Guidance for Selection of Protective Clothing for MDI Users

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Purpose

The purpose of this document is to provide useful guidance for selecting the appropriate personal protective equipment (PPE) for working with methylene diphenyl diisocyanate (MDI) and to analyze the performance characteristics of several gloves, coveralls, splash suits, and other protective garments commonly used when working with MDI and polymeric MDI (PMDI).[1] MDI is a solid white to yellow flake at room temperature; however, it can be sold in a heated (molten) form when it is in a liquid state. PMDI is a liquid at room temperature and typically is a mixture of monomeric forms of MDI (2,4 and 4,4-MDI) and higher molecular weight oligomers of MDI.

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Health and Safety Information

During the handling, processing, and application of MDI/PMDI, contact with vapor, liquid, or aerosol/mist may cause adverse health effects to the skin, eyes, and respiratory system. Inhalation of MDI vapors or aerosol/mist at concentrations above the occupational exposure limit (e.g., ACGIH-TLV or OSHA –PEL) can irritate the respiratory system (nose, throat, lungs) causing runny nose, sore throat, coughing, chest discomfort, shortness of breath, or reduced lung function. Persons with a pre-existing condition, non-specific bronchial hyper-reactivity, can respond to airborne concentrations below the TLV or PEL with similar symptoms as well as an asthma attack or asthma-like symptoms. As a result of previous repeated overexposures (above the TLV or PEL) or a single large dose, certain individuals may develop sensitization to diisocyanates (asthma or asthma-like symptoms) that may cause them to react to a later exposure to diisocyanates at levels well below the threshold limit value (TLV) or permissible exposure limit (PEL).

Direct skin contact with MDI/PMDI may cause irritation with symptoms of reddening, swelling, rash, and, in some cases, skin sensitization. Animal tests and other research indicate that skin contact with MDI can play a role in causing sensitization and respiratory reaction.

Engineering controls (e.g. local exhaust ventilation) and sound workplace practices may be the first line of defense against potential exposure to MDI/PMDI, and guidelines have been established by OSHA to help individuals avoid overexposure and adverse health effects[1]. It is important that employees wear PPE recommended for their specific job functions to prevent direct skin/eye contact with PMDI liquid or inhalation of MDI vapors/mist.

Eye Protection and Respiratory Protection

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

Eye Protection

In situations where there is splash potential (e.g., when directly handling liquid product), wear chemical goggles and, depending on the extent of potential contact, a faceshield. These situations may include line-breaking (transfer hose disconnect), transfer of material using a drum pump, etc. MDI may irritate the eyes and can be difficult to remove, so prevention is very important.

Respiratory Protection

Airborne MDI concentrations greater than the ACGIH TLV or OSHA PEL can occur in inadequately ventilated environments when MDI is sprayed, aerosolized, or heated. In such cases, wear respiratory protection. The type of respiratory protection selected must comply with the requirements set forth in OSHA's Respiratory Protection Standard (29 CFR 1910.134). The use of air purifying respirators (APRs) is acceptable in certain situations as part of a comprehensive respiratory protection program[2]. An organic vapor cartridge with a particulate filter (e.g. OV/P100) may be used with the APR where the concentration of MDI in air can be documented and where the protection factor will not be exceeded. A cartridge change out schedule is required to be part of the respiratory protection program by OSHA. When concentrations of MDI exceed or are likely to exceed the protection afforded by a cartridge respirator (e.g. emergency situations or identified high exposure potential activities), a supplied-air respirator (SAR) is necessary under OSHA's standard.

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[1] For details, see CPI Guidance Document AX205, *Working With MDI and Polymeric MDI: What You Should Know*, available at www.polyurethane.org.

[2] For more details on the use of air purifying respirators under the OSHA Standard, please refer to Guidance Document AX 246, CPI *Model Respiratory Protection Program for Compliance With the Occupational Safety and Health Administration Respiratory Protection Standard 29 CFR §1910.134* available at www.polyurethane.org.

Selecting Protective Clothing

Understand and adhere to safe handling practices for MDI/PMDI and other chemicals that pose potential health hazards. This may include wearing eye protection, respiratory protection, gloves, boots and coveralls or lab aprons. For individuals who work with MDI/PMDI, appropriate protective clothing is essential for the prevention of skin exposures.

When selecting protective clothing, consider the following factors:

- *Chemical Resistance of Glove or Garment:* To be effective, the protective clothing should resist permeation by the chemical or chemicals being handled. Use of disposable gloves and clothing is often preferred, because proper decontamination of reusable items may be difficult. Protective gloves and garments should also be resistant to permeation by solvents used in combination with MDI/PMDI.

- *Specific Job Functions:* The nature of the job being performed will greatly influence the selection and features of protective clothing. 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.

- When the manual dexterity requirements of some jobs require the use of thin, form-fitting gloves that offer limited amounts of protection time, *change the gloves with sufficient frequency*.

- *Potential for Exposure:* The degree of exposure for individual job functions dictates the degree of personal protection required and the appropriate clothing for the job. For instance, work conducted in a laboratory environment, where the potential for exposure to the skin and eyes is limited, may need gloves, eye protection, and a lab apron or lab coat. On the other hand, a project that presents a greater risk of acute exposure to the skin and eyes, such as loading and unloading tank cars, may need to use hooded coveralls, boots, and more substantial gloves (heavy duty and light duty) to ensure adequate protection.

- *Duration of Exposure:* The length of time that an individual is working with or handling MDI/PMDI influences the type of protective clothing selected. When working with MDI for extended time periods, protective clothing that offers the greatest level of chemical resistance is appropriate.

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 Approach

The International Isocyanate Institute (III) sponsored a study in which Texas Research Institute (TRI) 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 offered by each garment.

The III research measured the length of time it took polymeric MDI (PMDI) to permeate through the protective clothing material under conditions of continuous contact and complete surface coverage with PMDI.

Following that survey, CPI asked TRI to conduct solvent and PMDI breakthrough testing on several different gloves and eight solvents, each containing one percent PMDI by weight.

Discussion of Tables

Tables 1 and 2 are organized by glove or garment type, and, within each category, are arranged in descending order according to the protection time provided[3]. Research included the trade name, manufacturer, thickness, and durability of each item.

The PMDI protection times presented in Tables 1 and 2 are the times required for PMDI to penetrate the chemical protective glove or garment material, and are the maximum suggested use times. Change gloves and garments with sufficient frequency to avoid exceeding the listed protection times. For example, if a job requires the use of thin, flexible gloves with a 30 minute protection time, then the wearer should change gloves within 30 minutes of initial contact with PMDI.

Table 1 - Protective Gloves for Polymeric MDI (PMDI) by type (light, medium, heavy duty); within type, by protection time

Glove Type	Material	Manufacture	Trade Name	Model #	Thickness (mil)	Durability*	Dexterity*	PMDI Protection Time (hours)
Heavy Duty	Neoprene	Ansell Edmont	Neox	9-924	72.0	High	Low	>8.0
Heavy Duty	Neoprene	Ansell Edmont	Scorpio	8-352	38.5	Medium	Medium	>8.0
Heavy Duty	PVC	Best	Black Night	7712R	51.0	High	Low	>8.0
Heavy Duty	Nitrile	Best	Ultraflex	21R	42.0	High	Medium	>8.0
Heavy Duty	PVC	Jomac	--	8112	57.0	High	Low	6.5
Heavy Duty	PVC	Jomac	--	7112	39.0	High	Low	3.5
Medium Duty	Butyl	North	--	B-131	11.5	Low	High	>8.0
Medium Duty	Laminated PE/EVAL	Safety 4 (Ansell Edmont)	4H	(87400)	2.0	Low	Medium	>8.0
Medium Duty	Butyl	North	--	B-161	17.5	Medium	Medium	>8.0
Medium Duty	Laminated PE/EVAL	North	SilverShield	(7094)	4.0	Low	High	>8.0
Medium Duty	Nitrile	Perfect Fit	Stansolve	AF-18	18.5	Medium	Medium	>8.0
Medium Duty	Natural Rubber	Perfect Fit	--	L118	11.0	Low	High	1.5-2.0
Medium Duty	Natural Rubber	Ansell Edmont	Canners & Handlers	392	20.0	Medium	Medium	1.5
Medium Duty	Natural Rubber	Marigold	--	326Y	18.0	Low	High	1.5
Light Duty	Nitrile	Best	N-Dex	9005	6.0	Low	High	>8.0
Light Duty	Nitrile	Best	N-Dex	7005	4.0	Low	High	>8.0
Light Duty	PVC	Perfect Fit	Pylox	212 (V-10)	9.0	Low	High	2.0
Light Duty	Polyurethane	Ansell Edmont	Poly-D	35-112	1.5	Low	High	1.0
Light Duty	Natural Rubber	Johnson & Johnson	Microtouch	(1)	5.0	Low	High	<0.25
Light Duty	Natural Rubber	Best	Dermathin	1005	7.0	Low	High	<0.25

*Based on subjective evaluation – information provided as a guideline only.

Table 2—Body Protective Clothing for Polymeric MDI (PMDI) by garment type; within type, by protection time

Clothing Type	Material	Manufacturer	Trade Name	Model #	Thickness (mil)	Durability* P	MDI Protection Time (hours)
Coverall (Disposable)	Laminated	Kappler	Chemrel	-	9.0	High	>8.0
Coverall (Disposable)	Laminated	Kappler	CPFII	-	15.0	High	>8.0
Coverall (Disposable)	Nonwoven	DuPont	Tychem SL	-	7.0	Medium	>8.0
Coverall (Disposable)	Laminated	Keppler	Chemtuff	-	10.0	High	>8.0
Coverall (Disposable)	Laminated	DuPont	Barricade	-	14.0	High	>8.0
Coverall (Disposable)	Nonwoven	DuPont	Tychem QC	-	6.0	Low	>8.0
Coverall (Disposable)	Nonwoven	Kimberly Clark	Hazard Guard I	-	20.0	Low	<0.25
Coverall (Disposable)	Nonwoven	Kimberly Clark	Hazard Guard I	-	13.0	Low	<0.25
Coverall (Disposable)	Nonwoven	DuPont	Tyvek	-	5.0	Low	<0.25
Splash Suit (Level B)	Laminated	Kappler	Responder	-	14.0	High	>8.0
Splash Suit	Neoprene	Rainfair	Chem Tech II	1000-8552	7.0	High	>8.0
Splash Suit	PVC	River City	Wizard	300J	11.0	High	>8.0
Splash Suit	Polyurethane	Rainfair	Medallion	1100-1937	8.0	Low	>8.0
Splash Suit	PVC	Neese Rubber Co.	Universal	35	10.0	High	7.5 to >8.0

*Based on subjective evaluation – information provided as a guideline only.

[3]Protection times refer only to the time required for MDI to penetrate the garment and do not address permeation by solvents or PMDI-solvent combinations.

Table 3—CPI Glove Permeation Study: Summary of Permeation Test Results For Solvent Breakthrough Testing

Solvent with 1% PMDI by Weight	Ansell Edmont Solvex Nitrile 37-155(15 mil)			Ansell Edmont Solvex Nitrile 37-155(22mil)			Ansell Edmont Scorpio Neoprene		
	BT NBT		PR	BT	NBT	PR	BT	NBT	PR
Dipropylene Glycol Monomethyl Ether	>475 >478		<0.07	>480	>480	<0.02	-	-	-
Methyl Ethyl Ketone	3	3	NR	-	-	-	3	6	21*
Mineral Spirits	>480	>480	<0.002	-	-	-	108	191	5
Toluene/Xylene (50%/50%)	21 26		62*	-	-	-	6	19	27*
Dibasic Ester	160	160	3.0**	300	300	1.0**	-	-	-
Propylene Carbonate	163	172	14	379	402	5	-	-	-
N-methylpyrrolidone NMP	27 32		8*	-	-	-	-	-	-
NMP/Dibasic Ester/d-Limonene (33%/33%/33%)	38 45		46*	72	87	58*	-	-	-

Table 4—CPI Glove Permeation Study: Summary of Permeation Test Results For Solvent and PMDI Breakthrough Testing

Solvent with 1% PMDI by Weight	Ansell Edmont Solvex Nitrile 37-155(15 mil) Solvent Breakthrough			Ansell Edmont Solvex Nitrile 37-155(15 mil) PMDI Breakthrough		
	BT NBT		PR	BT	NBT	PR
Dipropylene Glycol Monomethyl Ether	>475	>478	<0.07	>480	>480	<0.007
Methyl Ethyl Ketone	3	3	NR	NT	NT	NT
Mineral Spirits	>480	>480	<0.002	>480	>480	<0.007
Toluene/Xylene (50%/50%)	21	26	62*	NT	NT	NT
Dibasic Ester	160	160	3.0**	280	410	NR
Propylene Carbonate	163	172	14	>480	>480	<0.007
N-methylpyrrolidone NMP	27	32	8*	60	60	NR
NMP/Dibasic Ester/d-Limonene (33%/33%/33%)	38 45		46*	80	80	NR

BT = Actual Breakthrough Time in minutes
NBT = Normalized Breakthrough Time in minutes (0.1ug/cm2*min)
PR = Maximum Permeation Rate in ug/cm2*min
NR = No Rate available due to catastrophic breakthrough
* = Rate may be artificially low due to detector saturation
** = Rate may be artificially low due to low volatility of chemical
NT = Not Tested

Tables 3 and 4 present various glove materials and the corresponding breakthrough times, in minutes, of several solvents and solvent-1% PMDI mixtures[4]. III assessed not only the degree to which protective garments prevent PMDI permeation, but also the degree to which they prevent permeation by any solvents used.

Although a large number of chemical protective gloves and garments were tested, this technical bulletin by III was 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 MDI, users may consult their protective clothing suppliers and MDI manufacturers to keep informed of new protective clothing developments.

[4] For details on the permeation of PMDI/solvent combinations see W. Robert, et al., “Protecting Workers from PMDI-Solvent Combinations—What Gloves Work Best?”.

Additional Information

For additional information on MDI 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 polymethylene polyphenyl isocyanates (PMDI) available from the supplier.

Working With MDI and Polymeric MDI: Things You Should Know (AX205), 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.

W. Robert, et al., *Protecting Workers from PMDI Solvent Combinations—What Gloves Work Best?* Proceedings of the Polyurethanes Technical Conference, 2000.

Model Respiratory Protection Program for Compliance With the Occupational Safety and Health Administration Respiratory Protection Standard 29 CFR §1910.134.

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