Guidance for Selection of Personal Protective Equipment for MDI 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 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. Throughout this document, the term MDI is used to address both monomeric MDI and polymeric MDI (pMDI).

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American Chemistry Council
Center for the Polyurethanes Industry

Health and Safety Information

During the handling, processing, and application of MDI, contact with vapor, liquid, or aerosols may cause adverse health effects to the skin, eyes, and respiratory system. Inhalation of MDI 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, and lungs) causing runny nose, sore throat, coughing, chest discomfort, shortness of breath, or reduced lung function. The odor threshold of MDI is above the established exposure limits. Therefore, odor should never be used to indicate the presence of MDI. As a result of previous 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 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 also have asthma-like symptoms when exposed to airborne concentrations below the TLV or PEL.

Understand and adhere to safe handling practices for MDI and other chemicals that pose potential health hazards. Direct skin contact with MDI may cause irritation with symptoms of reddening, itching, rash, and, in some cases, skin sensitization. Animal tests and other research indicate that skin contact with MDI 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 MDI, 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 MDI liquid or inhalation of MDI vapors or aerosols.

Eye Protection and Respiratory Protection

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

Eye Protection

MDI 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 MDI is immediately and thoroughly rinsed from the eye.

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 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

Airborne MDI concentrations greater than the ACGIH TLV or OSHA PEL can occur in inadequately ventilated environments, especially when MDI is sprayed, aerosolized, or heated. In such cases, wear respiratory protection. The type of respiratory protection selected must comply with 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. OSHA requires a cartridge change out schedule to be part of the respiratory protection program. 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 required under the OSHA standard.

Selecting Gloves and Protective Clothing

For individuals who work with MDI, appropriate protective clothing is essential for the prevention of skin exposures.

When selecting 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 MDI.

- **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 (TRI) 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 PMDI offered by each. 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 PMDI to permeate through the protective clothing material under conditions of continuous contact and complete surface coverage with PMDI. PMDI is commonly used in industry and is one of many commercial MDI products, but the data can be considered instructive for working with MDI in general. Always consult the supplier's Safety Data Sheets (SDS) for PPE indications for a particular MDI product.

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

Following the initial study, CPI asked TRI to conduct solvent and PMDI breakthrough testing on several different gloves and eight solvents, each containing one percent PMDI by weight. The results of those studies are shown in Tables 3 and 4 in Appendix B. Tables 3 and 4 present various glove materials and the corresponding breakthrough times, in minutes, of several solvents and solvent-1% PMDI mixtures[4]. TRI 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.

The key points from the testing are summarized below:

Glove Materials:

- Materials that provided long-term permeation protection in heavy contact with undiluted PMDI: laminated PE/EVAL, neoprene, butyl rubber, nitrile.
- Other materials that provided good permeation protection per unit of thickness: PVC.
- Nitrile gloves provided long-term permeation protection in heavy contact with PMDI (1%) in dipropylene glycol momomethyl ether, and PMDI (1%) in mineral spirits.
- 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:

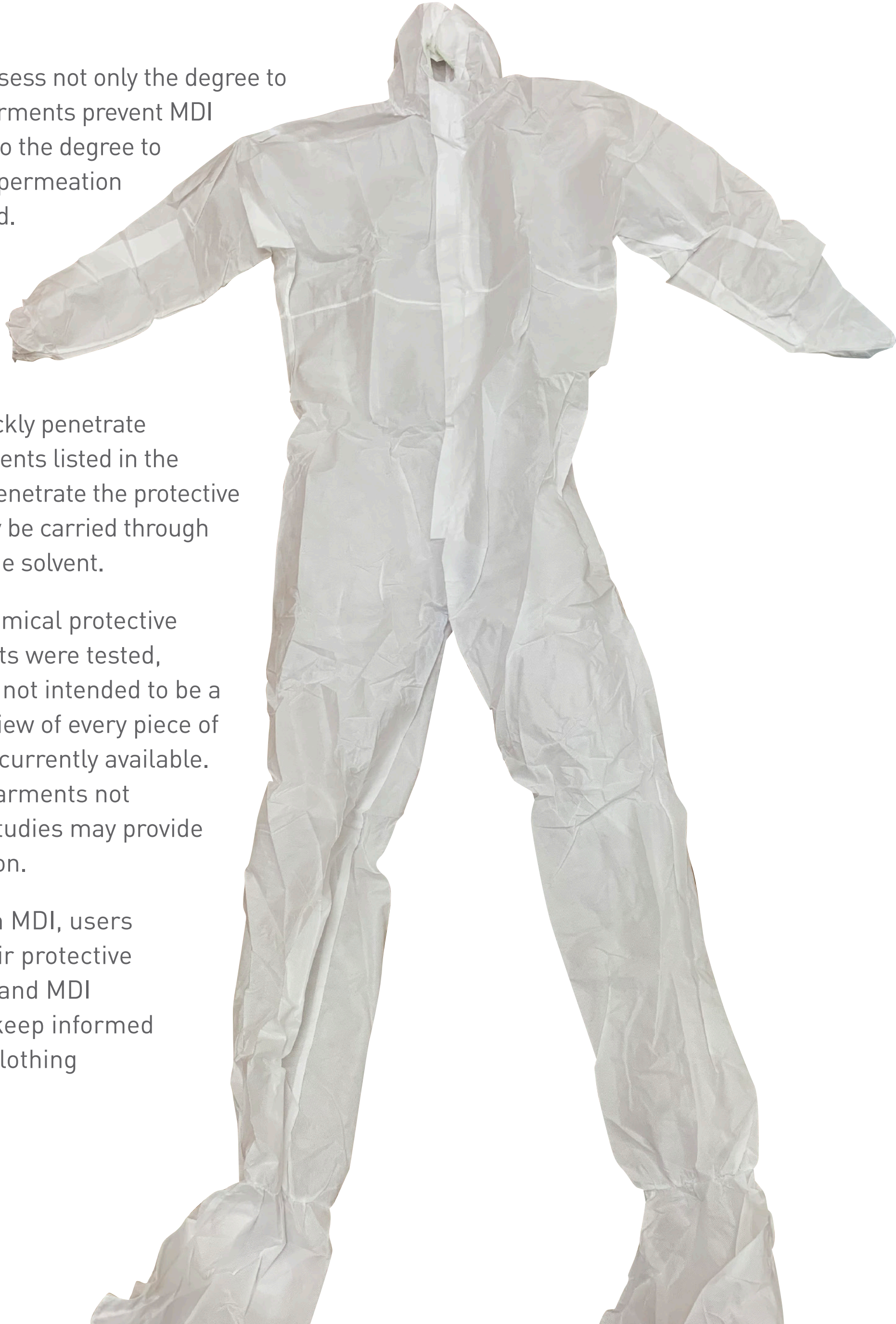
PE/EVAL inner glove	+	nitrile outer glove
		

Suit Materials:

- Materials that provided long-term permeation protection in heavy contact with PMDI: laminates, neoprene, PVC, and polyurethane.

- Non-woven materials offer limited protection, but may be useful in one-time use for protection if only slight incidental contact is anticipated

The MDI breakthrough times presented in the tables are the times required for MDI 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 MDI.



It is important to assess not only the degree to which protective garments prevent MDI permeation, but also the degree to which they prevent permeation by any solvents used. Methyl ethyl ketone and dibasic ester are just two examples. Some solvents are expected to quickly penetrate the protective garments listed in the tables. If solvents penetrate the protective garments, MDI may be carried through the garment with the solvent.

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

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

Footnotes

1 For details, see CPI Guidance Document AX205, Working With MDI: Things 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 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 MDI to penetrate the garment and do not address permeation by solvents or PMDI-solvent combinations.

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.

Legal Notice

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 MDI users. It is not intended to serve as a substitute for in-depth training or specific protective clothing requirements, 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 MDI 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.

For more information on material presented in this guidance document, please contact your supplier.

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; µg/cm2/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) of 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 judgment. 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 - Protective Gloves for Polymeric MDI (PMDI) by type (light, medium, heavy duty); within type, by protection time

Glove Type	Material	Manufacturer	Model Name/#	Thickness (mil)	Mechanical Durability*	Dexterity*	PMDI Breakthrough 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	Model Name/#	Thickness (mil)	Mechanical Durability*	PMDI Breakthrough 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.

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	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-methylpyrrolidoneNMP	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

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