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A Portable Chemical Protective Clothing Test Method: Application at a Chemical Plant*

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The National Institute for Occupational Safety and Health (NIOSH), in cooperation with Monsanto Chemical Company, conducted an on-site evaluation of chemical protective clothing at Monsanto's Nitro, West Virginia plant. The Monsanto plant manufactures additives for the rubber industry including antioxidants, pre-vulcanization inhibitors, accelerators, etc. This survey evaluated six raw materials that have a potential for skin absorption: aniline, cyclohexylamine, diisopropylamine, tertiary butylamine, morpholine and carbon disulfide. Five generic glove materials were tested against these chemicals: nitrile, neoprene, polyvinylchloride, natural latex and natural rubber. The NIOSH chemical permeation portable test system was used to generate breakthrough time data. The results were compared to permeation data reported in the literature that were obtained by using the ASTM F739-85 test method. The test data demonstrated that aniline has too low a vapor pressure for reliable analysis on the portable direct reading detectors used. The chemical permeation test system, however, provided comparable, reliable permeation data for the other tested chemicals. Monsanto has used this data to better select chemical protective clothing for its intended use.

Introduction

The proper selection of chemical protective clothing (CPC) can be difficult without specific information relative to the chemical(s) involved and the effects they will have on the CPC. Chemical permeation data are currently available for a number of chemicals and materials but often is limited to the more common chemicals and is not available for mixtures of chemicals.⁽¹⁾ The material safety data sheets for specific chemicals provide a great deal of information about the chemical, but fall short in specifying a type of glove or other CPC.⁽²⁾

Even when the specific CPC material is known for a chemical, there are several variables that may have an effect on its permeation rate. For instance, the thickness of the material may vary between manufacturers or even within the same manufacturer. This has been shown to be related directly to the permeation rate and is described by Fick's Law.⁽³⁾ Also chemicals used by a laboratory to test permeation rates are usually of a reagent grade and therefore do not contain the level of impurities found in industrial grade chemicals that may have an impact on the permeation rate.

This study's purpose was to evaluate the NIOSH Chemical Protective Clothing Portable Test Method at a chemical plant. This method differs from the ASTM F739-85 method in that it utilizes portable industrial hygiene monitoring equipment to detect chemical permeation rather than laboratory equipment.⁽⁴⁾ The NIOSH method is easy to transport, can be set up rapidly and can be performed in a limited space making it suitable for field use. A complete report on the chemical permeation field test method is available from NTIS.⁽⁵⁾

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

The testing was conducted at a Monsanto Chemical Company plant in Nitro, W. Va. This plant employs approximately 530 employees and predominantly makes intermediates for the rubber industry, such as accelerators, antioxidants and pre-vulcanization inhibitors. A wide range of organic and inorganic chemicals are used at this plant, including acids, bases, alcohols, amines, aliphatics, aromatics, chlorinated hydrocarbons and halogens. Most of the finished products are in a solid form, but interim process stages may involve liquids such as slurry solutions.

Gloves used in the plant before this survey were predominantly polyvinylchloride (PVC) floc-lined chemical gloves. Because of enclosed systems in the plant, liquid chemical exposure is rare and of short duration (*i.e.*, splash or contact with a wet surface not immersion of gloved hand(s) into chemicals with repeated or prolonged exposure).

Gloves used in the laboratory before this survey were usually thin surgical latex gloves. These were used since a high degree of manual dexterity is required.

Methodology

The glove/chemical combinations evaluated are summarized in Table I. The chemicals used were technical grade actually used in the plant. The gloves tested were laboratory and plant gloves that were available to the employee for his/her protection. During the course of the study, it became apparent that other glove materials would provide more protection than PVC. Therefore, several alternative glove materials were evaluated.

Prior to chemical permeation testing, a 2-in. (5.08 cm) circular specimen was cut from the palms of the gloves. Each specimen was measured for thickness at the 3, 6, 9 and 12 o'clock position and in the center. The mean then was com-

TABLE I
Glove/Chemical Combinations Tested

Glove	Aniline (AN)	Tertiary Butylamine (TBA)	Diisopropylamine (DIPA)	Cyclohexylamine (CHA)	Carbon Disulfide (CS ₂)	Morpholine (MORP)
JOMAC PVC (plant glove)	X	X	X	X	X	X
North NBr (laboratory glove)		X	X			X
Conform natural latex (laboratory glove)		X	X			X
Midland disposable PVC (laboratory glove)			X			
Edmont No. 29-870 (neoprene) (possible alternative)			X			X
Edmont natural rubber (possible alternative)						X

puted. The specimen was mounted in the cell for chemical permeation testing. Chemical permeation testing was conducted using a modified ASTM F739-85 standard test method (Figure 1). The cell used was not the ASTM standard cell, but a smaller, less expensive cell available from AMK Glass Co. (Vineland, N.J.). The two cells, however, yield comparable results.⁽⁶⁾ A DuPont P-4000 pump at 2.5 Lpm was used to circulate air, the collection medium, through the collection side of the cell. Only breakthrough times were measured. Three analytic detectors were evaluated as follows: 1) a Foxboro OVA 108 total hydrocarbon flame ionization detector; 2) an H-Nu Model PI 101 photo-ionization detector; and 3) a Photovac Model 10A10 portable gas chromatograph with a photo-ionization detector.

The OVA 108 and H-Nu operated according to expectations. The Photovac was only partially functional since it was discovered that the unit had leakage in one of the fittings and that most of its air supply was exhausted early in this study.

Results

The challenge chemicals are listed in Table II with their respective vapor pressures and Threshold Limit Values (TLVs®).

The test results are shown in Table III. Aniline (AN) has a low vapor pressure (0.6-mm Hg) and the JOMAC PVC glove has a nap jersey lining that can soak up the permeated

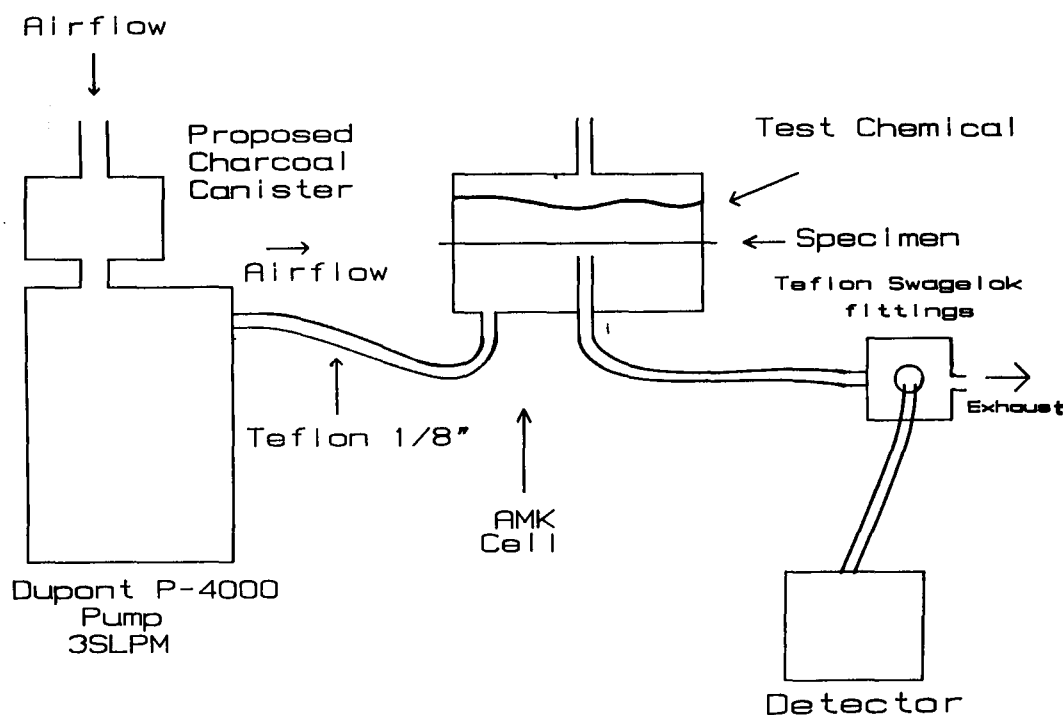


Figure 1 — Chemical permeation field test system.

TABLE II
Vapor Pressure and 1984-85 ACGIH TWA/STEL® Values for
Challenge Chemicals

Chemical	Vapor Pressure (mm Hg)	TWA (ppm)	STEL (ppm)	Comments
Aniline CAS no. 62-53-3	0.6 @ 20C	2	5	ACGIH skin notation
Morpholine CAS no. 110-91-8	7	20	30	ACGIH skin notation
Cyclohexylamine CAS no. 108-91-8	10.4	10	---	ACGIH skin notation
Diisopropylamine CAS no. 108-18-9	60	5	---	ACGIH skin notation
Tertiary butylamine ^A Butylamine CAS no. 009-73-9	400	5 ceiling limit	---	ACGIH skin notation
Carbon disulfide CAS no. 75-15-0	296	10	---	ACGIH skin notation

^AThe ACGIH booklet does not list tertiary butylamine. This CAS no. is for n-butylamine and not its isomer tertiary butylamine that is used in the plant. N-butyl may be an acceptable surrogate.

chemical. Because of factors, the results for aniline are suspect. From the literature, PVC gloves when evaluated vs. aniline yield a breakthrough time between 3 to 180 min depending on the manufacturer.⁽⁷⁾ The field chemical permeation test method is not able to measure permeation of low vapor pressure liquids.

Tertiary butylamine (TBA) breakthrough time for all detectors against the JOMAC glove was about 20 min. Diisopropylamine (DIPA) breakthrough times were 17 and 19 min with the OVA having the longer breakthrough time of 19 min. Cyclohexylamine (CHA) and morpholine (MORP) breakthrough times were about 40 min for the H-Nu and 50 min for the OVA.

Norton NBR gloves occasionally may be worn by laboratory personnel. This glove material has a 2-hr breakthrough time for tertiary butylamine (TBA), greater than 3.5 hr for diisopropylamine (DIPA), and 41 min for morpholine (MORP). These amines, however, did cause chemical degradation. After exposure, the specimens were mottled, quite stretchy and tore easily when compared to unexposed specimens. Conform natural latex gloves that resemble surgical latex gloves are used on occasion by laboratory personnel. Tertiary butylamine, diisopropylamine and morpholine breakthrough times were all 3 min or less. Another laboratory glove, Midland disposable PVC, was evaluated against only tertiary butylamine, the breakthrough time was 1 min. Natural rubber was tested only against morpholine and the experimentally observed breakthrough times were widely different. Neoprene was tested only against morpholine and tertiary butylamine. Morpholine breakthrough time was 35 min; TBA breakthrough time was greater than 30 min.

Discussion

The H-Nu, OVA and Photovac (once the air leakage problems was resolved) all performed as expected. AN has too

low a vapor pressure for reliable analysis on the detectors used in this study. For the other amines, the H-Nu, Photovac and OVA have different lower detection limits. The detection limits (ppm) appear in Table IV.

The difference between the lower detection limit of the detectors for the amines account for the observed breakthrough time for the JOMAC glove against morpholine and cyclohexylamine. The H-Nu is more sensitive as demonstrated by the early breakthrough time when compared to the OVA sensitivity and breakthrough time. Norton NBR according to the manufacturer literature has a morpholine breakthrough time for their LA142G glove of 48 min.⁽⁸⁾ This compares well with 41 min obtained in this investigation. Also, according to the Edmont chemical resistance guide. (Edmont Natural Rubber Glove, 36-124) has a 30-min breakthrough time against morpholine.⁽⁹⁾ The authors' test results were 51 min and 31 min. The variation in the authors' observed breakthrough times might be due to the variation in these glove materials (*e.g.*, thickness, batch-to-batch, *etc.*).

A system using a photo-ionization or flame ionization detector provides comparable and reliable permeation data for liquids that have a vapor pressure above approximately 10 mm Hg. About 10-mm Hg vapor pressure was selected based on laboratory and field permeation testing.⁽⁵⁾ Desorption of the permeated chemical into the airstream may be a problem much below 10-mm Hg vapor pressure. Also, a floc-lined glove may aggravate this situation further.

Follow-up Activities Since NIOSH Initial Testing

Since NIOSH testing, much activity has occurred at the Nitro Plant to expand glove testing and improve the selection of gloves. These activities are summarized below:

TABLE III
Chemical Permeation Field Test Method Results

Glove	Mean Thickness + Std. Dev. (mm)	Chemical	Breakthrough Time	Detector	Chemical Degradation
JOMAC PVC	0.285 ± 0.021	AN	> 60 min	H-Nu/OVA	V-slight hardening
JOMAC PVC	0.306 ± 0.026	AN	> 60 min	H-Nu/OVA	V-slight hardening
JOMAC PVC	0.358 ± 0.023	AN	> 16 hr	H-Nu	V-slight hardening
JOMAC PVC	0.356 ± 0.023	AN	> 16 hr	H-Nu	V-slight hardening
JOMAC PVC	0.372 ± 0.021	TBA	22 min	H-Nu/OVA	V-slight hardening
JOMAC PVC	0.328 ± 0.012	TBA	20 min	H-Nu	V-slight hardening
JOMAC PVC	0.350 ± 0.050	CS2	2 min	H-Nu/OVA	Slight
JOMAC PVC	0.294 ± 0.027	CS2	1.4 min	H-Nu	Slight
JOMAC PVC	0.352 ± 0.004	DIPA	17 min 19 min	H-Nu OVA	Slight
JOMAC PVC	0.323 ± 0.046	DIPA	17.5 min	H-Nu	Slight
JOMAC PVC	0.337 ± 0.035	CHA	41 min 50 min	H-Nu OVA	None
JOMAC PVC	0.313 ± 0.018	CHA	43 min	H-Nu	None
JOMAC PVC	0.366 ± 0.014	MORP	40 min 50 min	H-Nu OVA	V-slight hardening
JOMAC PVC	0.355 ± 0.024	MORP	42 min	H-Nu	V-slight hardening
Norton NBR	0.394 ± 0.004	TBA	> 60 min	H-Nu	Swells, stretchy
Norton NBR	0.383 ± 0.008	TBA	2 hr	H-Nu/OVA/10A10	Swells, stretchy
Norton NBR	0.361 ± 0.006	DIPA	> 60 min	H-Nu	Swells, stretchy
Norton NBR	0.347 ± 0.004	DIPA	> 3.5 hr	H-Nu/OVA/10A10	Swells, stretchy
Norton NBR	0.366 ± 0.003	MORP	41 min	H-Nu/OVA/10A10	Swells, stretchy
Norton NBR	0.380 ± 0.003	MORP	41 min	H-Nu	Swells, stretchy
Edmont Nat. Rub.	0.517 ± 0.006	MORP	51 min	H-Nu/OVA/10A10	Slow permeation rate
Edmont Nat. Rub.	0.507 ± 0.007	MORP	31 min	H-Nu	Slow permeation rate
Conform Nat. Lat.	0.142 ± 0.009	TBA	1.3 min	H-Nu	Rapid permeation rate
Conform Nat. Lat.	0.132 ± 0.008	TBA	1 min	H-Nu/OVA/10A10	Rapid permeation rate
Conform Nat. Lat.	0.126 ± 0.008	DIPA	0.2 min	H-Nu	Rapid permeation rate
Conform Nat. Lat.	0.150 ± 0.009	DIPA	0.2 min	H-Nu/OVA/10A10	Rapid permeation rate
Conform Nat. Lat.	0.141 ± 0.006	MORP	2 min	H-Nu/OVA/10A10	Rapid permeation rate
Conform Nat. Lat.	0.145 ± 0.006	MORP	2 min	H-Nu/OVA/10A10	Rapid permeation rate
Edmont neoprene	0.472 ± 0.018	MORP	35 min	H-Nu	Rapid permeation rate
Edmont neoprene	0.450 ± 0.012	TBA	> 30 min	H-Nu	Rapid permeation rate
Midland Dispos. PVC	0.126 ± 0.005	TBA	1 min	H-Nu	Rapid permeation rate

- 1) Survey of the plant glove users to select brands, sizes, linings, etc. and glove manufacturers for costs, customers services, etc.
- 2) Review of the literature to screen most likely CPC material candidates.
- 3) Expand the NIOSH test method to include 36 plant chemicals and 3 types of CPC materials: PVC (current glove material), neoprene, and nitrile.
- 4) The information was tabulated and provided to employees to explain proper glove selection.
- 5) New gloves (neoprene and nitrile) were ordered and stocked in the storeroom. Storeroom personnel were trained to question employees about what chemicals they will need gloves for. They then look up the chemical and respective CPC to select the proper type. Different sizes are available to maximize comfort and dexterity.
- 6) A follow-up audit will be performed to assure improvements are ongoing.

Conclusions

In the CPC selection process, laboratory data often are used to recommend a type of CPC against a given chemical. In many instances, no data are available. Since permeation cannot be accurately predicted as yet and currently available data probably do not reflect user conditions, NIOSH has undertaken the development of portable test methods.⁽⁵⁾ A portable test method to determine chemical permeation (*i.e.*, breakthrough time) demonstrates the utility of this method

TABLE IV
Detection Limits (ppm)

Detector	Chemical					
	AN	MORP	CHA	DIPA	TBA	CS2
OVA	0.6	>2	1.2	0.6	<0.3	<0.3
Photovac	0.4	0.7	0.3	0.3	<0.3	<0.3
H-Nu	0.4	0.7	0.3	0.1	<0.3	<0.3

in an industrial setting. This permits rapid evaluation of candidate materials to select expeditiously the most appropriate one. The portable test method under the stated limitation yields similar results to the ASTM F739-85 chemical permeation test method, these methods complement one another. The portable test method gives preliminary data; while the more versatile F739-85 test method is used to confirm the preliminary results.

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