PES REPORT

PART I. EVALUATION OF CHEMICAL PROTECTIVE CLOTHING FIELD TEST METHODS USING SELECTED GARMENT MATERIALS AGAINST METHYL ISOCYANATE

PART II. EVALUATION OF CHEMICAL PROTECTIVE CLOTHING AGAINST METHYL ISOCYANATE USING SOLUBILITY PARAMETERS

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ABSTRACT

Twenty-two different garment materials were evaluated for chemical permeation against methyl isocyanate. Only chemical permeation breakthrough times were measured. Most garment materials had a breakthrough time of under ten minutes. Solubility parameters of protective clothing and methyl isocyanate were evaluated. Use of most chemical protective clothing materials against methyl isocyanate is questionable.

DISCLAIMER

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

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INTRODUCTION

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

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

MIC's threshold limit value (TLV) 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 severely irritated. 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 mmHg of 39.1°C. The vapor pressure at 20°C is 348 mmHg. The vapor density is twice that of air[1]. MIC vapor thus will be concentrated near ground level.

(1) Methyl Isocyanate F-41443A, Union Carbide Corp., 270 Park Ave., New York, N.Y., 10017 (1976).

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

PART I. LABORATORY TESTING

EXPERIMENTAL DESIGN. H-Nu PI-101 and Century OVA 108 direct reading instruments were initially used but did not have a lower detectable limit of 1 ppm or less. Figure 1 shows the apparatus. The chemical permeation apparatus used throughout this study was a closed loop system consisting of a Miran 1A-CVF infrared direct reading instrument with a 1-inch diameter (2.54 cm) chemical permeation cell[2]. All tubing was Teflon, all connectors were Teflon or stainless steel. Air, the collection medium, was circulated by a Metal Bellows Corporation metal bellows pump at 8.0 sLpm. At this flow rate, the internal permeation cell pressure was 10 mmHg above atmospheric. Additionally, the metal bellows of the pump at this flowrate 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 slightly depressed then placed on the permeation fill tube (Figure 1). This created a slight negative pressure in the chemical reservoir which substantially reduced the severe agitation of MIC.

Before each test run the specimen thickness was measured using a dial gage. Readings were taken at five different points. The specimen was then 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) started.

(2) Available from AMK Glass Co. 610 South 3rd Avenue, Vineland, N.J., 08360

The system was run for 10 minutes. In this way, any contamination was easily seen. After 10 minutes, 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, then start the watch, place the aspirator bulb on the chemical permeation inlet tube, then start the pump.

This apparatus was evaluated initially using acetone-neoprene. The chemical permeation of acetone through neoprene demonstrates that our apparatus is comparable to the ASTM F739-81 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals[3]. In the ASTM F739-81 test method a standard 2-inch test cell is used. The mean breakthrough time for triplicate runs for our system was 12.3 $\pm$ 1.4 minutes compared to the ASTM F23 cell mean of 12.3 $\pm$ 0.4 minutes.

In a separate study, an attempt was made to obviate the induced specimen vibration by lowering the air circulation flowrate. Accordingly, a Dupont 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 $\pm$ 0.7 minutes versus 12.3 $\pm$ 0.4 minutes) demonstrates that there is insufficient airflow through the large volume of the apparatus (5.61). Therefore, the metal bellows pump was used through this study.

(3) S.P. Berardinelli et al, Chemical Protective Clothing: A Comparison with Chemical Permeation Test Cells and Direct-Reading Instruments. American Industrial Hygiene Association Journal 44(12): 886-889 (1983).

The lower limit of detection was determined by two different methods. A known amount of liquid MIC was injected into a large carboy (50 l), allowed to vaporize, and 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 value, 0.26 ppm, was used as the lower limit of detection for this study. 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 different garment materials used to fabricate total encapsulating suits were tested in triplicate unless otherwise stated against MIC. Only the breakthrough times were measured. The results appear on Table 1. The materials which exhibited the longest breakthrough time were a MSA® aluminum laminate and a Chem Fab® Teflon-Nomex laminate. However, the aluminum laminate when flexed cracked and the breakthrough time of the flexed specimens were vastly different as compared to unflexed. Cracking can be easily monitored by shining a flashlight on one site of the garment while

observing the other site. In a darkened room, light will shine through the small cracks, etc. 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 the rate of most other materials which permeate at a much more rapid rate; e.g., detector went off scale within 30 minutes of testing after breakthrough occurred. The other garment materials had a mean breakthrough time of less than ten minutes, except for MSA Chem Butyl (thirteen minutes).

CONCLUSIONS

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

There is no garment material which affords workers adequate protection for at least one hour. Of the test materials, only the MSA® aluminum laminate and Chem Fab® Teflon-Nomex laminate can be considered as a candidate material. However, the aluminum laminate 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 considering the breakthrough time and the rate of permeation after breakthrough.

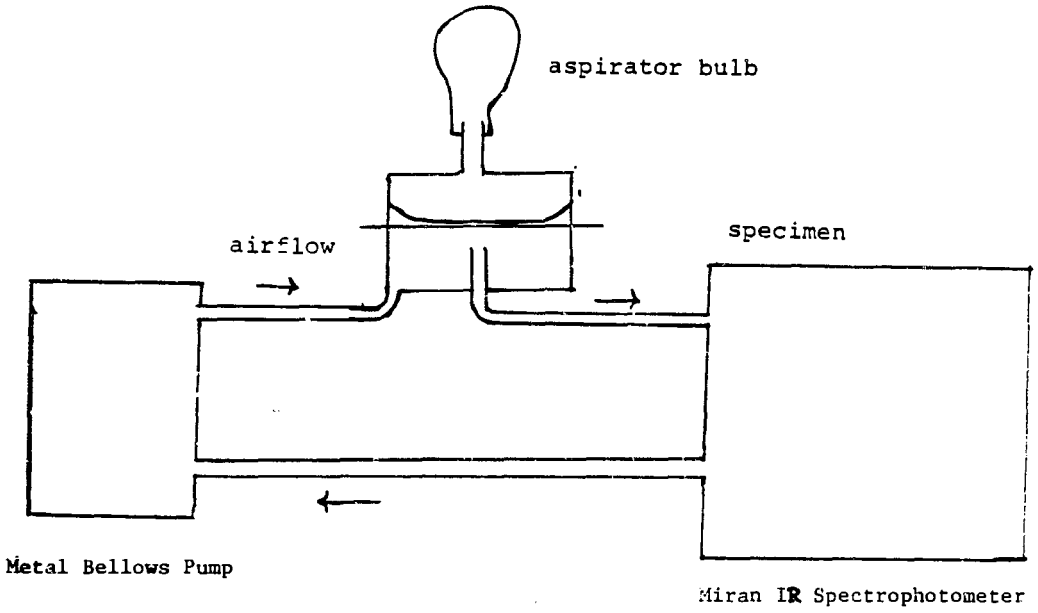
aspirator bulb
airflow
specimen
Metal Bellows Pump
Miran IR Spectrophotometer

FIGURE 1

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	0.47 ± 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 ± .002	0.45		
	(2)	0.138 ± .002	0.40	0.38 ± 0.08	
	(3)	0.134 ± .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 ± .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		

TABLE I LIQUID MIC PERMEATION THROUGH SELECTED GARMENT MATERIAL (CONT.)

Material	Run	Mean thickness (mm) ± Std. Dev.	Breakthrough time (min)	Mean breakthrough time (min) ± Std. Dev.	Comments
ILC DOVER CHLOROPEL (chlorinated polyethylene)	(1)	0.555 ± 0.002	5.50	5.95 ± 0.84	
	(2)	0.555 ± 0.004	6.50		
	(3)	0.552 ± 0.002	6.80		
	(4)	0.554 ± 0.003	5.00		
ILC DOVER URETHRANE	(1)	0.439 ± 0.009	4.30	4.42 ± 0.25	
	(2)	0.440 ± 0.009	4.25		
	(3)	0.436 ± 0.011	4.70		
FYREPEL VITON	(1)	0.227 ± 0.003	0.41	0.70 ± 0.43	
	(2)	0.226 ± 0.005	0.50		
	(3)	0.230 ± 0.002	1.20		
WHEELER VITON	(1)	0.230 ± 0.004	1.10	1.13 ± 0.06	
	(2)	0.230 ± 0.004	1.20		
	(3)	0.230 ± .001	1.10		
FYREPEL BUTYL	(1)	0.358 ± 0.002	7.10	6.77 ± 0.35	
	(2)	0.357 ± 0.002	6.40		
	(3)	0.359 ± 0.001	6.80		
PAIGE BUTYL 13 oz.	(1)	0.376 ± 0.004	8.0	8.0 ± 0.00	
	(2)	0.368 ± 0.007	8.0		
PAIGE BUTYL 6 oz.	(1)	0.180 ± 0.002	2.20	2.28 ± 0.10	
	(2)	0.182 ± 0.002	2.40		
	(3)	0.182 ± 0.002	2.25		

TABLE I LIQUID MIC PERMEATION THROUGH SELECTED GARMENT MATERIAL (CONT.)

Material	Run	Mean thickness (mm.) ± Std. Dev.	Breakthrough time (min.)	Mean breakthrough time (min.) ± Std. Dev.	Comments
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• ALUMINIUM LAMINATE	(1)	0.148 ± 0.001	>240		unflexed
	(2)	0.158 ± 0.001	>270		"
	(3)	0.149 ± 0.002	6.00		flexed
	(4)	0.150 ± 0.001	8.00		"
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		
CHEM FAB• NON WOVEN NOMEX• on TEFLON•	(1)	0.519 ± 0.006	30.0		unflexed
	(2)	0.519 ± 0.009	30.0	29.3 ± 1.1	"
	(3)	0.511 ± 0.014	28.0		"
	(4)	0.516 ± 0.007	28.0	28	flexed

TABLE I LIQUID MIC PERMEATION THROUGH SELECTED GARMENT MATERIAL (CONT.)

Material	Run	Mean thickness (mm.) ± Std. Dev.	Breakthrough time (min.)	Mean breakthrough time (min.) ± Std. Dev.	Comments
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		

Part II. Solubility Parameters

INTRODUCTION

The purpose of this study is to calculate the solubility parameters of methyl isocyanate (MIC) and methyl amine (MA) and to relate these numbers to current knowledge of systematically selecting protective clothing.

Solubility parameters are evaluated in the hopes of gleening additional information on the interaction of methyl isocyanate (MIC) and chemical protective clothing materials. Much of this report was prepared by Dr. Charles Hansen, a noted researcher in this area.

Three dimensional solubility parameters enables characterization of chemical protective clothing by solvents which dissolve (swell) them. Dr. Hansen has determined three categories of solutions interaction: Insoluable-little to no weight or volume change of protective clothing after contact with a solvent; soluable - large weight or volume change, and partially soluable - moderate weight or volume change.

The permeation rate of various penetrants through polyvinyl chloride glove membranes has been correlated by Henriksen with three dimensional solubility parameters[1]. There is an exponential increase in the permeation rate with

(1) Henriksen, H.R., Selection of Materials for Protective Gloves. Polymer Membranes to Protect Against Contact with Epoxy Products, Translation of Report No. 8/1982. The Danish National Labour Inspection Service, Copenhagen.

a variation of a factor of 1000 in the rate. In other words a very good solvent penetrates 1000 times faster than a bad one. Henriksen's reports which also includes similar data on other membrane types has been translated into English.

These Scandinavian efforts to correlate solubility parameters with penetration of protective clothing by organic materials are based on previous Scandinavian research. A doctoral thesis from 1967 includes the background for these developments[(2)]. A summary of how solubility parameters were and are still calculated is discussed in reference 3.

In actual practice, a series of chemicals (solvents) are tested against a specific chemical protective clothing. The data is then put into a computer which does a best fit for a sphere; that is the insoluable interactions should be outside the sphere, the soluable interactions inside the sphere and the partially soluable interactions near the surface of the sphere. Since the three dimensional solubility parameters for the solvents are known, the center of the sphere can be calculated. This is the three dimensional solubility parameter for the specific chemical protective clothing tested. Also, the radius of the sphere is called the interactive distance. Solvents whose solubility parameters lie inside the sphere will dissolve that protective

(2) Hansen, C.M., Doctoral Dissertation, Danmarks tekniske Hojskole, Danish Technical Press, Copenhagen (1967).

(3) Hansen, C.M., and K. Skaarup, Dansk Kemi, 48, 81(1967).

clothing. Mathematically the distance between the center of the sphere and the solvent is less than the radius, R_A.

The penetration of membranes depends on both the solubility, S, and the diffusion coefficient, D. The usual equation for the permeation rate, P, is

$$P = DS$$

An increase in solubility leads to a proportional increase in the permeation rate for D being the same. Solubility correlates with the solubility parameter. It has been shown many places (see ref. 2-5, for example) that the diffusion coefficient varies exponentially with penetrant concentration. This is general behavior for penetrant polymer systems. The penetrant plasticizes more as its concentration increases and the mobility (diffusion coefficient) in the system increases. Thus, the solubility and hence the solubility parameter also play a role in the diffusion rate because of these effects.

The Solubility Parameter and Membrane Solubility

The most widely used solubility parameter concept today is the extension of Hildebrands concepts attributable to Hansen[2]. A recent CRC handbook by

(4) Hansen, C.M., Ind. Eng. Chem. Fundamentals, 6, No. 4, 609 (1967).

(5) Hansen, C.M., J. Appl. Polym. Sci., 26, 3311 (1981).

Barton is recommended as the most recent comprehensive treatment of the field in general[6].

Hansen divided the cohesion energy into three parts to account for the three independent energy types commonly called dispersion (London), permanent dipole-permanent dipole, and hydrogen bonding. These are the major energy types which cause interactions between organic materials.

When these energies are suitable well matched for two materials, solubility occurs. Solubility regions can be defined. In crosslinked polymeric materials this matching of energies causes swelling by penetrant. The first correlation of swelling of crosslinked polymeric with these solubility parameters was by Beerbower[7]. Beerbower later collaborated with Hansen in a general article on solubility parameters[8]. In general the better the solvent quality the greater the swelling up to a maximum.

(6) Barton, A.F.M., Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press Inc., Boca Raton, Florida, 1983.

(7) Beerbower, A. and Dickey, J.R., A.S.L.E. Transactions 12, 1 (1969).

(8) Hansen, C.M. and Beerbower, A., Encyclopedia of Chemical Technology, Suppl. Vol. 2nd Ed., p. 889-910, John Wiley and Sons Inc., New York, 1971.

A present problem of some dimension is that only a relatively few polymeric types used in protective clothing are characterized by these techniques. These are to be found in Henriksens report (reference 2 and to some extent in reference 9).

The use of group contribution methods to calculate solubility parameter relations for polymers is too imprecise to do. There are far too many parameters influencing behavior to allow relatively simple calculations having a respectable degree of reliability.

A warning is in order at this point. What is generally called polyethylene for example in this trade is in fact a polyethylene product modified for example with other monomers to improve laminating properties or other properties. Data on polyethylene as such or any other polymer as such can be misleading. One should really examine the membrane materials in question. It can be said from experience, however, that the number of solvents having

(9) Saarnak, A. and Hansen, C.M., Solubility Parameters - Characterization of Coatings, Binders, and Polymers, Report T 10-82, Scandinavian Paint and Printing Ink Research Institute (1982).

affinity for a given polymer type is not reduced by altering its structure i.e., by including co-monomers. In other words the solubility parameter regions are generally made larger by co-polymerizing, and Dr. Hansen has never seen them become smaller.

Use of Polymer Solubility Parameter Data for Protective Clothing

Recent discussions with the researchers in this area in Denmark have led to the following current view of how to use solubility parameter data for polymers in selecting protective clothing.

If the affinity of the penetrant is such that it is within the region characterizing the polymer, then this polymer is not to he selected for protective purposes unless very critical evaluation of thicknesses etc. clearly shows that it can be use. Such a high affinity must generally indicate an unsuitable combination. Thus rapid screening of unsuited combinations is possible.

On the other hand, the fact that the affinities are low enough to place the penetrant outside the solubility (specified percent swell) range does not mean the combination can be used without critical review. Water, for example penetrates polyethylene to some extent. Their solubility parameters are widely different; they have very low affinities for each other. No membrane can be considered perfect for use forever, and the break through times and permeation rates which can be tolerated will depend on the given situation. In general, however, the larger the differences between the penetrant and polymer solubility parameters, the more secure the system will be.

An important extension to this lack of affinity leading to improved barrier properties is as follows: If data are available on given penetrant/polymer combinations indicating they retard penetration to a safe level for a given purpose, then penetrants having similar molecular sizes and shapes (i.e., approximately the same diffusion coefficients[2]) which have lesser affinities for the polymer should also be satisfactory. The relative toxicological effects of the penetrants must also be considered, of course.

The solubility parameters for MIC have never been determined; therefore, the first step is to calculate them. The next section demonstrates these calculations.

Solubility Parameter Calculations

When the solubility parameters for two materials are known, one can calculate an energy difference which reflects their affinities for each other. The equation which has been used for this purpose for many years is:

$$R_A^2 = 4(\delta_{D_1} - \delta_{D_2})^2 + (\delta_{P_1} - \delta_{P_2})^2 + (\delta_{H_1} - \delta_{H_2})^2$$

where the subscripts 1 and 2 denote the materials involved, and R_A is the energy difference between them in solubility parameter space. The 4 enters as an empirical factor to allow data to be plotted as spherical regions of solubility. This allows easier computer treatment of data as well.

R_A is then compared with the reported data for the solutes or polymers which are given in the tables or experimentally determined as a characteristic radius, R. If R_A is less than R for a polymer, solubility is predicted. Dr. Hansen has recently begun reporting the value R_A/R as a relative energy difference parameter (RED number). For RED numbers of 0 there is a perfect match of energies. The solubility parameters are identical. RED number of 1.0 means a boundary solvent and higher RED numbers mean greater energy differences and lower affinities. This seems to be an easier concept for those who are not technically trained.

Calculation of the Solubility Parameters for Penetrants - General

Group contribution methods are not advisable if they can be avoided, and are not used for the compounds evaluated here. No data are available for the isocyanate groups, and since $-NH_2$ gives widely different behavior, in various molecules, this is a particularly questionable group to used in this manner. In general experimental evidence on solubilities would be helpful. Customary practice in the past has been to calculate, as is done here, the three parameters to the extent possible, and then to confirm these by evaluating whether or not solubility is found for a number previously characterized polymers. This experimental procedure is not possible in the present case either.

The dispersion parameters were calculated by the methods given in reference 10. Those results are consistent with previous experience. Comparisons are made at the same corresponding states with hydrocarbons of the same molecular volume.

An article "Some Aspects of the Three Dimensional Solubility Parameter" gives the equations used for the polar parameters[3]. This article also includes a comparison of such calculated values with values assigned based on over 10,000 experimental data print. The agreement is good. Likewise Dr. Hansen is confident that the calculations below yield results which are consistent with everything he has done with the solubility parameter over the past 20 years[11-12].

The hydrogen bonding parameter must be found by difference in the present cases. There is no alcohol group. The equation used is

$$\Delta E_H = \Delta E_{TOT} - \Delta E_D - \Delta E_P$$

The hydrogen bonding solubility parameters found are consistent with what would be expected from related compounds.

The conversion multiplying factor from the older $(cal/cm^3)^{1/2}$ units to newer SI units $(J/cm^3)^{1/2}$ is 2.045.

(10) Hansen, C.M., J. Paint Technology, 39, No. 505, 104 (1967).

(11) Hansen, C.M., J. Paint Technology, 39, No. 511, 404 (1967).

(12) Hansen, C.M. and Skaarup, K., J. Paint Technology, No. 511, 511 (1967).

Solubility Parameters for Methyl Isocyanate

$CH_3 - N = C = O$

δ_P The following data are needed for the calculations:

Molecular weight	M = 57.05
Density	ρ = 0.951
Dipole Moment	μ = 2.28 Debye
Dielectric Constant	ε = 2.175
Refractive Index	n_D = 1.3695

Molar Volume $V_M = \frac{M}{\rho} = 60$

$$\delta_P^2 = \frac{12108}{V_M^2}\left(\frac{\varepsilon-1}{2\varepsilon+n_D}\right)^2 \quad (n_D^2 + 2)\mu^2 = 12.79$$

$$\delta_P = 3.6 \quad (cal/cm^3)^{1/2} = 7.3 \quad \left(\frac{J}{cm^3}\right)^{1/2}$$

$$\Delta E_P = (3.6)^2(60) = 768 \text{ cal/mole}$$

δ_D Using Figure 1 (Ref. 10).

Reduced Temperature not available.

Assume T_R = 0.60 from similarity to other compounds.

$V_M = 60$

ΔE_D = 3500 Cal/mole (from Figure)

$\delta_D = \left(\frac{3500}{60}\right)^{1/2} = 7.6 \ (Cal/cm^3)^{1/2} = 15.6 \ (J/cm^3)^{1/2}$

δ_H A total solubility parameter is in the literature (Hoy, K., Tables of Solubility Parameters, Union Carbide Corp., Research and Development Dept. Tarrytown, N.Y., 1975).

$\delta_T = 10.60$

$\Delta E_T = (10.60)^2(60) = 6742$ Cal/mole

$\Delta E_H = \Delta E_T - \Delta E_P - \Delta E_D = 2474$ Cal/mole

$\delta_H = \left(\frac{2474}{60}\right)^{1/2} = 6.4 \ (Cal/cm^3)^{1/2} = 13.1 \ (J/cm^3)^{1/2}$

The solubility Parameters in SI units for methyl isocyanate are:

$\delta_D : \delta_P : \delta_H = 15.6 : 7.3 : 13.1$

Solubility Parameters for Methyl Amine

CH_3NH_2

δ_P In a similar manner as with Methyl Isocyanate:

$M = 44.4$

$\mu = 1.30$ Debye

$n_D = 1.3527$

ϵ_{liq} (not available) = 7 estimated from

Dimentyl Amine	= 5.26
Ammonia	= 22.4
Triethyl Amine	= 2.42
Trimethyl Amine	= 2.44

(This parameter is not too critical)

$\delta_P = 3.6\ (Cal/cm^3)^{1/2} = 7.3\ (J/cm^3)^{1/2}$

$\Delta E_P = (3.6)^2(44.4) = 575$ Cal/mole

(An equation proposed elsewhere[13] gives $\delta_P = 3.8$ which is good agreement.)

δ_D

$V_M = 44.4$
$T_C = 156.9^oC$ (Langes Handbook)
$T_R = 0.69$
From Fig 1 (ref. 10)
$\Delta E_D = 1.8$ Kcal/mole

$$\delta_D = \left(\frac{1800}{44.4}\right)^{1/2} = 6.36\ (cal/cm^3)^{1/2} = 13.0\ (J/cm^3)^{1/2}$$

δ_H

From Barton p. 147, Ref. 6

$\delta_{TOT} = 22.9$ at 25^o (SI units) = 11.2 (old units)

$\Delta E_T = (11.2)^2(44.4) = 5568$ Cal/mole

$\Delta E_H = 5568 - 575 - 1800 = 3193$ Cal/mole

$\delta_H = 3193/44.4)^{1/2} = 8.5\ (Cal/cm^3)^{1/2} = 17.3\ (J/cm^3)^{1/2}$

The solubility parameters in SI units for methyl amine are:

$\delta_D : \delta_P : \delta_H = 13.0 : 7.3 : 17.3$

Comparisons with related compounds (amines) indicate these are reasonable values.

(13) Koenhen, D.M. and Smolders, C.A., J. Appl. Poly. Sci., 19, 1163(1975). (See equ. 24a).

Relation to Skin Absorption

There exists a correlation between the swelling of psoriasis scales (Keratin) and the solubility parameter[14]. This is expressed by the numbers δ_D: δ_P: δ_H: R in SI units as 24.64: 11.94: 12.92: 19.04.

Using the equation for R_A given above, the following data are obtained with the solubility parameters calculated here:

	R_A	RED
Methyl isocyanate	18.6	0.98
Methyl Amine	24.1	1.27

The prediction is that MIC as a small, linear molecule just within the area of interaction, will penetrate (neglecting reactions!) while MA would not present a specific danger by this route unless exceptionally high toxicity indicated very low amounts are sufficient to justify concern for entry by this route.

Suitable Protective Clothing

All data are in SI units. Polyisobutylene (PIB) rubber with δ_D : δ_P : δ_H : R equal to 14.2 : 2.5 : 4.6 : 12.4 is used as a reference for hydrocarbon type membranes. The affinity to MIC is high with RED = 0.81. The affinity to MA is marginal with RED = 1.11. Hydrocarbon type membranes would not appear generally acceptable.

(14) Hansen, C.M., The Absorption of Liquids into the Skin, Report T 3-82, Scandinavian Paint and Printing Ink Research Institute (1982).

Dr. Hansen suggests looking at lower energy (lower solubility parameter) membranes, but he has no data. Silicone types generally have lower solubility parameters than hydrocarbon types, and fluorinated types are potentially still lower than these. Perhaps a look at Viton would be appropriate and one could also work in a water spray.

Comparison of Chemical Permeation Data to Solubility Parameters

According to Dr. Hansen, butyl rubber should have an approximate breakthrough time of one hour. However, in our laboratory testing, a much lower breakthrough time was observed. The elastomers in Table 1 have recorded solubility parameters. Accordingly, the energy difference, R_A, was calculated for each elastomer and MIC. The breakthrough times of many of these elastomers were experimentally obtained and were under 10 minutes as shown in Table 1. By inference, other elastomers of Table 1 with similar energy difference; i.e., R_A, should exhibit a rapid breakthrough. Neoprene, silicone, and natural rubber meet these criteria and therefore are unsuitable garment materials. Further, some of these elastomers are used in self-contained breathing apparatuses (SCBA), e.g. hoses, exhalation values, diaphragms, etc., They must be monitored carefully if worn to protect the worker against MIC. Under disaster conditions-very high concentration of MIC - elastomeric components of an SCBA may degrade.

Against monomethyl amine (MA), nitrile, butyl and Viton elastomers have a breakthrough time greater than 4 hours. Neoprene and polyvinyl chloride have a breakthrough time between 1 and 4 hours; while natural rubber and polyvinyl

alcohol are under 1 hour. By inference, silicone should have a breakthrough time between 1 and 4 hours.

Table 1. Solubility Parameters $(cal/cm^3)^{1/2}$

Elastomers (min)	δ P	δ H	δ D	R_A	MIC Mean Breakthrough Time (min)
Neoprene	1.5	1.3	9.4	6.6	ND
Nitrile	4.3	2.0	9.1	5.4	2
PVC	3.7	4.1	8.9	3.5	1
Silicone	1.8	2.2	8.0	4.6	ND
PE	0	0	8.1	7.4	1
Butyl	0.9	3.0	8.2	4.5	6
Viton	5.2	3.0	8.3	4.0	1
Nat. Rubber	1.0	3.5	9.0	4.8	ND
PIB	1.2	2.2	6.9	6.1	ND
Reagents					
Methyl amine	3.6	8.5	6.4		
MIC	3.6	6.4	7.6		

ND = Not determined

$(Cal/cm^3)^{1/2}$ is the older system to convert to SI units multiple by 2.045.

PES REPORT

Methyl Isocyanate Studies

PART III. LIQUID PERMEATION OF METHYL ISOCYANATE (MIC) THROUGH SELECTED RESPIRATOR DIAPHRAGMS

PART IV. LIQUID MIC PERMEATION THROUGH VITON® HAVING A DEAD AIR SPACE BETWEEN LAYERS

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Part III. Liquid Permeation of MIC Through Selected Respirator Diaphragms.

Introduction

Regulator diaphragms from four different closed circuits, positive pressure self-contained breathing apparatuses were tested for chemical permeation against liquid methyl isocyanate.

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

MIC used throughout this study was from Aldrich Chemical Company, lot no. 3317AL.

Experimental

The chemical permeation system has been discussed in detail in Part I. Some difficulty was encountered sealing the diaphragms into the permeation test cell due to their construction. Gortex expanded PTFE was used to affect a good seal in some instances. However, MIC does permeate through the compressed Gortex when used as a sealant. But, the permeation apparatus is a closed loop, positive pressure system so that this extraneous permeation is not a problem.

Table 1 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 two minutes. Also, Stannett and Yashuda[1] have demonstrated that saturated vapor yields similar permeation results to the liquid. Under extreme disaster conditions, saturated vapor (~ 500,000 ppm @ 20°C) may be encountered by emergency response personnel and the liquid MIC - diaphragm data of this report is directly applicable.

(1) V. Stannett and H. Yashuda, Liquid Versus Vapor Permeation through Polymer Films, J. Poly Sci, 289-293, (1963)

TABLE 1

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. Gortex used as sealant.	< 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 edge of elastomer, large metallic disc with 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. Tested specimen cut such that elastomeric material in metallic hole was evaluated.

Part IV. Liquid MIC Permeation Through Viton® Having a Dead Air Space Between Layers.

Introduction

Our Division Director suggested that a quick study be conducted using protective clothing with a dead air space between layers. This is an excellent idea based on sound theory since permeation is highly diffusion dependent. The uniqueness is the dead air space. From permeation theory, there will be one set of boundary conditions for permeation of the liquid through the material into the dead air space. The maximum concentration of MIC in the dead air space would be the steady state concentration. Hence another set of boundary conditions exist for the permeation of vapor MIC in the dead space through the second layer of material. Qualitatively, a much longer breakthrough time is anticipated than if two layers of material were sandwiched together without a dead space.

Experimental

The chemical permeation test apparatus is discussed in Part I of this study. Wheeler Viton® was selected for study based on its short breakthrough time; i.e., 0.230 mm specimen mean breakthrough time is 1.1 minutes. In this experiment two 0.230 mm specimens were separated by a 2.62 mm gap between them (thickness of 2 Teflon® washers).

Two experiments were conducted using Viton® with a dead air space between layers. Breakthrough times were 9.1 minutes and 9.0 minutes. This can be compared to 1.1 minutes for a 0.230 mm single layer specimen which when normalized to correct for thickness yields 4.4 minutes for a 2 x 0.230 mm thick specimen (0.460 mm).

Conclusion

Use of a dead air space between layers is a better alternative than increasing material thickness. However, chemical protective clothing is not fabricated with dead air spaces. Once the clothing is contaminated, decontamination would be practically impossible.

PES REPORT

Methyl Isocyanate Studies

PART V. VAPOR PERMEATION OF METHYL ISOCYANATE (MIC) THROUGH SELECTED RESPIRATOR DIAPHRAGMS AND CHEMICAL PROTECTIVE CLOTHING

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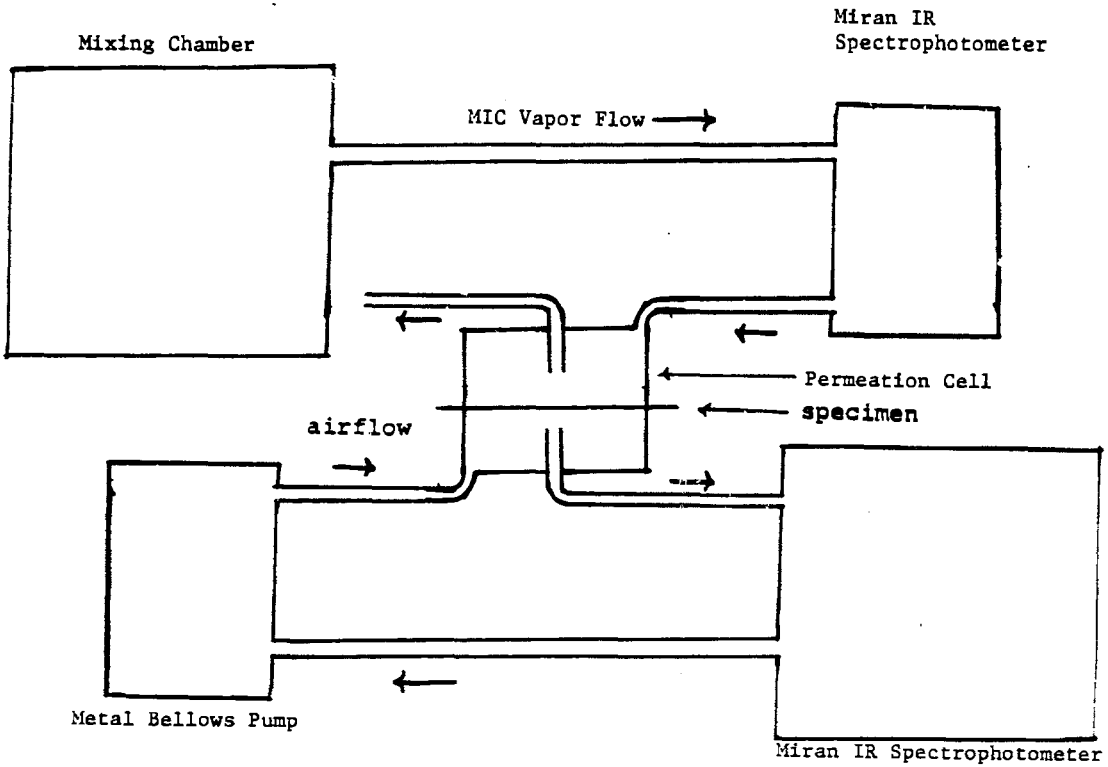
Mixing Chamber
Miran IR
Spectrophotometer
MIC Vapor Flow
Permeation Cell
specimen
airflow
Metal Bellows Pump
Miran IR Spectrophotometer

FIGURE 1

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

Introduction

Diaphragms from four different closed circuits, positive pressure self-contained breathing apparatuses of Part III and three chemical protective clothing materials of Part I were tested for chemical permeation against vapor methyl isocyanate.

MIC vapor were used as challenge agents in dry air and with 73% relative humidity.

MIC used throughout this study was from Aldrich Chemical Company, lot no. 3317AL.

Experimental

The chemical permeation system has been discussed in detail in Part I except two collection sides were used as shown in Figure 2. About 800 ppm MIC vapor was continuously passed through one side using 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 quantitately injection MIC liquid into a 95 sLpm air stream. Adequate mixing was insured since the MIC-air mixture fed into a mixing chamber (8 X 12 X 16 inches). A Miller-Nelson Research Inc. control box was used to condition the air before

mixing with MIC. At 73% relative humidity, MIC can decompose into monomethyl amine, MMA. Hence, both MIC and MMA must be monitored.

Table 1 contains the permeation test results and diaphragm information. 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-concentration for MIC/MMA are 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 minutes 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, breakthrough times appear shorter than 800 ppm MIC (dry air) breakthrough times. In the event of

an MIC vapor exposure the respirator diaphragm may be the weakest link; 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.

TABLE 1

Diaphragm/ NIOSH Approval NUMBER	Construction	Liquid MIC Mean Breakthrough Time	Vapor MIC Mean MIC Conc (ppm)	Vapor MIC Breakthrough time (min.)	Steady State Permeation Rate ppm/min·Cm^2	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	0.062 0.081	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	0.024 0.027 0.030	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	.078 ND	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	.012 .094 .034	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	---ND ---ND ND ND	None None 73
Fyrepel Polyvinyl Chloride	0.359 ± 0.003 mm	0.50 ± 0.05	Run 1 894 ± 21	>45	ND	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	ND ND ND	None 73

ND = Not determined.