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TEST AND EVALUATION FOR CHEMICAL RESISTANCE OF GLOVES WORN FOR PROTECTION AGAINST EXPOSURE TO H-70 HYDRAZINE

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This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continued)

during routine maintenance tasks; however, if liquid H-70 contact is observed, the gloves should not be reused. Gloves should be decontaminated with 5% bleach before disposal. This report lists a second group of gloves that performed only a little less satisfactorily and could be used in emergency situations. The second group includes the readily available and federal stock-listed aircrew gloves by Norton and Edmont-Wilson. Gloves are mentioned by manufacturer and model number rather than by material, thickness, and other more objective parameters because of observed discrepancies between glove specifications and test results. For example, nitrile gloves of the same thickness but from different manufacturers gave breakthrough times of greater than 6 hr versus less than 10 min at 20°C. It appears that the most important specification to insure adequate chemical resistance from a glove is to have representative glove samples of various styles and construction from each manufacturer pass a chemical resistance test for the specific chemical of interest.

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TEST AND EVALUATION FOR CHEMICAL RESISTANCE OF GLOVES WORN FOR PROTECTION AGAINST EXPOSURE TO H-70 HYDRAZINE

INTRODUCTION

The F-16 is an electronically controlled (fly-by-wire) aircraft that requires an emergency power unit (EPU) to provide short-term electric and hydraulic power. The EPU runs on a monopropellant hydrazine fuel mixture, H-70, which contains 70% hydrazine (N_2H_4) , 30% water, by weight. Because H-70 is highly reactive, very caustic, and a suspect carcinogen, it and systems containing it must be handled with care to prevent exposure of maintenance and support personnel. During maintenance of the F-16 EPU, workers must wear gloves to prevent skin contact with liquid H-70 in the event of a spill and/or a leak. Present use of the heavy-duty rocket fuel handler's (RFH) glove (NSN 845-00-916-2817) provides adequate skin protection; however, the glove is bulky and does not allow for adequate dexterity in connecting or disconnecting the fuel quick-disconnect fittings. The dexterity/flexibility deficiencies of the rocket fuel handler's gloves in the F-16 application have contributed to accidents which resulted in H-70 skin contact. At the start of this study, no commercially available or federally stocklisted glove with adequate H-70 permeation resistance and dexterity had been fully tested and qualified for use with H-70 on the F-16 EPU.

The objective of this effort was to investigate the chemical resistance of various commercially available gloves and glove materials to liquid H-70 over a temperature range of 0°C to 40°C. Those gloves exhibiting resistance to H-70 penetration were subjectively tested and evaluated for dexterity. Results of testing were provided to the USAF Occupational and Environmental Health Laboratory (USAF OEHL) and the F-16 System Program Office (SPO) for aid in selection of a disposable (one-time-use) glove to replace those currently authorized for use on the F-16 EPU system and with associated support gear.

EXPERIMENTAL PROCEDURE

Sample gloves were obtained from the manufacturers and other sources listed in Table 1. Model numbers and other pertinent information obtained from the manufacturers' literature are given in Table 2. All gloves tested were from the same batch and lot.

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Because of time constraints and the lack of a standard procedure for testing chemical resistance of glove materials, a modification of a National Institute for Occupational Safety and Health (NIOSH) recommended method (1) was adopted and used. The major difference between the modification and the NIOSH method was our testing of an entire uncut glove in contrast to NIOSH testing that is done with material specimens.

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TABLE 1. MANUFACTURERS SUPPLYING GLOVES FOR H-70 CHEMICAL RESISTANCE TESTING

Perry Company Massilon OH 44646

Pioneer Division of Sherwood Medical St Louis MO 63103

Norton Company P.O. Box 4367 Charleston SC 29405

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International Playtex Company Industrial Gloves Division 888 Seventh Avenue New York NY 10019 Granet Division ESB Rayovac P.O. Box 588 25 Loring Drive Framingham MA 01701

Edmont-Wilson Division of Becton & Dickenson & Company Coshocton OH 43812

Surety Rubber Company P.O. Box 97 611 N. High St. Carrollton OH 44615

Renco Corporation 2060 Fairfax Avenue Cherryhill NJ 08003

TABLE 2. GLOVES USED IN H-70 RESISTANCE TESTING

				Thickness	
Glove	Manufacturer	Model No.	Material	cm (mil)	Size
A	Perry	Surgeons NSN 655-00-782-6476	Latex	.018 (7)	8 1/2
В	Pioneer	A-10	Nitrile	.025 (10)	9
с	Pioneer	A-15	Nitrile	.038 (15)	9
D	Norton	NSN 8415-00-753-6551	Butyl rubber	.076 (30)	M
E	Norton	NSN 8415-01-025-9378	Neoprene	.043 (17)	9
F	Playtex	835	Neoprene-latex	.051 (20)	L
G	Granet	490	Nitrile	.038 (15)	XL
н	Edmont-Wilson	29-845	Neoprene	.043 (17)	8
I	Edmont-Wilson	37-165	NBR	.056 (22)	10
J	Edmont-Wilson	26-665	Rubber	.046 (18)	10
ĸ	Edmont-Wilson	36-755	Rubber	.102 (40)	10
L	Surety	10-112L	Nitrile	.028 (11)	10
М	Surety	10-132R	Nitrile	.036 (14)	9
N	Surety	10-136R	Nitrile	.051 (20)	9
0	Surety	10-156R	Nitrile	.066 (26)	10
P	Surety	10-166R	Nitrile	.066 (26)	10
Q	Surety	10-186R	Nitrile	.038 (15)	10
R	Renco	RN-12	Nitrile	.030 (12)	9

Test Procedure

Basically, the testing procedure followed used the apparatus illustrated in Figure 1. A 500-ml aliquot of perspiration simulant (4.8 g NaCl, 0.4 g CaCl₂, 0.4 g KCl, and 2 g lactic acid per liter of distilled water) was added to the clean 1-liter apparatus jar. The glove to be tested was turned inside out, partially inserted in the jar, and filled with 300 ml of Mil Std H-70. The glove then was repositioned to bring outside and inside liquids to the same level (approximately 500 cm² of glove surface area was exposed to H-70). The apparatus was sealed with a glass top and clamp which also secured the glove in place. A magnetic stirrer was used to keep the perspiration simulant in vigorous motion.



Figure 1. USAFSAM/VNL apparatus for testing chemical resistance of gloves.

Testing was done in a walk-in environmental chamber controlled at 0°C, 20°C, and 40°C. Gloves, apparatus, liquids, etc. were placed in the test environment for at least 3 hr before start of an experiment to permit attainment of temperature equilibrium.

Gloves were tested as received from the manufacturer, except for one series of tests at 40°C where glove samples were pretreated by immersion in a hydrazine spill decontamination fluid (5% aqueous solution of sodium hypochlorite), for 1 hr followed by thorough water rinsing and drying. The hypochlorite treatment was done to see if the decontaminant degraded glove resistance to H-70.

Analytical Procedure

The analytical measurement technique chosen was a colorimetric method based on the reaction between hydrazine and paradimethylaminobenzaldehyde (PDAB) (2). Sampling was done by extracting 10-ml-sample aliquots through a serum septum at 10-min intervals, starting with a background sample taken 10 min before addition of H-70 to the glove. The aliquot removed was replaced with 10 ml of fresh simulant before withdrawal of the next sample to keep the total volume of perspiration simulant at a constant 500 ml. Sampling continued for 6 hr, after which testing was terminated. The 10-ml samples were analyzed within 3 hr of test completion. (A pretest study showed hydrazine to be stable in the perspiration simulant for at least 48 hr.) Sensitivity of the analytical method for a 10-ml sample was $0.2 \ \mu g$.

All concentration data presented were corrected for this discrete sampling procedure using the following formula:

$$C_{\eta} = c_{\eta} + \frac{v_{s}}{v_{p}} \sum_{i=1}^{n-1} c_{i}$$

where

- i = an indexing number assigned to each discrete sample taken, starting with i=1 for the first sample.
- ci = the concentration of harmful liquid found in discrete sample number
 i.
- n = the number of the most recent discrete sample taken.
- c_{η} = the concentration of harmful liquid found in discrete sample number n_{\bullet} .
- C_{η} = the corrected concentration of harmful liquid in the perspiration simulant at the time of discrete sample number n.

 V_s = the volume of each discrete sample taken (10 ml).

 V_{p} = the volume of perspiration simulant in the test cell (500 ml).

Other Measurements

Glove material thickness was measured on palm, back-of-the-hand, and finger specimens to 0.0025 cm (0.001 inch or 1 mil). Measurements were made on dry gloves before and after exposure to H-70.

Dexterity Testing

Dexterity tests were conducted using the Arthur D. Little test method reproduced in the NIOSH reference (1).

RESULTS AND DISCUSSION

General

The gloves tested were chosen by F-16 SPO and USAF OEHL personnel who relied on manufacturers' recommendations. Eighteen kinds of gloves made of latex, butyl rubber, natural rubber, neoprene, acrylonitrile, and acrylonitrile-butadiene rubber were tested. Other materials such as polyvinylchloride (PVC) were not tested because of their poor resistance to UDMH reported in the NIOSH document (1). Batch and lot were not a consideration at this time; the main concern being chemical resistance as a function of material and thick-Testing was limited to 6-hr exposures because of time constraints ness. imposed on the program. Because the NIOSH-recommended standard for generalpurpose protective resistance of clothing and hand coverings to carcinogens (1) is 1 hr, those gloves showing breakthrough times of less than 1 hr at room temperature (20°C) were not tested further. The NIOSH standard must be met under worst-case direct continuous challenge conditions which we feel was satisfied by the 40°C testing sequence. The analytical sensitivity of the PDAB method used is estimated at 0.02 µg/ml or 0.2 µg for a 10-ml sample aliquot. In terms of total chemical permeation through a typically exposed 500-cm² surface area of glove material, sensitivity is 10 μ g (0.01 mg) of hydrazine.

Breakthrough Time

In this testing effort, breakthrough time is defined as the time between initial contact of H-70 with the outside surface of the glove and the time at which hydrazine was detected in the perspiration simulant contacting the inside surface of the glove. Breakthrough data are presented in Table 3 for the temperatures, $0^{\circ}C$ ($32^{\circ}F$), $20^{\circ}C$ ($68^{\circ}F$), and $40^{\circ}C$ ($104^{\circ}F$), with $40^{\circ}C$ being the worst-case test as expected. Data given in Table 3 with standard deviations are the result of a minimum of three replicate glove samples. Where no standard deviation is given, only one glove was tested.

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Chemical Permeation

Assessing the degree of protection a glove gives to the wearer during chemical exposure requires knowledge of both breakthrough time and the TABLE 3. BREAKTHROUGH TIME FOR GLOVES IN CONTACT WITH LIQUID H-70

		Breakthro	ough time (min) ^a	
Glove	0°C	20°C	40°C	40 °C ^b
A	80	<10	_	-
В	NBC	190 ^d	77 ±7	80
с	NB	NB	135 ±7	130
D	NB	NB	NB	NB
E	NB	NB	100 ±14	105 ±7
F	NB	87 ±15	27 ±6	-
G	NB	NB	130 ±21	130 ±21
н	NB	NB	70 ±2	80
I	NB	NB	268 ±22	320
J	NB	73 ±12	< 10	-
ĸ	NB	NB	60 ±0	-
L	60	< 10	-	-
м	NB	NB	105 ±7	110
N	NB	NB	184 ±47	190
0	NB	NB	300 ±50	300
Р	NB	NB	300 ±28	290
Q	NB	NB	90 ±0	70
R	NB	NB	110 ±10	100

Breakthrough time (min)^a

^aBreakthrough time defined as time hydrazine first detected. Lower limit of detection was 0.02 μ g/ml.

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 $^{\rm b}{\rm Gloves}$ were soaked for 1 hr in 5% aqueous sodium hypochlorite and rinsed, before testing.

^CNB indicated no breakthrough during duration of testing (6 hr).

^dTwo glove samples showed no breakthrough; one glove failed at the time shown.

permeation rate of the chemical. Most of the gloves examined here did not result in a steady-state permeation rate because of the limited testing time. However, while not as readily comparable as steady-state rates, equally informative rate data were obtained by measuring the total amount of hydrazine permeating through the glove and into the perspiration simulant 3 and 6 hr after glove exposure to H-70 (Table 4). For example, although gloves B and H basically have a similar breakthrough time of about 70 minutes, permeability of glove B is on the order of 400 times that of H at 6 hr. Hydrazine permeability rates for the gloves are graphically illustrated in Figures 2 through 6. The illustrated graphs are normalized to a standard H-70 exposed glove area (500 cm²).

	Breakthrou	gh (40°C)		ligrams (40°C) ^b	
Glove	Time (min)	Rank ^C	3 hr	6 hr	Rank ^C
В	77 ±7	12	97.5 - 337d	2800 - 4250	13
с	135 ±7	6	0.1 - 12.5	185 - 2000	12
D	NBe	1	0	0	1
E	100 ±14	10	0.06	1	6
G	130 ±21	7	0.2	75	10
н	70 ±2	13	0.2	10	7
I	286 ±22	4	0	0.05	4
M	105 ±7	9	0.4	10.5	9
N	184 ±47	5	0	1	5
ο	310 ±50	2	0	0.03	3
P	300 ±29	3	0	0.03	2
Q	90 ±0	11	0.3	9	8
R	110 ±10	8	4.2 - 70	644 - 1360	11

TABLE 4. GLOVES SHOWING HIGH RESISTANCE TO H-70 PENETRATION^a

Hydrazine permeability

 $^{\rm a}{\rm Gloves}$ showing breakthrough at 20°C were rejected from consideration for further testing.

^bHydrazine permeation through glove into sampling solution after 3-hr and 6-hr testing. Concentration normalized to $mg/500 \text{ cm}^2$.

^CRanking is from most desirable (1) to least desirable (13) property.

^dWhere ranges are given, it indicates a wide variability of hydrazine permeation between tested glove sample (>20%).

^eNB indicates no breakthrough during duration of test (6 hr).



Figure 2. Permeation of H-70 through industrial glove material as a function of time.



Figure 3. Permeation of H-70 through industrial glove material as a function of time.

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Figure 4. Permeation of H-70 through industrial glove material as a function of time.

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Figure 5. Permeation of H-70 through industrial glove material as a function of time.

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Figure 6. Permeation of H-70 through industrial glove material as a function of time.

Glove surface areas contacting H-70 and perspiration simulant were estimated by cutting the tested glove at the emersion level line and weighing the dried material specimen. The weight of an accurately cut 25 cm piece of glove (back of hand) was used to determine the density of the material and hence to calculate the surface area of the glove exposed to H-70.

Surface Area =
$$\frac{\text{Wt of Glove Section Affected}}{\text{Wt of 25-cm}^2 \text{ Section}} \times 25$$

Glove Material Thickness

Glove materials showed a relatively uniform thickness between glove samples and parts of gloves from the same manufacturer which is in good agreement with the manufacturers' specifications and findings reported elsewhere (3).

Typical data supporting these observations are reproduced in Table 5. Data on the effect of a 6-hr H-70 exposure and a 1-hr pretreatment with Clorox (5% aqueous sodium hypochlorite) are included for completeness.

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The Surety gloves were exceptions to the uniform thickness observation in that all samples were thinner in the fingertips than in other parts of the glove. For example, the Surety 10-156R measured .066 cm (26 mil) to .074 cm (29 mil) at palm, back, and finger--compared to manufacturers' stated value of .066 cm (26 mil)--but measured only .051 cm (20 mil) at the fingertips. The thinner fingertips may account for the relatively high rating the Surety gloves got in the subjective dexterity testing.

				• • •			
- M Glove	lanufacturer: data	-	glove	6 1 H-70 co			hr ox soak
		20°C	40°C	20°C	40°C	20°C	40°C
Pioneer A-15 (Nitrile) ^a	5 15	15.0 15.2 15.0	15.5 15.4 15.6	15.3 15.2 15.4	15.9 15.8 15.7	15.6 15.7 15.3	15.3 15.7 15.8
Edmont-Wilso 29-845 (Neoprene) ¹	-	16.8 17.0 16.9	17.6 17.6 17.1	19.2 19.3 19.1	19.7 19.7 19.7 19.9	19.7 19.8 19.8	19.6 19.7 20.0

TABLE 5. THICKNESS OF GLOVES BEFORE AND AFTER EXPOSURE TO LIQUID H-70

Thickness (mil)

^aBack-of-hand measurement. ^bMiddle-finger measurement.

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Thickness is obviously not usable as a measure of protection unless the density of the material is also known. This was demonstrated by the large differences in breakthrough times (Table 3) observed for the two acrylonitrile gloves B (Pioneer A-10) and L (Surety 10-112L). Both gloves have similar thickness (B/L = 10/11) but differ in "density" (B/L = .694/.656). "Density" values quoted are the observed weights of a 25-cm² glove specimen. Corrected for the slight difference in thickness, the density ratio becomes even larger, B/L = .694/.588. Thus, the thicker glove, L in this case, had breakthrough at much lower temperature than B which appeared to be mainly a function of material density. Thinner fingertips for L, the glove manufactured by Surety, do not appear to be a significant factor in the large differences observed in breakthrough times and temperature in this case since fingertip measurement values were on the order of 0.025 cm (10 mil) vs. 0.28 cm (11 mil) for the glove as a whole and never much less than glove B thickness.

Dexterity Testing

A test method recommended by NIOSH (1) was used to determine the dexterity of those gloves investigated for chemical resistance. The gloves were tested at ambient temperature $(20^{\circ} \pm 2^{\circ}C)$ in new condition as received from the manufacturer. The basic intent of the dexterity test was to establish the ability of a gloved hand to pick up a smooth stainless-steel pin, 5.0 mm (0.20 in) in diameter and 40.0 mm (1.6 in) in length, under dry and wet conditions within a specified period of time. Testing consisted of the gloved subject sequentially using each of the four possible combinations of thumb and finger to pick up the pin by its circumference from a flat stainless-steel surface. The attempt was timed with success defined as completion of the test within 30 sec. Since all gloves passed the 30-sec test (averaged values ranged between 2.1 - 11.9 sec for both dry and wet testing), it was decided to rank the gloves according to the relative speed needed to complete each test. The somewhat subjective results are summarized in Table 6 and agree with expectations based on glove characteristics such as thickness.

Rank ^a , b	Dry pin test	Wet pin test
1	L Surety 10-112L	B Pioneer A-10
2	Q Surety 10-186	L Surety 10-112
3	N Surety 10-136	G Granet
4	B Pioneer A-10	C Pioneer A-15
5	C Pioneer A-15	N Surety 10-136
6	F Playtex	Q Surety 10-186
7	G Granet	F Playtex
8	E Norton Aircrew	H E-W 29-845
9	H E-W 29-845	J E-W 26-665
10	I E-W 37-165	E Norton Aircrew
11	J E-W 26-665	I E-W 37-165
12	D Norton Tox	D Norton Tox
13	P Surety 10-166	P Surety 10-166
14	K E-W 36-755	K E-W 36-755

TABLE 6. RESULTS OF DEXTERITY TESTING

^aMost dexterous (1) to least (14).

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^bThe Surety 10-156R and 10-132R and the Perry Surgeons gloves were not tested. It is expected the Surety 10-156R would perform similar to the 10-166R glove, while the other two gloves would be equal to or better than the top five.

CONCLUSION AND RECOMMENDATIONS

Results of the testing program are summarized in Table 7. Gloves are listed in groups of nearly equivalent performers based on chemical permeability and breakthrough times under the worst-case test condition of 40° C. Gloves ranked 1 through 3 showed no detectable hydrazine permeation after 3 hr of testing with very small amounts of hydrazine found after 6 hr of testing. Gloves ranked 4 and 5 showed barely detectable hydrazine permeation after 3 hr with a significant increase in permeation rate thereafter. All 5 groups showed no H-70 breakthrough over a 6-hr exposure period at the lower temperatures studied, 20°C and 0°C. All 5 groups satisfied the NIOSH criteria for

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GLOVES SHOWING HIGHEST RESISTANCE TO H-70 PENETRATION AT 40°C. RANKED IN ORDER OF DECREASING RESISTANCE TABLE 7.

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	Kank	X				and the second	
Group	Group Resistance Dexterity	Dexterity	Glove/style	Material	Length (in)	CIII (mil)	Sizes
-	-	12	D Norton Tox	Butyl rubber	14	.076 (30)	TX-SX
7	N	13	0 Surety 10-156R	Nitrile	16	.066 (26)	9-10-11
		13	P Surety 10-166R	Nitrile	18	.066 (26)	9-10-11
m	m	11	I Edmont-Wilson 37-165ª	NBR	14	.056 (22)	9-10-11
		£	N Surety 10-136R	Nitrile	12	.051 (20)	8-9-10-11
4	4	6	E Norton Aircrews	Neoprene	12	.043 (17)	7-8-9
Ŋ	'n	œ	H Edmont-Wilson 29-845	Neoprene	12	.043 (17)	7-8-9
		2	Q Surety 10-132R	Nitrile	12	.036 (14)	8-9-10-11
		e	M Surety 10-186R	Nitrile	18	.038 (15)	9-10-11

^aEquivalent but longer length glove (18 in) is Edmont-Wilson 37-185.

general-purpose protective clothing use which call for 1-hr chemical resistance to carcinogens and suspect carcinogens.

It is concluded that gloves in the 1 through 3 grouping are adequate for one-time use during spill cleanup operations if rocket fuel handler's gloves are unavailable or unsuitable because of task dexterity requirements. The best choice of this glove grouping for satisfying dexterity needs is the Surety Model Number 10-136R; however, regardless of choice, maximum dexterity/flexibility requires proper fit obtained only by having the appropriate sizes in stock. The group 1-3 gloves may be used during routine maintenance tasks until they are mechanically damaged or observed contacting liquid H-70. Gloves exposed to liquid H-70 should be decontaminated with 5% bleach and disposed, not reused.

Gloves ranked 4 and 5, while not as highly recommended as the 1-3 groups, did satisfy the NIOSH criteria and could be used (treated as disposable) in an emergency when none of the other discussed gloves can be found. This second group of gloves fortuitously includes the aircrew gloves by Norton and Edmont-Wilson which are readily available at most flying bases.

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