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Final Report
for Allied-Signal Aerospace Company
Kansas City Division
on
Protective Glove Permeation Analysis
ICO Q428285

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MASTER

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(January 1989)	

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Executive Summary

We conducted 25 separate glove fabric permeation studies during this project. The permeations were carried out in the small (1 inch) glass ASTM cell using the LLNL modification of the ASTM F739-85 procedure (the inside surface of the glove is rinsed at regular intervals with one mL of an appropriate solvent and each rinse volume is analyzed for the breakthrough analyte). One other permeation study was carried out with a large (two inch) modified ASTM cell for comparison with the small cell results. We also compared the LLNL procedure from both large and small cells with the standard ASTM test procedure which uses a liquid solution on the breakthrough side of the fabric (the liquid is then sampled on a periodic basis). In all comparisons we observed a close correlation in breakthrough times between the two procedures and the two cell sizes. These data were reported in the first status report to Fred Larsen at Allied-Signal Aerospace, Kansas City Division (see attachment).

In the course of this study, we tested ten different glove materials. These included neoprene (original ASTM round-robin sheet stock, 16 mil thickness), Edmont Sol-Vex (nitrile), Pioneer nitrile, Pioneer Pylox (polyvinyl chloride), North Viton (trademark for fluoroelastomers), North SilverShield (Norfoil, trademark for a flexible metallized laminate), Safety 4 4H (patented plastic laminate), and QRP PolyTuff (polyurethane) 20G-2000 (5 mil), 23G-2300 (1.5 mil), and 25G-2500 (1.5 mil). Three of the glove materials, Viton and Silver Shield (North), and 4H (Safety 4), did not allow any permeation measurable by our system to either 1,2-dichloroethane or 3% diphenylmercury (in 1,2-dichloroethane) for a period greater than six hours. A fourth material, QRP Poly Tuff 20G-2000, did not allow any measurable penetration of Asilamine (an aromatic diamine) for a time period of greater than 4 hours. Breakthrough times and curves were obtained for all other tested materials.

Eleven different chemicals were used to challenge the glove materials. These included acetone, Asilamine (an aromatic diamine), 1,2-dichloroethane, dichloromethane, isopropyl alcohol, a mixture of 3% diphenylmercury in 1,2-dichloroethane (w/w), phenol, and Iso Verre Stripper, 4,4'-methylenedianiline (MDA), 1,3-phenylenediamine (MPDA), and Shell Epon (R) curing agent Z (a mixture of MDA and MPDA). The aromatic amines in particular are low vapor pressure materials and are water insoluble. As such, they do not lend themselves readily to the standard ASTM permeation testing procedure. The LLNL modified procedure was originally developed for testing compounds with these properties.

In our work with the modified method, we had not previously observed an effect on permeability or structural integrity of glove fabric with an aliphatic hydrocarbon rinse solution (usually isooctane, occasionally pentane or hexane). Because of the solvent strength of methanol (which was the mildest solvent we could find that dissolved the aromatic diamine compounds) we conducted a blank analysis of selected glove fabrics with methanol. To do this, we applied methanol in the standard rinse procedure on the fabric surface for a period of sixty minutes (eleven one mL rinse volumes at the designated time intervals) prior to testing the same fabric with Shell Z. We observed a decreased breakthrough time (increased permeation) on the prewashed fabric and conclude that our results on the Shell Z permeation are conservative due to the increase in permeability caused by the wash solution.

Introduction

The Safety Science Group (Hazards Control Department, Special Projects Division, LLNL) was asked by Fred Larsen of Allied-Signal to carry out permeation studies on fabrics and chemicals of interest to the Kansas City Division (KCD). The studies were intended to contribute to the ongoing health and safety activities of KCD and provide protective clothing information not currently available in the literature. Protective clothing fabrics and challenge chemicals were chosen by Allied personnel for addition to the testing schedule as the work progressed. Methods were to be developed as necessary to carry out the work and all work was to be related to some common format or recognized testing protocol.

We compared our results to the standard ASTM permeation protocol (ASTM F739-85, Resistance of Protective Clothing Materials to Permeation by Liquids and Gases). Because the chemicals chosen by Allied as challenge liquids were high viscosity, low vapor pressure and non-water soluble, LLNL requested that an effort be devoted to further develop a modification of the ASTM protocol (the modification was already used in several previous studies of interest to KCD). Allied concurred with this request, and the published ASTM procedure was compared to the LLNL modified version using standard ASTM neoprene sheet stock. These data were provided in the previous progress report and are included as an appendix to this document. This work was conducted under an initial Integrated Contract Order, ICO Q428056, and the follow on Order, ICO Q428285.

Test Results of QRP PolyTuff Glove Material

Three products from QRP, Inc. were tested in the final part of this permeation study. These were the 20G-2000 (5 mil) glove, the 23G-2300 (1.5 mil), and the 25G-2500 (1.5 mil). Results from testing of these products were not available for the previous reports. Each glove was challenged separately with the aromatic diamines MDA and MPDA. The two thinner gloves, 23G and 25G, allowed permeation of either compound within three minutes. Given the response time of the rinse method (i.e., not real time, but data points are taken only when a rinse is made), permeation was almost immediate.

The thicker 20G glove did not allow breakthrough of MPDA until 27.5 minutes and MDA until 50 minutes (the average of two runs in each case). From a protection standpoint alone against these two compounds (or the Shell product Curing Agent Z which contains them both) the 20G product provides greater protection against exposure to Shell Z components. The increased protection in this case is no doubt due to the thickness of the fabric. We tested the 20G glove against Asilamine (another aromatic diamine product), and did not observe any penetration for a period longer than four hours. Solvent tests of the 20G glove showed 20 minutes until breakthrough of isopropyl alcohol and 3.5 minutes until breakthrough of acetone. A summary of these results is shown in the table in Appendix A and by graphic analysis in Figures 5 and 6 respectively.

The Effect of the Wash Solvent on QRP Glove Testing

There is always a question of what effect the wash solvent will have on the integrity of the glove fabric being tested. In our work in Special Projects, we have always used the simplest hydrocarbon molecule with the highest vapor pressure that would act as a good solvent for the chemical being studied. Solvents that have been successfully used before are pentane, hexane, and isooctane (2,2,4-trimethylpentane). We have observed these aliphatic compounds to evaporate quickly from the surface of the material and to have little or no degradation effect on the structural integrity or permeability. During our study of Shell Z (and its components MDA and MPDA) we could not use the previous wash compounds because of their poor solvent properties for the challenge chemicals of interest. A systematic evaluation showed that methanol is a good solvent for Shell Z.

To evaluate the effect of methanol on the glove fabric, we carried out a complete wash cycle of a fabric sample. This included a preliminary rinse and then timed washes of the surface exactly as if there were test compounds on the challenge side. After a complete wash cycle had been conducted, MPDA and MDA were added as single components in separate experiments and a breakthrough profile was determined. These results are provided in graphical form for comparison with an unwashed Polytuff breakthrough study in Figures 7-12. It was shown repeatedly that with either MDA or MPDA the breakthrough was accelerated due to the effect of the methanol on the PolyTuff material. The magnitude of acceleration was approximately six minutes for MPDA and fifteen minutes for MDA. Since we cannot completely resolve the effect on the breakthrough measured with unwashed material, we can only say that breakthrough time by these Shell Z compounds in the absence of methanol would be longer than that observed when methanol is used as the wash fluid.

Test Results of Magid Polyethylene Gloves

We also tested the Magid polyethylene gloves (# MR 100) supplied by Fred Larsen of Allied-Signal. These gloves were a thin clear translucent material supplied in sheet form and peeled from a protective backing material before testing. All testing was done with the LLNL modified ASTM procedure using a one inch diameter cell. The fabric samples taken from the gloves had an average thickness of 0.5 mil (the average of multiple measurements on multiple samples). The material was first tested separately against each of the two organic components of the Iso Verre Stripper, phenol and dichloromethane, and then against the product itself. We observed phenol to break through within two minutes and dichloromethane within one minute. When we used the Iso Verre product we observed both phenol and dichloromethane to break through in one minute. These permeation results are shown in Figures 1-4 and in the table in Appendix A. Penetration is rapid through this material, either with single components or as a mixture. Furthermore, since the two major organic components penetrated so quickly, we did not pursue testing for penetration of the other components of Iso Verre (formic acid and hydrofluoric acid). This glove is not an acceptable choice for hand protection from the product IsoVerre.

Analytical Chemistry

A summary of the gas chromatography conditions used to analyze all solvents discussed in this project was provided in a previous report (11/30/88). A copy of that document is attached to this report. To analyze MDA, MPDA, Shell Z (which contains the two aromatic amines MDA and MPDA), and the aromatic diamine in Asilamine we used high performance liquid chromatography (HPLC). That work was done with a Hewlett-Packard 1084B HPLC with a variable wavelength detector. The analytical wavelength was 254 nm and the reference wavelength was 430 nm. We used a 5cm by 4.6mm LC-8 column from SUPELCO with a 5 um particle diameter. The isocratic mobile phase was 50/50 water/acetonitrile at a flow of 2 mL/min and the injection volume was 25 uL. With these conditions we observed a detection limit of <0.5 ppm for each of the aromatic amines.

Conclusion

In this project, we were able to demonstrate a close similarity in performance between the standard ASTM fabric testing procedure and the LLNL modification of the ASTM F739 method. This modification is simple and easy to use and particularly useful when non-water soluble materials are tested or when the test fluid has a very low vapor pressure. The materials that were requested for testing by Allied-Signal were in this category on both counts. This project thus allowed development of an important extension to current methods of testing glove fabrics.

Several of the glove products that we evaluated did not allow penetration of the challenge materials during extended periods of testing. These results are summarized in the table in Appendix C. North SilverShield and Safety-4 4H were never observed to allow penetration to any of the challenge materials. The Safety-4 product had a much better tactile sensation for working with hand tools or grasping items in the laboratory than the SilverShield glove. North Viton gloves did not allow penetration to 1,2-dichloroethane alone or with 3% (w/w) diphenylmercury for a period greater than six hours. The QRP 20G-2000 gloves did not allow penetration of Asilamane for a sixty minute period. This information can be used by the health and safety professional to select the correct glove for employee protection at KCD as well as other DOE facilities in the weapons complex.

Glove Product Suppliers

Edmont
1300 Walnut Street
Coshocton, OH 43812-6000
614-622-4311

North Hand Protection
P.O. Box 70729
Charleston, SC
803-554-0660

Pioneer Industrial Products
500 Skokie Blvd., Suite 222
Northbrook, IL 60062

QRP, Inc.
P.O. Box 1814
Santa Cruz, CA 94061
408-425-1667

Safety 4, Inc.
2920 Wolff Street
Racine, WI 53404
414-632-8133

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Figure 1. Graph of methylene chloride breakthrough concentration (in ppm) from pure methylene chloride challenge vs time for Magid polyethylene (MR-100) glove material.

Figure 2. Graph of methylene chloride breakthrough concentration (in ppm) from Iso Verre challenge vs time for Magid polyethylene (MR-100) glove material.

Figure 3. Graph of phenol breakthrough concentration (in ppm) from pure phenol challenge vs time for Magid polyethylene (MR-100) glove material.

Figure 4. Graph of phenol breakthrough concentration (in ppm) from Iso Verre challenge vs time for Magid polyethylene (MR-100) glove material.

Figure 5. Graph of isopropyl alcohol breakthrough (in ppm) from pure isopropyl alcohol challenge vs time for QRP 20G-2000 glove material.

Figure 6. Graph of acetone breakthrough (in ppm) from pure acetone challenge vs time for QRP 20G-2000 glove material.

Figure 7. Graph of 1,3-phenylenediamine (MPDA) breakthrough (in ppm) from Shell Z challenge vs time for unwashed QRP 20G-2000 glove material.

Figure 8. Graph of 1,3-phenylenediamine (MPDA) breakthrough (in ppm) from Shell Z challenge vs time for prewashed (with methanol) QRP 20G-2000 glove material.

Figure 9. Graph to compare 1,3-phenylenediamine (MPDA) breakthrough (in ppm) from Shell Z challenge vs time for unwashed and methanol prewashed QRP 20G-2000 glove material.

Figure 10. Graph of 4,4'-methylenedianiline (MDA) breakthrough (in ppm) from Shell Z challenge vs time for QRP 20G-2000 glove material.

Figure 11. Graph of 4,4'-methylenedianiline (MDA) breakthrough (in ppm) from Shell Z challenge vs time for QRP 20G-2000 glove material that was previously washed with methanol.

Figure 12. Graph to compare breakthrough (in ppm) of 4,4'-methylenedianiline (MDA) from Shell Z challenge vs time for unwashed and methanol prewashed QRP 20G-2000 glove material.

Figure 13. Graph of 1,3-phenylenediamine (MPDA) breakthrough (in ppm) from Shell Z challenge vs time for QRP 23G-2300 glove material.

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Figure 16. Graph of 4,4'-methylenedianiline (MDA) breakthrough (in ppm) from Shell Z challenge vs time for QRP 25G-2500 glove material.

Figure 1. Methylene Chloride Permeation
Tests #1, #2, & #3

Figure 2. IsoVerre Permeation
(Methylene Chloride)
Tests #1, #2, & #3

Figure 3. Phenol Permeation Tests #1, #2, & #3

Figure 4. IsoVerre Permeation (Phenol)
Tests #1, #2, & #3

Figure 5. Isopropyl Alcohol Permeation
Tests #1 & #2

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Tests #1 & #2**

Figure 7. Shell "Z" Permeation
1,3-Phenylenediamine (MPDA)
Tests #1 & #2

Figure 8. Shell "Z" Permeation
1,3-Phenylenediamine (MPDA)
Post Wash Tests #1, #2, & #3

Figure 9. Shell "Z" Permeation
1,3-Phenylenediamine (MPDA)
Unwashed vs Post Methanol Washed

Figure 10.

Shell "Z" Permeation
4,4'-Methylenedianiline (MDA)
Tests #1 & #2

Figure 11. Shell "Z" Permeation
4,4'-Methylenedianiline (MDA)
Post Wash Tests #1, #2, & #3

Figure 12. Shell "Z" Permeation
4,4'-Methylenedianiline (MDA)
Unwashed vs Post Methanol Washed

Figure 13. Shell "Z" Permeation
1,3-Phenylenediamine (MPDA)
Tests #1, #2, & #3

Figure 14. Shell "Z" Permeation
4,4'-Methylenedianiline (MDA)
Tests #1, #2, & #3

Figure 15.

Shell "Z" Permeation
1,3-Phenylenediamine (MPDA)
Tests #1, #2, & #3

Figure 16. Shell "Z" Permeation
4,4'-Methylenedianiline (MDA)
Tests #1, #2, & #3

Appendix A
Summary of Breakthrough Times
for

- 1. ASTM neoprene**
- 2. Edmont Sol-Vex nitrile
Pioneer nitrile**
- 3. Magid MR-100**
- 4. North SilverShield**
- 5. North viton**
- 6. Pioneer Pylox**
- 7. QRP PolyTuff
20G-2000
23G-2300
25G-2500**
- 8. Safety 4 4H**

GLOVE TEST
MATERIAL vs CHEMICAL TEST # BREAKTHROUGH TIME (min)

Material:

ASTM neoprene (18 mil)

1 14.0

Challenge:

acetone (1 inch cell)

2 14.0

3 14.0

4 16.0

Wash Solution:

Deionized Water

5 14.0

6 14.4

average
standard deviation

0.8

Material:

ASTM neoprene (18 mil)

1 18.0

2 16.0

3 14.0

Challenge:

acetone (2 inch cell)

4 14.0

5 16.0

6 14.0

Wash Solution:

Deionized Water

average
standard deviation

15.3

1.5

Material:

Edmont Sol-Vex nitrile (16 mil)

1 9.0

2 9.5

Challenge:

1,2-Dichloroethane

3 9.5

4 9.5

5 9.5

Wash Solution: Isooctane

(2,2,4-Trimethylpentane)

6 9.5

7 11.0

average
standard deviation

9.6

0.6

Material:

Edmont Sol-Vex nitrile (16 mil)

1 11.0

2 12.5

Challenge:

3% Diphenylmercury
(w/w in 1,2-Dichloroethane)

3 14.0

average
standard deviation

12.5

1.5

Wash Solution: Isooctane

(2,2,4-Trimethylpentane)

GLOVE TEST
MATERIAL vs CHEMICAL TEST # BREAKTHROUGH TIME (min)

Material:

Pioneer nitrile (38 mil)	1	8.0
	2	<u>9.5</u>

Challenge:

(1,2-Dichloroethane)	average	8.8
	standard deviation	1.1

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material:

Pioneer nitrile (38 mil)	1	<u>12.5</u>
	average	n/a
	standard deviation	n/a

Challenge:

3% diphenylmercury
(w/w in 1,2-Dichloroethane)

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material: Magid # MR-100

Polyethylene (1 mil)	1	3.0
	2	1.0

Challenge: Methylene chloride
(Dichloromethane)

3	<u>1.0</u>
average	1.6
standard deviation	0.9

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material: Magid # MR-100

Polyethylene (1 mil)	1	3.0
	2	1.0

Challenge: phenol

3	<u>1.0</u>
average	1.6
standard deviation	0.9

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

GLOVE TEST
MATERIAL vs CHEMICAL TEST # BREAKTHROUGH TIME (min)

Material: Magid # MR-100
Polyethylene (1 mil)

1

1.0

2

1.0

Challenge: IsoVerre Strip
(Methylene chloride)

3

1.0

average

1.0

standard deviation

0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material: Magid # MR-100
Polyethylene (1 mil)

1

1.0

2

1.0

Challenge: IsoVerre Strip
(Phenol)

3

1.0

average

1.0

standard deviation

0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material: North SilverShield
(5 mil)

1

>360

2

>360

Challenge: 1,2-dichloroethane

3

>360

average

>360

standard deviation

0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material:
North SilverShield (5 mil)

1

>360

2

>360

Challenge:
3% diphenylmercury
(w/w in 1,2-Dichloroethane)

3

>360

average

>360

standard deviation

0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

GLOVE TEST
MATERIAL vs CHEMICAL TEST # BREAKTHROUGH TIME (min)

Material: North viton (10 mil)
Challenge: 1,2-dichloroethane
Wash Solution: Isooctane
 (2,2,4-Trimethylpentane)

1	>360
2	>360
3	>360
average	>360
standard deviation	0.0

Material: North viton (10 mil)
Challenge: 3% diphenylmercury
 (w/w in 1,2-Dichloroethane)
Wash Solution: Isooctane
 (2,2,4-Trimethylpentane)

1	>360
2	>360
3	>360
average	>360
standard deviation	0.0

Material:
 Pioneer Pylox (12 mil)
Challenge: isopropyl alcohol
Wash Solution:
 Deionized Water

1	55.0
2	60.0
3	30.0
average	48.3
standard deviation	13.1

Material: QRP PolyTuff (8 mil)
 Product #20G-2000
Challenge: isopropyl alcohol
Wash Solution:
 Deionized Water

1	25.0
2	15.0
average	20.0
standard deviation	5.0

GLOVE TEST
MATERIAL vs CHEMICAL TEST # BREAKTHROUGH TIME (min)

Material: QRP PolyTuff (8 mil)
 Product #20G-2000

	1		3.0
Challenge: acetone	2		<u>4.0</u>
		average	3.5
Wash Solution: Deionized Water		standard deviation	0.5

Material: QRP PolyTuff (8 mil)
 Product #20G-2000

	1		25.0
Challenge: 1,3-phenylenediamine (MPDA)	2		<u>30.0</u>
		average	27.5
Wash Solution: Methanol		standard deviation	2.5

Material: QRP PolyTuff (8 mil)
 Product #20G-2000

	1		50.0
Challenge: 4,4-methylenedianiline (MDA)	2		<u>50.0</u>
		average	50.0
Wash Solution: Methanol		standard deviation	0.0

Material: QRP PolyTuff (8 mil)
 Product #20G-2000

	1		>240
Challenge: Asilamine	2		<u>>240</u>
		average	>240
		standard deviation	0.0

Wash Solution: Isooctane
 (2,2,4-Trimethylpentane)

GLOVE	TEST		
MATERIAL vs CHEMICAL	TEST #	BREAKTHROUGH TIME	(min)

Material: QRP PolyTuff (2 mil)
Product #25G-2500

Challenge:	1	3.0
1,3-phenylenediamine (MPDA)	2	3.0
	3	<u>3.0</u>
Wash Solution: Methanol		average 3.0
		standard deviation 0.0

Material: QRP PolyTuff (2 mil)
Product #25G-2500

Challenge:	1	3.0
4,4'-methylenedianiline (MDA)	2	3.0
	3	<u>3.0</u>
Wash Solution: Methanol		average 3.0
		standard deviation 0.0

Material: QRP PolyTuff (2 mil)
Product #23G-2300

Challenge:	1	3.0
1,3-phenylenediamine (MPDA)	2	3.0
	3	<u>3.0</u>
Wash Solution: Methanol		average 3.0
		standard deviation 0.0

Material: QRP PolyTuff (2 mil)
Product #23G-2300

Challenge:	1	3.0
4, 4'-methylenedianiline (MDA)	2	3.0
	3	<u>3.0</u>
Wash Solution: Methanol		average 3.0
		standard deviation 0.0

GLOVE MATERIAL vs	TEST CHEMICAL	TEST #	BREAKTHROUGH TIME (min)
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Material: Safety 4 4H (3 mil)	1		>360
	2		>360
	3		<u>>360</u>
Challenge: 1,2-dichloroethane		average	>360
		standard deviation	0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Material: Safety 4 4H (3 mil)	1		>360
	2		>360
	3		<u>>360</u>
Challenge: 3% diphenylmercury		average	>360
		standard deviation	0.0

Wash Solution: Isooctane
(2,2,4-Trimethylpentane)

Appendix B

Summary of Wash Method Testing (Time vs Analyte Concentration)

for

**Magid MR-100 gloves
QRP PolyTuff gloves
and
Methanol prewash experiment
on
PolyTuff 20G-2000 gloves**

Glove: Magid MR-100 (polyethylene)
Challenge: Methylene Chloride (pure reagent)
Wash Solution: 2,2,4-Trimethylpentane

	<u>Test #1</u>		<u>Test #2</u>		<u>Test #3</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	Area Counts	PPM
1	n/a	4627	132	4791	137	
2	n/a	15668	467	14033	417	
3	3644	102	22271	667	24154	724
4	n/a	22112	662	23935	717	
5	12369	367	24885	746	23834	714
10	8726	256	12707	377	10662	315
15	6034	175	10443	308	9366	276
20	7001	204	22570	676	13804	410
25	8102	237	9671	285	7660	224
30	6327	184	9375	276	8135	238

Glove: Magid MR-100 (polyethylene)
Challenge: Methylene Chloride (in IsoVerre Strip)
Wash Solution: 2,2,4-Trimethylpentane

	<u>Test #1</u>		<u>Test #2</u>		<u>Test #3</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	Area Counts	PPM
1	1465	37	2622	72	3260	91
2	6951	203	10266	303	13668	40
3	10899	322	14726	438	18043	539
4	10381	307	19766	591	22099	661
5	16460	491	16495	492	24267	727
10	7838	229	15985	476	10759	318
15	6074	176	11325	335	9139	269
20	9268	273	10938	323	12456	369
25	6642	193	13916	414	10694	316
30	6911	201	13491	401	8249	242

Glove: Magid MR-100 (polyethylene)
Challenge: Phenol (pure reagent)
Wash Solution: 2,2,4-Trimethylpentane

	<u>Test #1</u>		<u>Test #2</u>		<u>Test #3</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	Area Counts	PPM
1	n/a	n/a	360	<1	310	<1
2	n/a	n/a	1473	7	1189	5
3	608	1	2688	14	2167	11
4	n/a	n/a	1890	9	2188	11
5	1992	10	2390	12	2280	12
10	1299	5	2856	15	1617	7
15	800	2	2810	15	1144	4
20	1212	5	3165	17	1852	9
25	1050	4	2609	14	1404	6
30	950	3	3000	16	1409	6

Glove: Magid MR-100 (polyethylene)
Challenge: Phenol (in IsoVerre Strip)
Wash Solution: 2,2,4-Trimethylpentane

	<u>Test #1</u>		<u>Test #2</u>		<u>Test #3</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	AreaCounts	PPM
1	n/a	n/a	82	<1	137	<1
2	182	<1	715	2	1562	7
3	961	3	1336	6	1398	6
4	1095	4	2077	10	1737	8
5	1691	8	1810	9	1819	9
10	1555	7	4389	25	1537	7
15	966	3	3685	20	1595	7
20	983	3	3279	18	2174	11
25	1009	4	4249	24	2484	13
30	894	3	3079	17	1267	5

Glove: QRP PolyTuff 20G-2000 (Polyurethane)

Challenge: 2-Propanol (isopropanol)

Wash Solution: Deionized Water

	<u>Test #1</u>		<u>Test #2</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
3	0	0	0	0
5	0	0	0	0
10	0	0	1	0
15	0	0	11	0
20	0	0	49	5
25	2	0	216	37
30	6	0	257	45
40	71	9	854	159
50	308	54	1827	344
60	719	133	1851	349

Glove: QRP PolyTuff 20G-2000 (Polyurethane)

Challenge: 2-propanone (Acetone)

Wash Solution: Deionized Water

	<u>Test #1</u>		<u>Test #2</u>	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	n/a	n/a	0	0
2	n/a	n/a	0	0
3	2924	3029	0	0
4	n/a	n/a	120	123
5	5498	5697	1408	1458
10	7262	7526	4784	4957

Glove: QRP PolyTuff 20G-2000 (Polyurethane)
Challenge: Shell Epon (R) Curing Agent Z
Wash Solution: Methanol

<u>Test #1</u>					<u>Test #2</u>				
MPDA			MDA		MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0	1	0	0	0	0
3	0	0	0	0	3	0	0	0	0
5	0	0	0	0	5	0	0	0	0
10	0	0	0	0	10	0	0	0	0
15	0	0	0	0	15	0	0	0	0
20	0	0	0	0	20	0	0	0	0
25	1	0	0	0	25	0	0	0	0
30	11	4	0	0	30	3	2	0	0
40	15	5	0	0	40	8	4	0	0
50	26	9	2	0	50	28	10	1	1
60	65	21	9	1	60	79	27	5	1

Methanol PreWashed Permeation Results

Glove: QRP PolyTuff 20G-2000 (Polyurethane)
Challenge: Shell Epon (R) Curing Agent Z
Wash Solution: Methanol

<u>Test #1</u>					<u>Test #2</u>				
MPDA			MDA		MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM	Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0	1	0	0	0	0
3	0	0	0	0	3	0	0	0	0
5	0	0	0	0	5	0	0	0	0
10	0	0	0	0	10	0	0	0	0
15	0	0	0	0	15	0	0	0	0
20	1	1	0	0	20	3	1	0	0
25	12	5	0	0	25	13	5	0	0
30	41	14	1	1	30	36	12	1	0
40	72	25	6	1	40	57	19	4	1
50	188	63	45	7	50	79	26	10	2
60	233	78	73	11	60	159	52	45	6

Methanol PreWashed Permeation Results
(continued)

Test #3

MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0
3	0	0	0	0
5	0	0	0	0
10	0	0	0	0
15	0	0	0	0
20	6	2	0	0
25	18	6	0	0
30	31	10	1	0
40	59	19	10	2
50	105	34	24	4
60	195	63	50	7

Glove: QRP PolyTuff 23G-2300 (Polyurethane)

Challenge: Shell Epon (R) Curing Agent Z

Wash Solution: Methanol

Test #1

MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0
3	1312	148	0	3
5	944	11	524	1
10	4240	50	3684	22
15	7982	94	11770	75

Test #2

MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0
202	3	148	0	
5	1419	16	648	2
10	5464	62	5877	31
15	8148	92	12400	67

Test #3

MPDA			MDA	
Wash Time (min)	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0
3	210	2	76	0
5	1453	15	689	2
10	5654	60	5912	30
15	8546	91	12520	66

Glove: QRP 25G-2500 Gloves
Challenge: Shell Epon (R) Curing Agent Z
Wash Solution: Methanol

Test #1

Wash Time (min)	MPDA		MDA	
	Area Counts	PPM	Area Counts	PPM
1	0	0	0	
3	1093	5	359	1
5	4292	19	2307	4
10	9588	43	13080	25
15	10010	44	17390	34

Test #2

Wash Time (min)	MPDA		MDA	
	Area Counts	PPM	Area Counts	PPM
1	0	0	0	
3	2742	13	1120	2
5	8016	37	6572	12
10	10110	47	17500	33
15	11000	51	18690	35

Test #3

Wash Time (min)	MPDA		MDA	
	Area Counts	PPM	Area Counts	PPM
1	0	0	0	0
3	1312	6	1104	2
5	6289	28	3952	7
10	9964	44	16870	31
15	11000	49	18340	33

Appendix C

Summary of Testing That Showed No Measurable Breakthrough

**North SilverShield
North Vlon
QRP Poly Tuff 206-2000
Safety 4 4H**

ASILAMINE PERMEATION TESTS

Gloves tested - QRP, Inc. 20G-2000, 5.0 mil thick

Wash solution analyzed by HPLC under the following isocratic conditions:

flow: 2.0 ml/min

injection volume: 25 ul

column: 5 x 5 LC-8 by Supelco

mobile phase: 50/50 - water/acetonitrile

attenuation: 2

wavelength: signal - 254 to 430

Standards run: 1, 5, 10, 100, & 1000 PPM

Detection limit: < 0.5 PPM

Results:

First run - washed at 1, 3, 5, 10, 15, 20, 25, 30, 40, 50, & 60 min with no detectable breakthrough.

Second run - repeated cycle of first test plus 2, 3, & 4 hr washings, again no detectable breakthrough.

Wash Solution: Isooctane (2,2,4-Trimethylpentane)

3% diphenylmercury In 1,2-dichloroethane Permeation Tests

Gloves tested: North Viton (10 mil)
North SilverShield (5 mil)
Safety 4 -4H (3 mil)

All solutions analyzed on a Varian model 3700 gas chromatograph under the following conditions;

column:	30m x .25mm SUPELCOWAX 10 capillary
temperature program:	100°C (hold 2 min) then to 260°C @ 20/min (hold 7 min)
detector range:	10 ⁻¹² A/mV
detector attenuation:	64
injector temperature:	280
detector temperature:	300
standards run:	1 - 1000 ppm
detection limit:	> .5 ppm

Results showed no detectable breakthrough for any of the glove materials under the following wash cycles;

North Viton	10 min, 30 min, 1-7 hours and 23 hours (one wash on the hour)
North SilverShield	10 min, 30 min, 1-7 hours (one wash on the hr.)
Safety 4 -4H	10 min, 30 min, 1-6 hours (one wash on the hr.)

Each wash cycle for each glove material was repeated three times during the test series.

1,2-dichloroethane Permeation Tests

Gloves tested: North Viton (10 mil)
 North SilverShield (5 mil)
 Safety 4- 4H (3 mil)

All solutions analyzed on a Varian model 3700 gas chromatograph under the following conditions;

column:	30m x .25mm SUPELCOWAX 10 capillary
temperature program:	100°C (hold 2 min) then to 260°C @ 20/min (hold 7 min)
detector range:	10 ⁻¹² A/mV
detector attenuation:	64
injector temperature:	280
detector temperature:	300
standards run:	1 - 1000 ppm
detection limit	> .5 ppm

Results showed no detectable breakthrough for any of the glove materials under the following wash cycles;

North Viton	10 min, 30 min, 1-6 hours (one wash on the hr.)
North SilverShield	10 min, 30 min, 1-8 hours (one wash on the hr.)
Safety 4- 4H	10 min, 30 min, 1-6 hours (one wash on the hr.)

Each wash cycle for each glove material was repeated three times during the test series.

Appendix D

Interim Report on Glove Permeation Testing January 1989

A Glove Permeation Study

for

**Allied-Signal Inc.
Bendix Kansas City Division
Fred N. Larsen, Sponsor**

**Peter M. Swearengen
James S. Johnson
Allen R. Grayson
Stephen J. Priante**

Lawrence Livermore National Laboratory

Summary

We studied glove fabric permeation for Allied-Signal Corporation. We first compared our experimental data on acetone permeation through neoprene to published ASTM data and observed nearly identical results. We repeated the test with a one inch diameter permeation cell and these data were also quite similar. We then conducted a permeation test with neoprene and acetone and used a modified one inch cell that allowed periodic rinsing of the breakthrough side of the fabric. Breakthrough parameters with this third type of cell were again similar to those obtained previously. All further permeation testing was conducted using the one inch rinse type of test cell.

The solvent 1,2-dichloroethane (DCE) was used to challenge nitrile, viton, SilvershieldR, and a Safety4 4HR glove fabrics. In addition, 3% w/w solutions of diphenylmercury in 1,2-dichloroethane were used to challenge the same fabrics. The pure solvent and the mixture began to penetrate the nitrile fabric in about twelve minutes. Neither the solvent alone or the mixture penetrated the other three fabrics after six hours of continual challenge. These materials would be the protective fabric choice for solvent or solvent mixtures of this type.

Introduction

Special Projects Division of LLNL conducted a glove permeation study for the Allied-Signal Corporation. The goal of the study was to determine the best protective wear for personnel exposed to mixtures of organometallic compounds in solvents. We selected diphenylmercury as a representative compound and 1,2-dichloroethane (DCE) as the representative solvent. Allied-Signal provided three glove materials for the study, nitrile, viton, and SilverShield, and LLNL provided the 4H glove fabric. The nitrile gloves included samples from two manufacturers, Pioneer and Edmont (Sol-Vex).

Personnel in the Special Projects Division have developed a method for use with compounds that have low vapor pressure and/or are not soluble in water. The compound diphenylmercury fits in this category since it has a very low vapor pressure (partial pressure) when dissolved in DCE and is not soluble in water. To verify this method, we first compared test results obtained using our procedure with tests conducted using ASTM permeation procedures.¹ We wanted to reproduce the published ASTM results which measured the permeation of acetone through neoprene fabric in a standard test cell. We also wanted to introduce the use of a smaller test cell with modifications in both cell and procedure. We first measured permeation with the standard two inch cell and then repeated the procedure with a one inch diameter cell. The breakthrough times we measured with a standard cell and water as a collection medium were nearly identical to the published ASTM results with the conventional two inch cell and water collection medium. We then obtained similar results using a one inch cell, and also with our modified cell and collection procedure. Once we showed that our procedure gave similar results, we conducted the rest of the permeation study using our method.

Experimental

A picture of the ASTM permeation cell is provided in Figure 1. This is the cell against which our comparisons were made. The cell is designed to use a fluid collection medium on the breakthrough side of the fabric. Either a flowing gas or a liquid solution are the common media. In the case of a circulating gas, the system usually has a closed loop arrangement, with either dynamic or intermittent analysis of the gas stream. Change in concentration of the analyte of interest is recorded on a continual or intermittent basis, according to the analysis scheme.

When a liquid is used for the collection medium, it is usually water (to approximate body fluid). Very small samples are periodically withdrawn from the water for analysis. The standard cell provides for a stirring mechanism to ensure that a representative sample is taken.

We used a standard two inch cell to reproduce the ASTM results. We then switched to an identical cell of one inch diameter to repeat the permeation test for acetone and neoprene. We did not provide for stirring in either cell. Both standard cells were purchased from Pesce Lab Sales.² We fabricated a modified cell from standard one inch conical system glass process pipe.³ For the experiment to duplicate the ASTM report on acetone permeation of neoprene, we used 0.40mm-thick (16 mil) neoprene.⁴ This material was from the same stock of neoprene that was used in the original round-robin evaluation of the ASTM permeation test method. All chemicals used in the testing were reagent grade.

We analyzed all the chemicals discussed in this report by gas chromatography (Varian 3700, FID; column: DB-1, 30m x 0.53mm I.D., 5 micron film thickness⁵). The output from the chromatograph was processed by a Varian 402 data system. The detection limits observed with this system were: acetone, 0.8ppm; 1,2-dichloroethane, 0.5ppm; and diphenylmercury, 0.8 ppm. Each compound was identified by its retention time and quantitated by comparison of peak areas to a standard calibration curve generated by injecting known concentrations of the chemical into the chromatograph and measuring peak areas. For the ASTM procedure we used water as the collection medium, and took microliter amounts from the water at prescribed time intervals for gas chromatographic analysis. For the modified method we used a syringe to inject one milliliter volumes of a wash solution (water for the acetone permeation, and isooctane (2,2,5-trimethylpentane) for the diphenylmercury and 1,2-dichloroethane permeations) onto the breakthrough side of the exposed glove fabric. Each injection was done at a specified time interval, and the syringe was manipulated to carefully wash the entire exposed surface. The one milliliter wash solution volumes were collected through a teflon valve into a two milliliter glass vial and sealed until analysis. A diagram of the modified cell is shown in Figure 2 in a side view, and in frontal views of each cell half in Figure 3.

The one inch and two inch test cells were evaluated for equivalency by duplicating the procedure specified in ASTM F 739-85. Breakthrough times and permeation rates were measured for both cells. The mean values of these measurements were tested for equivalency by an analysis of variance, where statistical significance was comparable at a 99% confidence level for breakthrough times and permeation rates.⁶ A summary of our testing results for acetone and neoprene is shown in Table 1 and the results for breakthrough observed on the two types of nitrile gloves are shown in Table 2.

Breakthrough was not observed on the three other types of gloves that were tested for permeation, North viton, SilverShield, and 4H. The summary of all the permeation testing done on the organometallic solutions is shown in Table 3. A final check of our system with other reported permeation values was done with isopropyl alcohol against Pioneer Pylox (Polyvinyl chloride) gloves. For three trial runs we observed a mean breakthrough time of 55 minutes with a standard deviation of 8.7 minutes. This compared quite closely to the reported breakthrough time of one hour under continuous immersion conditions.⁷

Conclusions

The superior performance of three of the gloves in this study, Silver Shield, 4H, and viton, show that these materials would provide good protection against organometallic solutions of the type observed here. Other consideration to be included in a frequent use environment are the relative cost of these items and the type of exposure, which are not within the scope of this paper. We have previously observed viton and Silver Shield gloves to be impervious to aromatic amine compounds such as Diethyltoluenediamine (DETDA) in solution with salicylic acid, and Shell curing agent Z (32% 4,4'-Methylenedianiline (MDA), 44% 1,3-Diaminobenzene (MPDA), and 24% proprietary products). The inclusion of 4H gloves in this study broadens the choice of marketplace gloves that appear to resist permeation to a very broad range of chemicals.

References

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3. Corning Glass Works, Big Flats, NY 14814. Phone: 607-974-0299
4. Fairprene Industrial Products Company Inc., 85 Mill Plain Rd., Fairfield, CT 06430. Phone: 203-259-3351.
5. J&W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630. Phone: 800-223-3424.
6. Taylor, J. K., Quality Assurance of Chemical Measurements, Lewis Publishers, Inc., Chelsea, Michigan, 1987, pp. 29-31.
7. Pioneer Industrial Products Co., Form No. 1084, p. 21., 512 East Tiffin Street, Willard, Ohio 44890. Phone: 800-537-2897.
Allied-Signal Glove Study

Table 1 - Summary of breakthrough times for acetone and neoprene study

Cell Type	Collection Medium	Breakthrough Time, min.
Large ASTM	water	18
		20
		16
		<u>14</u>
		mean = 17
	standard deviation	2.6
Small ASTM	water	14
		<u>14</u>
		mean = 14
		standard deviation 0
Large wash	water*	14
		16
		<u>14</u>
		mean = 14.7
		standard deviation 1.2
Small wash	water*	14
		16
		<u>14</u>
		mean = 14.7
		standard deviation 1.2

* by syringe injection of 1 cc volumes

Table 2 - Summary of breakthrough times for nitrile fabric with 1,2 - Dichloroethane and diphenyl mercury

Fabric	Solution Type	Breakthrough Time, min.
Edmont Sol-Vex nitrile	1,2-Dichloroethane	9
		9.5
		9.5
		<u>9.5</u>
		mean = 9.4
	standard deviation	0.2
	<u>1,2-Dichloroethane</u> (with 3% diphenyl mercury, w/w)	9.5
		9.5
		<u>11.0</u>
		mean = 10
		standard deviation 0.9
	same solution, diphenyl mercury component	11.0
		12.5
		<u>14.0</u>
		mean = 12.5
		standard deviation 1.5
Pioneer nitrile	1,2-Dichloroethane	8
		<u>9.5</u>
		mean = 8.8
		standard deviation 1.1
		diphenyl mercury 12.5
		N/A

Table 3 - Summary of solvent/organometallic permeation study

Breakthrough Time

	Solvex Nitrile	Pioneer Nitrile	North Viton	Silver Shield	4H
1,2-Dichloroethane (min)	9.4	8.8	>360	>360	>360
Diphenyl mercury (min)	12.5	12.5	>360	>360	>360
Fabric thickness (mm)	0.36	0.8*	0.346	0.102	0.062

*Includes liner

Standard ASTM permeation test cell.

MODIFIED PERMEATION CELL

MODIFIED PERMEATION CELL

PORT FOR
CHALLENGE LIQUID
14/35

WASHING PORT

INJECTION
RINSE PORT

COLLECTION RINSE TUBE

Comparison of large and small cells—ASTM method (acetone vs neoprene)

Acetone vs neoprene test with 2-in. cell

Acetone vs neoprene test with 1-in. cell

Comparison of large and small cells—wash method (acetone vs neoprene)

Solvent breakthrough of Solvex nitrile glove

Solvent with mercury compound breakthrough curve for Solvex nitrile glove

Solvent breakthrough of Pioneer nitrile glove

Solvent with mercury compound breakthrough curve for Pioneer nitrile glove

Comparison of Pioneer and Solvex nitrile gloves (solvent: 1,2,-dichloroethane)

Isopropanol breakthrough of Pioneer Pylox (average of three runs)

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