Manufacturer	Trade Name / Model #	Thick-ness (mil)	Mechanical Durability*	TDI Breakthrough Time (hours)
Coverall (Limited use)	Laminated	Kappler	Chemrel	9.0	High	>8.0
Coverall (Limited use)	Laminated	Kappler	CPFII	15.0	High	>8.0
Coverall (Limited use)	Laminated	DuPont	Tychem SL	7.0	Medium	>8.0
Coverall (Limited use)	Laminated	Keppler	Chemtuff	10.0	High	>8.0
Coverall (Limited use)	Laminated	DuPont	Barricade	14.0	High	>8.0
Coverall (Limited use)	Nonwoven	DuPont	Tychem QC	6.0	Low	0.25
Coverall (Limited use)	Nonwoven	Kimberly Clark	Hazard Guard I	20.0	Low	<0.25
Coverall (Limited use)	Nonwoven	Kimberly Clark	Hazard Guard I	13.0	Low	<0.25
Coverall (Limited use)	Nonwoven	DuPont	Tyvek	5.0	Low	<0.25
Splash Suit (Reusable)	Laminated	Kappler	Responder	14.0	High	>8.0
Splash Suit (Reusable)	Neoprene	Rainfair	Chem Tech II 1000-8552	7.0	High	1.33
Splash Suit (Reusable)	PVC	River City	Wizard 300J	11.0	High	<0.25
Splash Suit (Reusable)	Polyurethane	Rainfair	Medallion 1100-1937	8.0	Medium	<0.25
Splash Suit (Reusable)	PVC	Neese Rubber Co.	Universal 35	10.0	High	<0.25

**Mechanical Durability*: resistance to cuts, abrasion and tearing (subjective qualitative assessment for guidance only)

¹ *Material notes:*

'Nonwoven' – fabric made from polyethylene or polypropylene, typically by 'spin binding' or 'meltblowing' processes

'Laminated' – single or multiple layer barrier film laminated to nonwoven fabric



Center for the
Polyurethanes Industry

American Chemistry Council

700 2nd Street, NE
Washington, DC 20002
(202) 249-7000

www.americanchemistry.com