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Methyl Isocyanate Liquid and Vapor Permeation Through Selected Respirator Diaphragms and Chemical Protective Clothing*

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Initially, a study was undertaken to evaluate selected chemical protective clothing suitable for use by emergency response personnel confronted with methyl isocyanate (MIC). Twenty-two chemical protective clothing materials were tested against liquid methyl isocyanate. Chemical permeation breakthrough times for these clothing materials demonstrate that only one of these garments can be considered as a candidate material against liquid MIC. In a subsequent study, three chemical protective clothing materials were evaluated against approximately 800 ppm MIC vapor. Chemical permeation breakthrough times demonstrate that these materials can be considered candidate materials. A final study tested self-contained breathing apparatus (SCBA) diaphragms. Four SCBA diaphragms were tested and all experienced rapid breakthrough when exposed to liquid MIC. Next, three SCBA diaphragms were exposed to approximately 800 ppm MIC vapor. The data demonstrate that the SCBA should be worn inside a total encapsulating suit.

Background

The December 1984 Bhopal, India disaster has raised concerns regarding the selection of protective equipment for use by emergency response personnel against methyl isocyanate (MIC). These concerns are especially pertinent since this chemical is manufactured and stored in the U.S.

MIC is manufactured only by the Union Carbide Corporation's plant located in Institute, West Virginia; MIC is an intermediate in the production of carbamate pesticides. MIC is reactive, toxic and volatile and reacts with water and other hydroxyl compounds, such as alcohols. Other chemicals such as amines and acids react as well. MIC also reacts with itself, (*e.g.*, polymerization).[1]

The Threshold Limit Value (TLV®) for MIC is 0.02 ppm; the OSHA Permissible Exposure Limit (PEL) is 0.02 ppm. MIC attacks the respiratory system, eyes and skin; eye and skin burns occur on contact. The respiratory system can be irritated severely. Human subjects — when exposed to MIC — experienced nose, throat and eye irritation at 2 ppm, but at 0.4 ppm no effects were noticed. At 21 ppm such irritation was unbearable.[1]

MIC has a boiling point at 760 mm Hg of 39.1°C. The vapor pressure at 20°C is 348 mm Hg. The vapor density is twice that of air.[1] Thus, MIC vapor will be concentrated near ground level.

Part I. Liquid Permeation of MIC Through Selected Protective Clothing

Introduction

Twenty-two chemical protective clothing total encapsulating suit materials were evaluated for chemical permeation against liquid methyl isocyanate. This selection represents many types of elastomers used in these commercial products. No chemical permeation data for these products were found in the literature. Therefore, a study was undertaken to fill this information gap.

Materials

MIC used in this study was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin (Lot No. 3317AL, 37-39°C b.p.).

Air was house air that was passed through a dryer, sorbent and high efficiency filter to remove residual contaminants.

Experimental Design

H-Nu PI-101 and Century OVA 108 direct-reading instruments were used initially but did not have a lower detectable limit of 1 ppm or less. The chemical permeation apparatus used throughout the liquid permeation portion of this study was a closed-loop system consisting of a Miran® IA-CVF infrared (IR) direct-reading instrument with a (2.54 cm) 1-in. diameter chemical permeation cell (see Figure 1).† This chemical permeation cell is described completely in Reference 2. All tubing was Teflon®; all connectors were Teflon or stainless steel. Air, the collection medium, was circulated by a Metal Bellows Corporation, Model MB-41, metal bellows pump at 8.0 sLpm. At this flow rate, the internal permeation cell pressure was 10 mm Hg above atmospheric pressure. Additionally, the metal bellows of the pump at this flow rate and pressure induced a rapid vibration in the test specimen. This vibration, in turn, caused the MIC to churn inside the permeation cell. To minimize the vibration, a rubber aspirator bulb was depressed slightly, then placed on the permeation fill tube (Figure 1). This created a slight negative pres-

*Mention of a company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

†Chemical permeation cell available from AMK Glass Co., 610 South Third Avenue, Vineland, NJ 08360.

sure in the chemical reservoir, which reduced substantially the severe agitation of MIC.

Before each test run, the specimen thickness was measured with a dial gauge. Readings were taken at five different points. The specimen then was mounted in the permeation cell. The stop watch was started, the rubber aspirator bulb was put on the fill tube, and then the circulation pump (closed loop) was started. The system was run for 10 min. In this way, any contamination was seen easily. After 10 min, if no contamination was detected, an actual run was made by introducing 1 mL of MIC into the chemical permeation cell. The procedure was to stop the pump and stop watch, add 1.0 mL of MIC, start the watch, place the aspirator bulb on the chemical permeation inlet tube, then start the pump.

The apparatus was evaluated initially with the use of acetone-neoprene. The chemical permeation of acetone through neoprene demonstrated that this apparatus is comparable to the ASTM F739-81 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals.[2] In the ASTM F739-81 test method, a standard 2-in. test cell is used. The mean breakthrough time and standard deviation for triplicate runs for the system were 12.3 ± 1.4 min compared to the ASTM F739-81 cell mean of 12.3 ± 0.4 min. The breakthrough time is defined as the time interval between initial contact of the liquid or gas challenge chemical on the outside surface of the protective clothing material and detection at the inside surface of the material by a chosen analytical method.

An attempt was made to obviate the induced specimen vibration by lowering the air circulation flow rate. Accordingly, a Du Pont P-4000 pump at 3.5 sLpm in a closed-loop arrangement was used in lieu of the metal bellows pump. Acetone-neoprene mean breakthrough time of this study as compared to the standard ASTM cell (16.5 ± 0.7 min *vs.* 12.3 ± 0.4 min) demonstrates that there is insufficient airflow through the large volume of the apparatus (5.6 L). Therefore, a metal bellows pump and not a Du Pont pump was used throughout this study.

The lower limit of detection was determined by two different methods. The closed-loop calibration method was not used since the injection volumes of MIC were too small (< 1 μL). A known amount of liquid MIC was injected into a

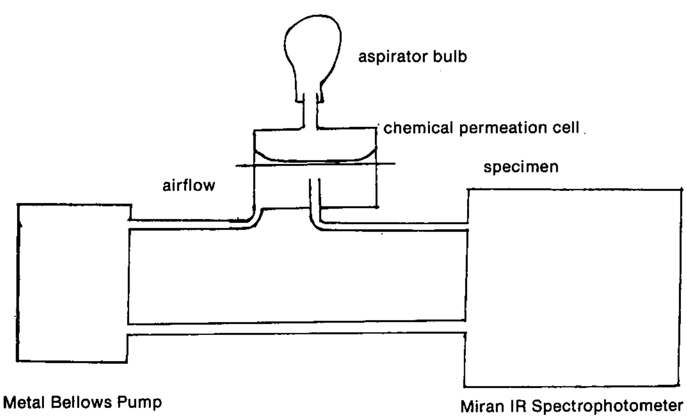

Figure 1 — Liquid MIC chemical permeation test system.

large carboy (50 L) and allowed to vaporize; then aliquots were injected into the closed loop. In the other method, head space samples of MIC vapor at 20° C (vapor in contact with liquid MIC) were injected into the closed loop. The lower limit of detection was 0.20 ppm by the former method and 0.32 ppm by the latter. The mean of these two values, 0.26 ppm, was assumed to be the lower detection limit for this instrument. The minimum detectable concentration claimed by the manufacturer is 0.6 ppm. During these experiments the following IR conditions were used:

0 - 0.100	absorbance scale
11.6 μm	wavelength
20.25m	path length
1 sec	response
1 mm	slit width

Results

Twenty-two garment materials were tested in triplicate against MIC, unless otherwise stated. Only the breakthrough times were measured. The results appear in Table I. The materials which exhibited the longest breakthrough time were an MSA® aluminum laminate and a Chem Fab® Teflon-Nomex® laminate. The aluminum laminate, however, cracked when flexed. Breakthrough times of the flexed specimens were vastly shorter as compared to unflexed. Cracking can be demonstrated easily when one shines a flashlight on one side of the garment while observing the other side. In a darkened room, light will shine through the small cracks. One specimen of Teflon-Nomex laminate was flexed, then tested. Flexing did not affect breakthrough time. Also, the permeation rate was very low when compared to most of the other tested materials whose permeation rates were large (*i.e.,* the detector went off scale). The other garment materials had a mean breakthrough time of less than 10 min, except for MSA Chem Butyl® (13 min).

Conclusions

A one-sided direct contact of MIC with a vibrating test specimen may represent a worst-case condition. But such a condition may simulate movements of emergency response workers during a disaster.

There is no garment material which affords workers adequate protection for at least 1 hr. Of the test materials, only the MSA aluminum laminate and Chem Fab Teflon-Nomex laminate can be considered as candidate materials against liquid MIC. The aluminum laminate, however, may crack, and in this state affords the worker no better protection than most other materials. The Chem Fab laminate, flexed or unflexed, affords the worker the most protection when the breakthrough time and the rate of permeation after breakthrough are considered.

Part II. Liquid Permeation of MIC Through Selected Respirator Diaphragms

Introduction

A limited study was undertaken to determine the effect of liquid MIC on respiratory protective equipment. Regulator

TABLE I
Liquid MIC Permeation Through Selected Garment Material

Material	Run	Mean Thickness (mm) ± Std. Dev.	Breakthrough Time (min)	Mean Breakthrough Time (min) ± Std. Dev.	Comments
Fyrepel polyvinyl chloride	(1)	0.362 ± 0.002	0.50	0.48 ± 0.03	
	(2)	0.355 ± 0.003	0.45		
	(3)	0.359 ± 0.003	0.50		
Wheeler polyvinyl chloride	(1)	0.446 ± 0.004	1.40		
	(2)	0.450 ± 0.002	1.50	1.45 ± 0.07	degradation observed
Fab Ohio vinyl 0.020″ thick	(1)	0.519 ± 0.002	3.20		
	(2)	0.520 ± 0.001	2.60		
	(3)	0.520 ± 0.001	3.10	2.97 ± 0.32	
Fab Ohio vinyl 0.006″ thick	(1)	0.138 ± 0.002	0.45		
	(2)	0.138 ± 0.002	0.40	0.38 ± 0.08	
	(3)	0.134 ± 0.002	0.30		
Fab Ohio vinyl Reinforced vinyl	(1)	0.353 ± 0.002	0.50		
	(2)	0.350 ± 0.001	0.80	0.67 ± 0.15	
	(3)	0.351 ± 0.001	0.70		
Fab Ohio No. T-55 reinforced polyethylene	(1)	0.130 ± 0.019	1.00		
	(2)	0.128 ± 0.019	1.10	1.03 ± 0.06	
	(3)	0.126 ± 0.026	1.00		
ILC Dover chloropel (chlorinated polyethylene)	(1)	0.555 ± 0.002	5.50		
	(2)	0.555 ± 0.004	6.50		
	(3)	0.552 ± 0.002	6.80	5.95 ± 0.84	
	(4)	0.554 ± 0.003	5.00		
ILC Dover urethrane	(1)	0.439 ± 0.009	4.30		
	(2)	0.440 ± 0.009	4.25	4.42 ± 0.25	
	(3)	0.436 ± 0.011	4.70		
Fyrepel Viton®	(1)	0.227 ± 0.003	0.41		
	(2)	0.226 ± 0.005	0.50	0.70 ± 0.43	
	(3)	0.230 ± 0.002	1.20		
Wheeler Viton	(1)	0.230 ± 0.004	1.10		
	(2)	0.230 ± 0.004	1.20	1.13 ± 0.06	
	(3)	0.230 ± 0.001	1.10		
Fyrepel butyl	(1)	0.358 ± 0.002	7.10		
	(2)	0.357 ± 0.002	6.40	6.77 ± 0.35	
	(3)	0.359 ± 0.001	6.80		
Paige butyl 13 oz.	(1)	0.376 ± 0.004	8.0		
	(2)	0.368 ± 0.007	8.0	8.0 ± 0.00	
Paige butyl 6 oz.	(1)	0.180 ± 0.002	2.20		
	(2)	0.182 ± 0.002	2.40	2.28 ± 0.10	
	(3)	0.182 ± 0.002	2.25		
Wheeler butyl	(1)	0.287 ± 0.004	4.40		
	(2)	0.290 ± 0.001	5.00		
	(3)	0.290 ± 0.001	4.80	4.73 ± 0.31	
MSA aluminum laminate	(1)	0.148 ± 0.001	>240		unflexed
	(2)	0.158 ± 0.001	>270		unflexed
	(3)	0.149 ± 0.002	6.00		flexed
	(4)	0.150 ± 0.001	8.00		flexed
MSA Chem butyl Butyl on nylon	(1)	0.382 ± 0.003	12.50		
	(2)	0.380 ± 0.001	14.50	13.17 ± 1.15	
	(3)	0.378 ± 0.002	12.50		
MSA Betex® Butyl on polyester on neoprene	(1)	0.494 ± 0.004	7.00		
	(2)	0.492 ± 0.004	7.03	7.03 ± 0.06	
	(3)	0.489 ± 0.002	7.10		
MSA Vautex® Viton on nylon on neoprene	(1)	0.659 ± 0.002	3.30		
	(2)	0.661 ± 0.001	3.25	3.25 ± 0.05	
	(3)	0.654 ± 0.004	3.20		

TABLE I (cont.)

Material	Run	Mean Thickness (mm) ± Std. Dev.	Breakthrough Time (min)	Mean Breakthrough Time (min) ± Std. Dev.	Comments
Chem Fab	(1)	0.519 ± 0.006	30.0		unflexed
Non-woven Nomex on	(2)	0.519 ± 0.009	30.0	29.3 ± 1.1	unflexed
Teflon	(3)	0.511 ± 0.014	28.0		unflexed
	(4)	0.516 ± 0.007	28.0	28	flexed
Edmont (55-530) spunbonded polyethylene	(1)	0.010	~ 5 sec		
Edmont (37-155) nitrile glove	(1)	0.482 ± 0.018	2.0		palm
	(2)	0.338 ± 0.009	2.0	1.93 ± 1.12	back
	(3)	0.364 ± 0.004	1.8		back
Travenol surgeon's latex	(1)	0.180 ± 0.001	~ 5 sec		
	(2)	0.182 ± 0.003	~10 sec		
	(3)	0.176 ± 0.001	~10 sec		

diaphragms from four different closed-circuit, positive-pressure self-contained breathing apparatuses (SCBA) were tested for chemical permeation against liquid methyl isocyanate. Regulator diaphragms were selected for chemical permeation testing, since the authors believe that these diaphragms are the most vulnerable component of a SCBA.

Materials

Mr. Sam Terry, NIOSH, DSR, Certification Branch, Air Supplied Respirator Section, kindly provided diaphragms from the following manufacturers: Scott, MSA, U.S. Divers (Survivair) and Globe (Guardsman).

Experimental

The chemical permeation system has been discussed in detail in Part I. Table II contains the permeation results and diaphragm construction information. Tests were done in duplicate.

Results/Conclusion

In the unlikely event that liquid MIC contacts the self-contained breathing apparatus diaphragm, high concentrations of MIC will permeate through the diaphragm in less than 2 min. Also, Stannett and Yashuda[3] have demonstrated that saturated vapor and liquid permeation may yield similar results. Under extreme disaster conditions, saturated vapor (~ 500 000 ppm @ 20° C) may be encountered by emergency response personnel, and at this high concentration of MIC, the tested respirator diaphragms would permit MIC permeation in less than 2 min.

TABLE II
Liquid MIC Permeation Through Respirator Diaphragms

Diaphragm/ NIOSH Approval Number	Construction	Mean Breakthrough Time
Globe (guardsman)/ TC-13F-43	Silicone elastomer 0.82 mm nominal thickness in center, 0.25 mm at edge of elastomeric material.	< 15 sec[A]
Scott/ TC-13F-40	Silicone elastomer 0.32 mm at edge, 1.12 mm in center. Segmented metallic disc laminated/ glued to material.	< 15 sec[A]
MSA/ TC-13F-30	Hycar® elastomer 0.475 center (disc removed), 0.310 mm at edge. Removable solid metallic disc on membrane. Solid metallic disc removed before testing.	1.5 min
U.S. Divers/ (survivair) TC-13F-30	Silicone elastomer 0.300 mm for elastomer in holes; 0.75 mm at diaphragm edge, large metallic disc having four 1″ holes laminated/glued to elastomeric material.	1.5 min[B]

[A]Tested specimens were cut so that ~ 1/2 of test area from center and ~ 1/2 from edge.
[B]Elastomeric material in 1″ hole was evaluated.

Part III. Vapor Permeation of MIC Through Selected Respirator Diaphragms and Chemical Protective Clothing

Introduction

A quick effort was undertaken to determine gross effects of MIC vapor on respirator diaphragms. Regulator diaphragms from four different closed-circuit, positive-pressure self-contained breathing apparatuses of Part II and three chemical protective clothing materials of Part I were tested for chemical permeation against MIC vapors. The challenge agent selected was 800 ppm MIC vapor in dry air and in 73% relative humidity. In an emergency spill scenario (*e.g.* Bhopal, India), this concentration of 800 ppm MIC might be expected.

Experimental

The chemical permeation system was discussed in detail in Part I except that two collection sides were used, as shown in Figure 2. About 800 ppm MIC vapor was passed continuously through one side of the permeation cell with the use of a stainless steel metal bellows pump (8 sLpm); the other side was connected to the IR. The methyl isocyanate vapor generation system used a motor-driven syringe to inject MIC liquid quantitatively into a 95-sLpm air stream. Adequate mixing was ensured since the MIC-air mixture fed into a mixing chamber (20 × 30 × 41 cm). A Miller-Nelson Research Inc. control box was used to condition the air before it was mixed with MIC. At 73% relative humidity, MIC can decompose into monomethyl amine (MMA); hence, both MIC and MMA must be monitored. MMA can be detected at 0.1 ppm with the IR. Calibration procedures are explained in Reference 4. Based on the rapid breakthrough times observed for these diaphragms against liquid MIC, 45 min was selected as a sufficient testing time.

Tests were done in duplicate where possible. MIC and MMA were not determined simultaneously on one specimen. Two specimens were used — one for MMA and one for MIC — so that the MIC challenge-concentrations for MIC/MMA were different.

Results/Conclusions

Permeation is a concentration-dependent phenomenon. Decreasing the MIC challenge concentration from neat liquid to 800 ppm should result in longer breakthrough times. This is the general trend for both respirator diaphragms and chemical protective clothing, as demonstrated by Table III. The number of tests is small so that only qualitative inference can be made. In these tests, humidity did not grossly affect breakthrough times for the chemical protective clothing.

Chemical protective clothing within the 45 min test time was not permeable to 800 ppm MIC vapor, but very permeable to the neat liquid. No MMA permeation was detected. These materials can be considered as candidate materials against 800 ppm MIC. Self-contained breathing apparatus diaphragms were permeable to liquid MIC as well as 800 ppm vapor. With 73% RH, MIC breakthrough times appear to be shorter than those in dry air for the respirator diaphragms. MMA was determined only at 73% RH, and breakthrough times appear shorter than 800 ppm MIC (dry air) breakthrough times. In the event of a MIC vapor exposure, the respirator diaphragm may be the weakest line (*i.e.*, possible greatest MIC exposure) in the personal protective equipment chain. Total encapsulating suits with the respirator inside the suit should be worn by personnel who may be exposed to MIC vapor and liquid spills during emergency response operations.

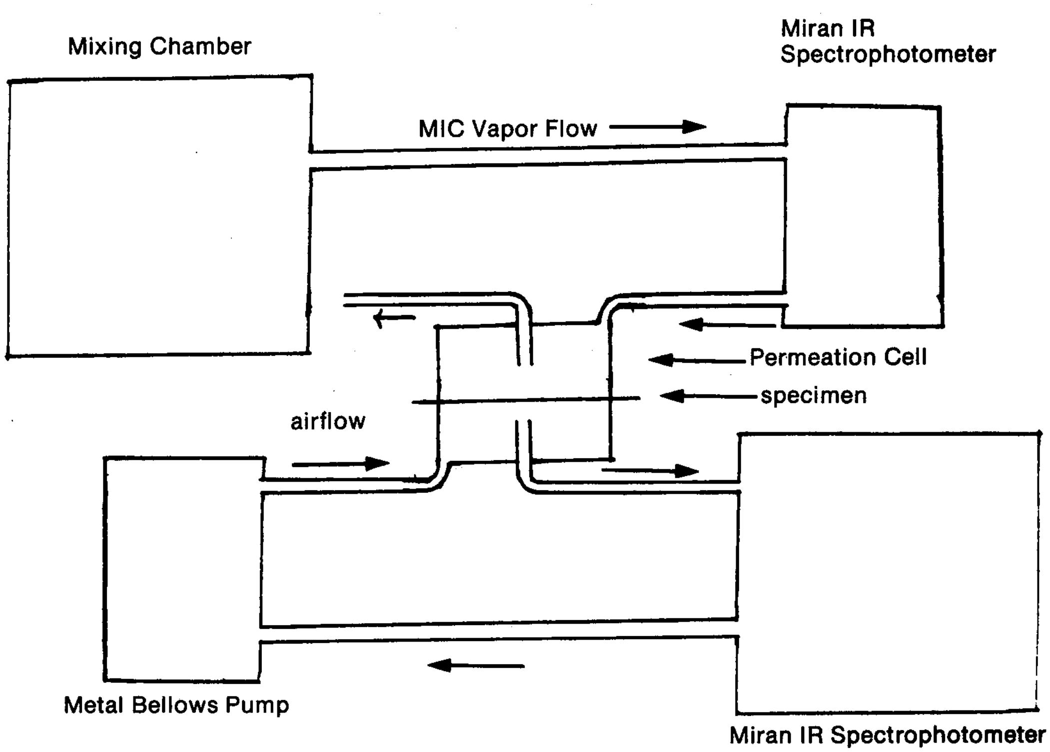

Figure 2 — Vapor MIC chemical permeation test system.

TABLE III
Permeation of Liquid and Vapor MIC Through Selected Diaphragms and Protective Clothing

Diaphragm/ NIOSH Approval Number	Construction	Liquid MIC Challenge Mean Breakthrough Time	Vapor MIC Challenge Mean MIC Conc (ppm) ± Std. Dev.	Vapor MIC Challenge Breakthrough Time (min)	Percent Relative Humidity
Globe/ TC-13F-43	Silicone elastomer 0.82 mm nominal thickness in center, 0.25 mm at edge of elastomeric material.	< 15 sec	Run 1 819 ± 22 Run 2 808 ± 38	2.5 3.0	None None
Scott/ TC-13F-40	Silicone elastomer 0.32 mm at edge, 1.12 mm in center. Segmented metallic disc laminated/glued to material. Gortex used as sealant.	< 15 sec	Run 1 820 ± 18 Run 1 948 ± 30 1047 ± 22	4 3 - MIC < 1 - MMA	None 73
MSA/ TC-13F-30	Hycar elastomer 0.475 center (disc removed), 0.310 mm at edge. Removable solid metallic disc on membrane. Solid metallic disc removed before testing.	1.5 min	Run 1 878 ± 100 Run 2 842 ± 18	23 31	None None
U.S. Divers/ TC-13F-30	Silicone elastomer 0.300 mm for elastomer in holes; 0.75 mm at edge of elastomer, large metallic disc with four 1″ holes laminated/glued to elastomeric material.	1.5 min	Run 1 820 ± 18 Run 1 1047 ± 22 948 ± 30	14 2 - MIC 4 - MMA	None 73
Chemical Protective Clothing					
Wheeler Viton	0.230 mm ± 0.004 mm	1.13 ± 0.06	Run 1 800 ± 174 Run 2 842 ± 18 Run 1 1069 ± 85 947 ± 30	>45 >45 >45 - MIC >45 - MMA	None None 73
Fyrepel polyvinyl chloride	0.359 ± 0.003 mm	0.50 ± 0.05	Run 1 894 ± 21	>45	None
Paige 6 oz. butyl	1.82 ± 0.002 mm	2.28 ± 0.10	Run 1 894 ± 21 Run 1 947 ± 38 1069 ± 85	>45 >45 - MIC >45 - MMA	None 73

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