REPORT SD-TR-83-51

Measurements of Hypergolic Fuels' and Oxidants' Permeation through Commercial Protective Materials

Part I: Inhibited Red Fuming Nitric Acid and Unsymmetrical Dimethylhydrazine

R. N. ABERNATHY and R. B. COHEN
Chemistry and Physics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

and

J. J. SHIRTZ
Bioenvironmental Engineering Office
Air Force Space Division
El Segundo, Calif. 90245

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AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

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Robert A. Skier

ROBERT A. SKIER, CAPT, USAF, BSC
Staff Bioenvironmental Engineer

Joseph Hess

JOSEPH HESS, GM-15, Director
West Coast Office, AF Space
Technology Center

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Protective equipment is used by Air Force and NASA personnel who participate in hypergolic propellant transfer and loading operations that entail potential exposure to hypergolic vapor or liquid. Forty materials (sections of protective suits, gloves, boots, and a hood window) that are now used or are under consideration for future use in hypergolic propellant transfer operations were tested to determine their resistance to permeation by the fuel, unsymmetrical dimethylhydrazine (UDMH), after exposure to liquid UDMH,

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and their relative resistance to permeation by nitrogen dioxide (NO_2) after exposure to the liquid oxidant, inhibited red fuming nitric acid (IRFNA). The material sections were clamped in a static test cell that permitted the fabric to be exposed to the fuel (or oxidant) on one side while UDMH (or NO_2) permeation was monitored by an electrochemical analyzer on the other side. The experiments were discontinued after 90 min if no permeation was detected. A new material section was used in each test; the test section was neither preconditioned nor was exposure repeated.

Only one suit fabric of the nine tested resisted both NO_2 and UDMH permeation for the full 90 min of the tests. One resisted UDMH for 90 min and was permeated rapidly (in 2 min) by NO_2, two resisted UDMH and NO_2 permeation from 20 to 30 min, and others were permeated in less than 5 min by both propellants. The palm sections of only four of the 28 glove palm sections resisted permeation by NO_2 and UDMH for 90 min. Both (very thick) boot sections and the only hood window resisted NO_2 and IRFNA permeation for 90 min.

Our results demonstrate that protective clothing should not be adopted without specific chemical compatibility testing and that procedures to ensure quality control are required for all protective equipment currently in use.

PREFACE

The authors gratefully acknowledge useful discussions with Dr. R. Rianda and the excellent laboratory support provided by S. A. Genova, J. E. Foster, and L. Tolentino.

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I. INTRODUCTION

The hypergolic rocket propellants used in Air Force and NASA operations include the oxidants N_2O_4 and hydrogen fluoride (HF) inhibited red fuming nitric acid (IRFNA), and the fuels hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine (UDMH). These chemicals are extremely hazardous to propellant handlers (skin contact can cause rapid and severe burns) and are highly toxic (they exhibit both acute and chronic toxicity). On the basis of their demonstrated oncogenic potential in laboratory animals,[1] the hydrazine family of fuels is listed among substances suspected of carcinogenic potential in man. Their use requires special protective equipment and operational procedures designed to maximize personnel safety during each phase of an operation. The complete cycle of operations for loading N_2O_4 into a Titan space launch vehicle booster, for example, may last several days and require the use of several combinations of protective gloves, suits, boots, and breathing equipment.

The Air Force Systems Command's Space Division (SD) is currently reviewing the protective equipment and procedures used in its propellant handling operations and is developing guidelines for the Space Transportation System (shuttle) operations to be carried out at Vandenberg Air Force Base. During the past decade, a variety of protective items have been adopted by the Air Force for relatively similar propellant handling operations. As specific compatibility tests for the materials and propellants involved are lacking, items such as gloves, protective suits, and boots have often been adopted as a result of a manufacturer's recommendations, extrapolation from experience with similar compounds, or practical experience. An examination of the literature on the permeation of protective clothing[2-22] established that chemical-material compatibility must be tested on an item-by-item basis, and that fabric composition, thickness, uniformity, age, and the extent of previous exposure are parameters that affect compatibility. Variations in the same material (e.g., PVC, nitrile, butyl rubber) are encountered from manufacturer to manufacturer,[7] and from sample to sample, when a single batch of gloves is examined.

The results of a screening study that measured permeation times for 40 protective materials exposed to liquid IRFNA and to liquid UDMH are reported here. Each experiment involved a previously unexposed section cut from an item of unused protective equipment. The suit fabric tests were conducted on samples cut from sheets of material. A permeation study involving exposure of these same materials to other hypergolic fuels and oxidants is under way. The results of this study of relative resistance to permeation by fuels and oxidizers will be considered in both the selection of protective equipment and in the review of the propellant-handling procedures for SD operations. The operational and systems-safety considerations relevant to choosing protective equipment for Air Force programs are addressed in the Appendix.

II. EXPERIMENTAL

A. APPARATUS

The permeation apparatus is illustrated schematically in Fig. 1. The test materials were clamped in a paraffin-coated glass apparatus by means of a Viton or butyl rubber O-ring to ensure an airtight seal on the sweep air side. The exposed area of material was 8 cm^2. The permeation of NO_2 was monitored by an Energetic Science, Inc. (ESI) Series 7000 Ecolyzer electrochemical detector. UDMH permeation was monitored by an Interscan Corp. model 1186 electrochemical hydrazine analyzer. Air Products breathing air for the IRFNA study or Air Products extra-dry nitrogen for the UDMH study was swept over the unexposed side of the test material at a rate of 2.0 ℓ/min and sampled by the Ecolyzer at 0.71 ℓ/min or by the Interscan at 1.2 ℓ/min. The excess sweep gas was vented into the duct of the hood in which the entire experimental apparatus was situated.

B. MATERIAL PREPARATION

Except for a brief visual examination for obvious defects, samples were tested as received (from the manufacturer) in this program. This permitted a sampling of both product variability and the manufacturer's quality control. Several test programs have used selection and preparation methods including leak-testing, washing, and solvent conditioning.[9-12] The prescreening approach is not relevant to this study.

C. REAGENTS

Military specification IRFNA was obtained from Vandenberg AFB storage and used as received. UDMH of 99% minimum purity was purchased from the Aldrich Chemical Company. The calibration gas, 100 ± 2 ppm NO_2 in air, was supplied by Matheson, who had verified its concentration. Independent tests indicate that the calibration gas concentration remained constant during the testing. Air Products breathing air was used as the sweep and dilution gas for the IRFNA study. It contains less than 1000 ppm carbon dioxide (CO_2) and has a dew point below 70 K. A UDMH permeation tube was obtained from Analytical

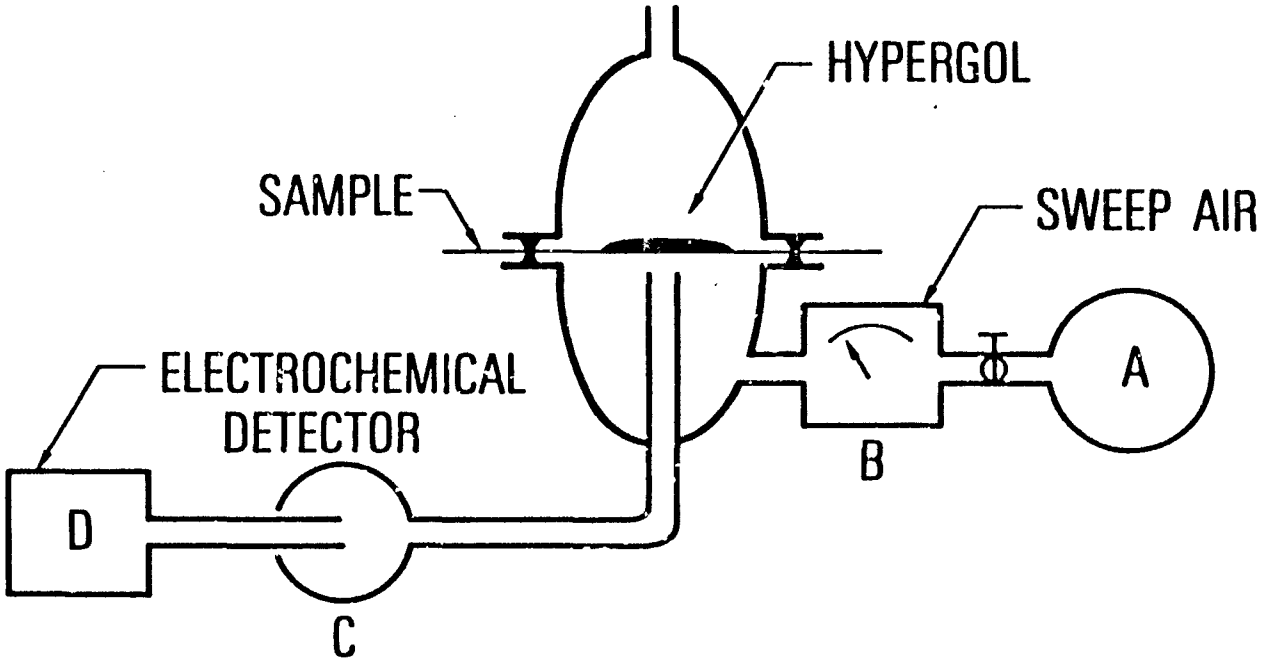

Fig. 1. Schematic of IRFNA and UDMH permeation apparatus. (A) Air for IRFNA or nitrogen for UDMH. (B) Rotameter. (C) Sampling port (allows the detector to withdraw aliquot while excess is vented). (D) Series 7000 Ecolyzer NO_2 analyzer for IRFNA study, or Interscan model 1186 hydrazine analyzer for UDMH study.

Instruments Development, Inc. Air Products extra-dry nitrogen was used as the sweep and dilution gas for the UDMH study.

D. PROCEDURES: IRFNA PERMEATION

In each experiment, 0.2 ml of liquid IRFNA was applied to the top of the fabric (t = 0.0 min.) and the concentration of NO_2 vapor below the fabric was detected by means of a Series 7000 Ecolyzer and recorded as a function of time. Since IRFNA may be described as nitric acid (HNO_3) with excess dissolved NO_2, the observation of NO_2 permeation is indicative of one type of fabric failure. Two characteristic permeation times are reported for each experiment: t_L, which is the time at which the NO_2 concentration reaches the lower detection limit of the Series 7000 Ecolyzer (0.3 ppm in 2 ℓ/min sweep air), and t_H, which is the time at which the NO_2 concentration reaches the upper detection limit (2.0 ppm in 2 ℓ/min sweep air). The instantaneous NO_2 permeation rate may be obtained from our concentration data by multiplying the concentration in ppm by 0.28 gm NO_2/m^2 hr ppm (e.g., 0.3 ppm NO_2 = 0.08 gm NO_2/m^2 hr).

The small pool of liquid IRFNA (which did not cover the entire surface of the fabrics) was typically observed on the surface throughout the duration of the test. An exposure volume of 0.2 ml was chosen as a compromise between the extremes of a minimum liquid volume and complete surface coverage. Determining the effect of exposure volume upon breakthrough times t_H and t_L, and (perhaps) upon the relative ordering of fabric permeation resistances, was beyond the scope of this study.

Liquid IRFNA contains 1% HF. No measurement of HF permeation was carried out. Tests showed that HF permeation would not have interfered significantly with the ability of the Series 7000 Ecolyzer to detect NO_2.

E. PROCEDURES: UDMH PERMEATION

The liquid UDMH permeation tests and data handling were carried out in the same manner as described for the liquid IRFNA permeation tests. Each test was initiated by the application of 0.2 ml of liquid UDMH to the test sample, and the small pool of liquid (which did not entirely cover the surface) was

observed to remain on the surface throughout the test. UDMH permeation was detected by the Interscan hydrazine analyzer, and the UDMH concentration in the sweep gas was recorded as a function of time. The characteristic times t_L and t_H for this system are determined at 20 ppb and 750 ppb levels of UDMH in 2 ℓ/min sweep nitrogen. For our setup the instantaneous permeation rate equivalent to a UDMH concentration in ppb is obtained by multiplying by the conversion factor 7.7×10^{-4} gm UDMH/m^2 hr ppb (e.g., 20 ppb UDMH = 7.4×10^{-3} gm UDMH/m^2 hr).

F. PROCEDURES: CALIBRATION

The Series 7000 Ecolyzer NO_2 analyzer has a usable dynamic range of one order of magnitude and can detect NO_2 at ~ 0.3 ppm with a signal-to-noise ratio of ~ 3. It was calibrated on a daily basis by means of Matheson-certified 100 ± 2 ppm NO_2 in air, a simple dilution apparatus, and rotameters. The Interscan hydrazine analyzer was calibrated on a daily basis by means of a UDMH permeation tube held at 70°C, a simple dilution apparatus, and rotameters. The rotameters were calibrated by means of a wet-test meter or the bubble displacement method, depending upon the flow rate. The UDMH concentrations generated by the calibration system were verified by traditional wet-chemistry colorimetric methods,[23-24] after they were collected with a solid sorbent.[24]

III. RESULTS

A. GLOVES

The 28 gloves studied in the liquid IRFNA and UDMH permeation tests are listed in Table 1. The manufacturer, model number, material composition, and average thickness are provided. The gloves are grouped mainly by composition within the major classifications of unsupported gloves (1-22) and supported gloves (23-28). The average thickness for each composition grouping is also given.

The permeation rate results are summarized in Table 1, which lists the measured breakthrough times t_L and saturation times t_H for glove palm sections. N indicates that no permeation was observed for 90 min. The experimental uncertainty in t_L and t_H is ± 1 min or less. The variation in t_L or t_H exhibited by several glove models is more likely to be due to variability in the quality control of the glove manufacturer than in our experimental procedure.

The individual breakthrough times for NO_2 and UDMH are plotted in Figs. 2 and 3, respectively, for the 28 glove models. The number in parenthesis represents the number of replicate data points that overlap within experimental uncertainty.

No permeation times were reported for the liquid IRFNA study of glove palms 10 and 11. Both gloves produced saturated negative responses on the Ecolyzer NO_2 analyzer within 1.5 min of the addition of 0.2 ml of IRFNA to the palm section. A mass spectrometric investigation into this phenomenon indicated that nitrous oxide (N_2O) and sulfur dioxide (SO_2) are released from the unexposed side of the fabric prior to NO_2 detection. Reaction (1) is thermodynamically spontaneous and exothermic,

$$4NO_2 + 3S \rightarrow 2N_2O + 3SO_2 \qquad (1)$$

Table 1. Breakthrough Times for Glove Palms following Exposure to Liquid IRFNA or UDMH

Glove No.	Manufacturer	Stock No.	Composition	Lining	Thickness (mm)	IRFNA		UDMH	
						t_B (min)	t_B (min)	t_B (min)	t_B (min)
1	Edmont Wilson	29-870	Neoprene	None	0.46	N[a]	N	39/38	47/54
2	Playtex	Blue 834	Neoprene/natural rubber	Flocked	0.41	N	N	9/8	11/10
3	Playtex	Yellow 834	Neoprene/natural rubber	Flocked	0.41	N	N	10/2	11/11
4	Playtex	Green 4156	Neoprene/natural rubber	None	0.41	N	N	9/7	12/9
5	Glover	SL-868	Natural rubber	Flocked	0.53	N	N	13/14	16/18
6	Granet	541	Natural rubber	None	0.46	N	N	6/7	8/9
7	Edmont Wilson	26-665	Case hardened natural rubber	Flocked	0.46	N	N	17/14	21/18
8	Edmont Wilson	46-322	Case hardened natural rubber	None	0.43	N	N	11/11	13/13
9	Edmont Wilson	26-669	Case hardened natural rubber	None	0.38	N	N	14/10	16/12
10	Edmont Wilson	46-321	Natural rubber (sprayed grip)	None	0.23	Neg. resp.	-	3.6/3.6	4.5/4.2
11	Edmont Wilson	46-320	Natural rubber (smooth)	None	0.23	Neg. resp.	-	3.6/3.6	4.2/4.2
12	Edmont Wilson	37-175	Case hardened nitrile	Flocked	0.38	N	N	16/14	23/19
13	Edmont Wilson	37-155	Case hardened nitrile	None	0.38	N	N	9.	15.
14	Edmont Wilson	37-145	Case hardened nitrile	None	0.28	N	N	6.	7.5/7.5
15	Norton	LA-111-EB	Nitrile	None	0.28	N	N	7/7	8/8
16	Norton	B-324	Butyl	None	0.91	N	N	N	N
17	Norton	B-174	Butyl	None	0.43	N	N	N	N
18	Norton	B-131	Butyl	None	0.33	N	N	N	N
19	Norton	F-121	Viton	None	0.30	N	N	13/12	13/13
20	Pioneer Rubber	V-30	PVC	None	1.02	41/34	44/37	47/41	61/61
21	Pioneer Rubber	V-20	PVC	None	0.51	13/12	14/13	14/13	16/16
22	Pioneer Rubber	V-10	PVC	None	0.25	4/9	4/9	2/3	3/3
23	Edmont Wilson	3-318	Supported PVC	Fabric	1.14-1.19	40/53	65/90	35/40	60/67
24	Edmont Wilson	4-454[b]	Supported PVC	Fabric	1.02-1.14	36/26	48/33	17/19	21/25
25	Edmont Wilson	13-158	Supported PVC	Fabric	0.94-1.02	55/70	84/>90	28/35	40/50
26	Edmont Wilson	9-928	Supported Neoprene	Fabric	1.27-1.35	N	N	67/79	>90/>90
27	Edmont Wilson	19-938	Supported Neoprene	Fabric	1.32-1.40	N	N	N	N
28	Edmont Wilson	15-554	Supported PVA	Fabric	0.94-1.02	0.1/0.4	0.1/0.2	8/16	12/22

[a] N indicates that there was no detectable permeation during the 90-min duration of the testing.
[b] The glove we tested was purchased from Standard Safety and had a stock number 505525. However, Standard Safety does not fabricate the glove, but merely modifies the gauntlet on the Edmont Wilson 4-454 glove.

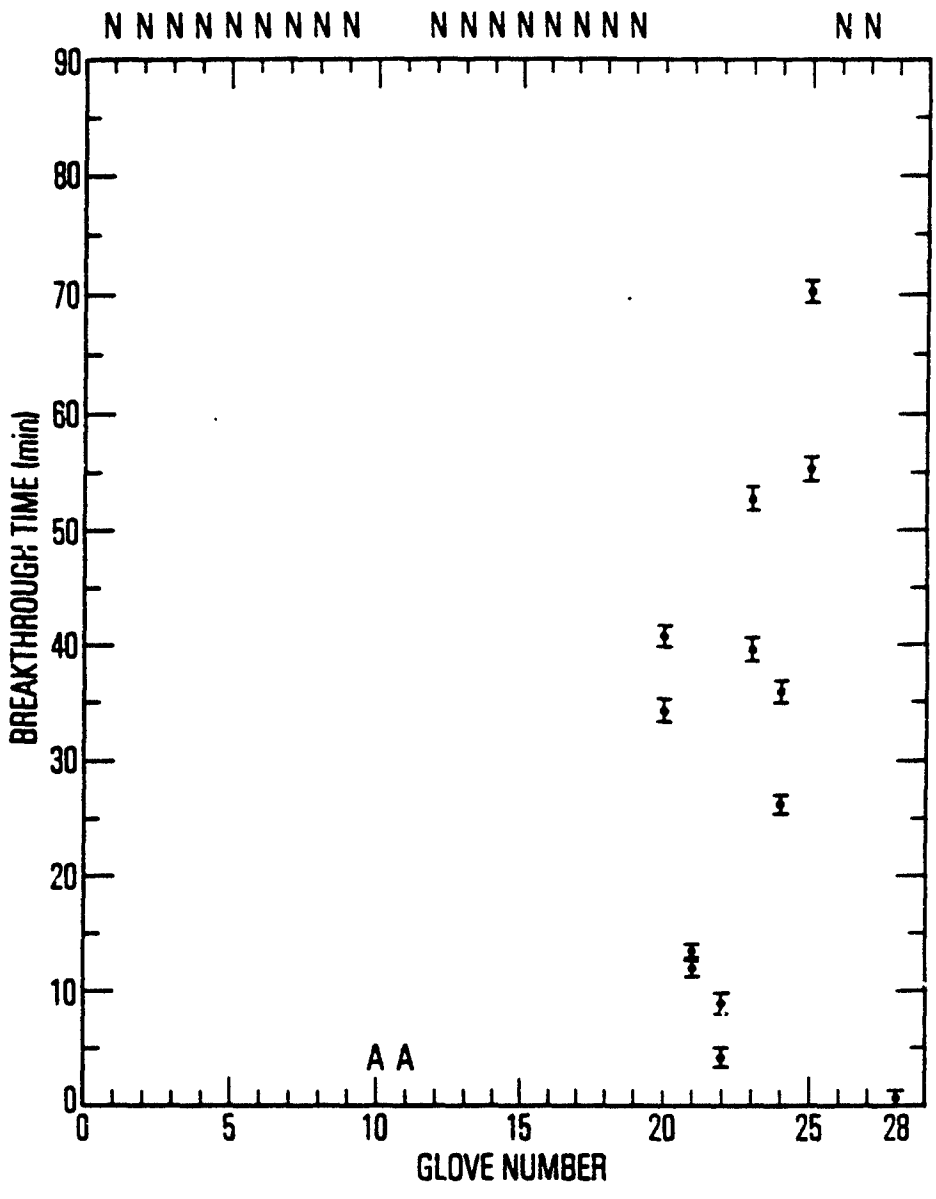

Fig. 2. NO_2 breakthrough times following exposure of glove palms to liquid IRFNA. N indicates that there was no detectable NO_2 permeation during the 90-min duration of the monitoring. ‡ indicates the error limits that can be assigned to experimental procedures, as opposed to the data scatter caused by variation in sample quality. (A) Glove palms found to be incompatible with our test procedure. (Therefore, no breakthrough times can be reported for their IRFNA testing.)

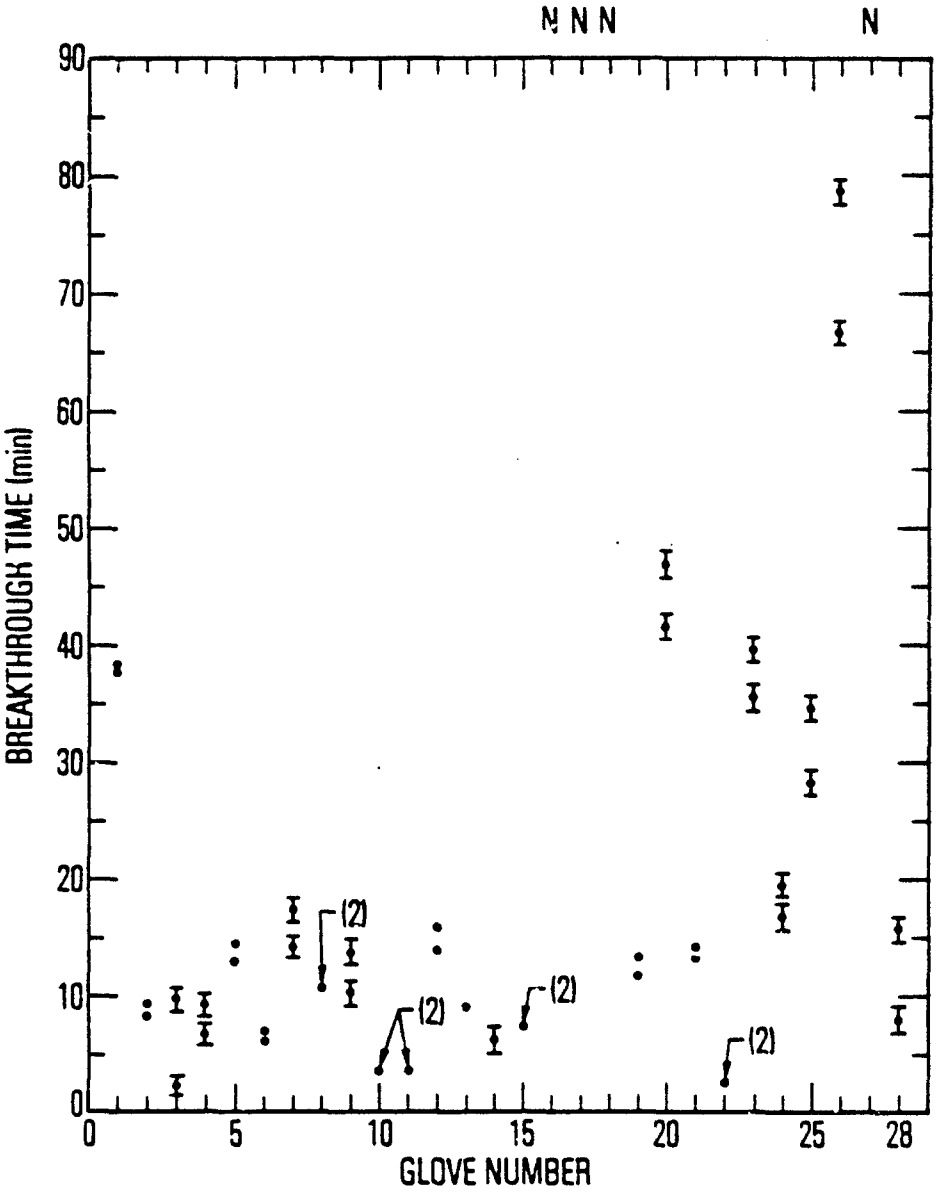

Fig. 3. UDMH breakthrough times following exposure of glove palms to liquid UDMH. N indicates that there was no detectable UDMH permeation during the 90-min duration of the monitoring. ± indicates the error limits that can be assigned to experimental procedures, as opposed to the data scatter caused by variation in sample quality.

and generically accounts for the N_2O and SO_2 as products of oxidation of sulfur (S) contained in the natural rubber. It was experimentally determined that the Ecolyzer registered no response to N_2O, whereas it registered a large negative response to 6 ppm SO_2 in air. Since the t_L and t_H values in Table 1 and Fig. 2 are defined in terms of NO_2 concentrations, no values can be reported for gloves 10 and 11 because of the presence of an unknown amount of SO_2 interference. When larger volumes (0.4 ml) of liquid IRFNA were applied to the palms of gloves 10 and 11, the initial negative Ecolyzer response was followed by a positive response occurring at 20 min (glove 10) and at 8 min (glove 11) after the IRFNA application. These results can be explained by the consumption of the smaller (0.2 ml) volume of IRFNA by reaction with the natural rubber, whereas with larger amounts of IRFNA, NO_2 permeates after locally depleting the sulfur in the glove sample.

We tested for permeation on sections cut from various portions of a few gloves. The results of two of these investigations illustrate the sensitivity of breakthrough times to the area sampled. IRFNA permeation testing was performed on sections of glove 27, with breakthrough times (t_L) ranging from no detectable permeation for 90 min for sections cut from either the palm or wrist, to 1.5 min for the gauntlet section. UDMH permeation testing was performed on sections cut from glove 12, with t_L ranging from 14 and 16 min for two palm sections, to no detectable permeation for 90 min for the wrist section.

B. SUIT FABRICS

Nine suit fabrics, described in Table 2, were subjected to liquid IRFNA and UDMH permeation tests. At least five permeation tests were performed on each fabric with each of the hypergols (using fresh samples for each test). The average values and the standard deviations are reported for t_L and t_H in Table 2. The individual values of t_L for the IRFNA and UDMH tests are presented in Figs. 4 and 5.

C. BOOTS AND HOOD WINDOW

Two Tingley boots and a hood window (Standard Safety) were tested for compatibility with the oxidant liquid IRFNA and the fuel liquid UDMH. Samples

Table 2. Breakthrough Times for Suit Materials following Exposure to Liquid IRFNA or UDMH

Fabric No.	Manufacturer	Stock Name or No.	Composition	Thickness Listing	(mm)	IRFNA		[redacted]	
						t_L (min)	t_B (min)	t_L (min)	t_B (min)
1	Aerohead Products	RFNCO[b]	Chlorobutyl-coated Nomex	None	0.51	[a]N(5)	[a]N(5)	N(5)	N(5)
2	ILC Dover	Chloropel	Chlorinated polyethylene	None	0.51	27 ± 1	28 ± 2	30 ± 2	30 ± 2
3	Standard Safety	Winter Glo 20	PVC Percale	0.71–0.76	15 ± 2	17 ± 1	9.6 ± 0.2	12.4 ± 0.3	
4	Rich Industries	3777	PVC/Nylon ocrin/PVC	None	0.30	7.0 ± 0.1	7.3 ± 0.1	4.5 ± 0.2	4.7 ± 0.2
5	Standard Safety	Ora-Lite 20	PVC Percale	0.71–0.76	22 ± 2	26 ± 3	20 ± 2	26 ± 3	
6	Standard Safety	Whiteside	PVC None	0.46–0.51	2.4 ± 0.3	4.4 ± 0.5	0.32 ± 0.26	1.2 ± 0.2	
7	Rich Industries	3778	Aluminized Mylar/nylon ocrin/PVC	None	0.38	1.9 ± 0.5	2.7 ± 0.9	N(5)	N(5)
8	Standard Safety	Ora-Lite	PVC Percale	0.58–0.64	4 ± 1	6 ± 2	3 ± 1	5 ± 2	
9	Standard Safety	Winter Glo	PVC None	0.46–0.51	0.34 ± 0.27	0.8 ± 0.3	1.4 ± 0.9	1.7 ± 0.7	

[a]N indicates that there was no detectable permeation during the 90-min. duration of the test. The number in parentheses indicates the number of experiments performed.

[b]RFNCO: This DuPont material, #23219-41-1, had been used in the RFNCO. Currently a different DuPont material, #23219-119-1, is being used in the RFNCO.

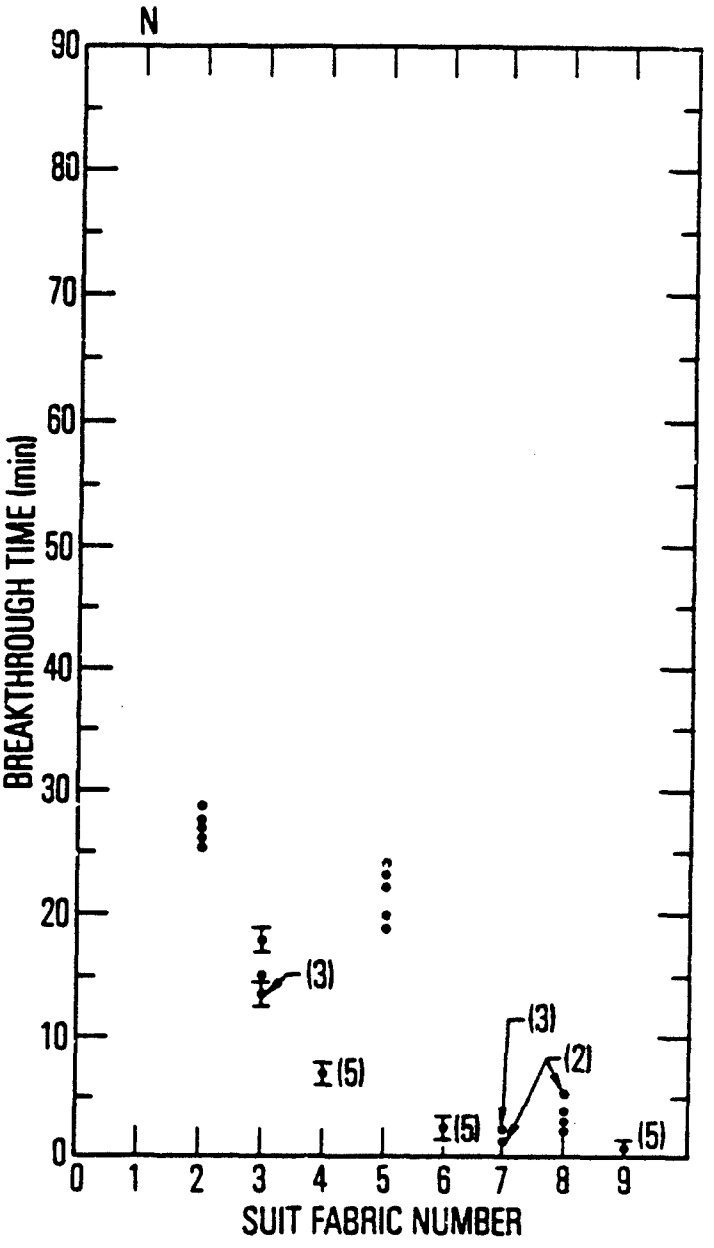

Fig. 4. NO_2 breakthrough times following exposure of suit fabrics to liquid IRFNA. N indicates that there was no detectable NO_2 permeation during the 90-min duration of the monitoring in five experiments. The numerals in parentheses indicate the number of experiments having the same outcome within experimental limits. ⧗ indicates the error limits that can be assigned to experimental procedures, as opposed to the data scatter caused by variation in sample quality.

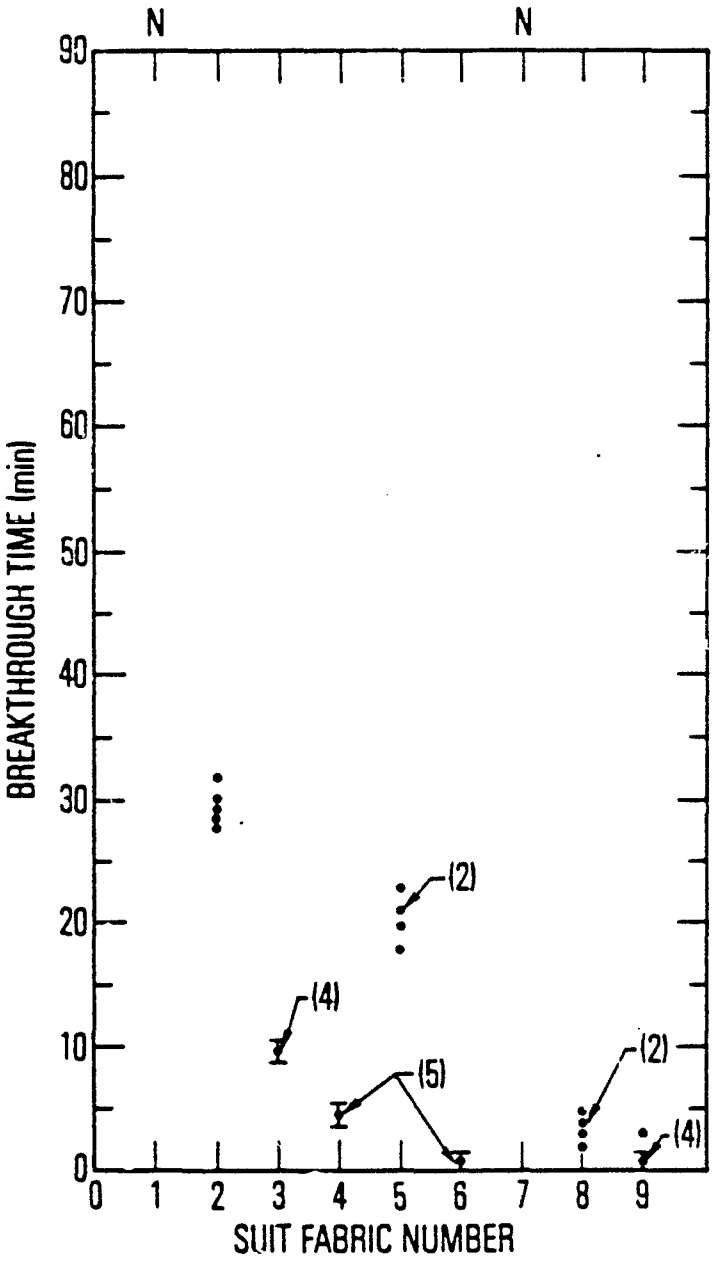

Fig. 5. UDMH breakthrough times following exposure of suit fabrics to liquid UDMH. N indicates that there was no detectable UDMH permeation during the 90-min duration of the monitoring in five experiments. The numerals in parentheses indicate the number of experiments having the same outcome within experimental limits. ‡ indicates the error limits that can be assigned to experimental procedures, as opposed to the data scatter caused by variation in sample quality.

were taken from the ankle region of the 45 ± 5 mil natural rubber (model 1400) and the 45 ± 5 mil Neoprene (model 1440) 254-mm-high (10-in.) Tingley boots. Both boots withstood the 90-min IRFNA and UDMH testing without detectable permeation. The 40-mil PVC hood window survived the 90-min oxidant and fuel exposure without detectable permeation but with impaired transparency.

IV. DISCUSSION

A. GLOVE PERMEATION

The relative resistance of 28 commercially available glove models to NO_2 permeation following exposure to liquid IRFNA, and to UDMH following exposure to liquid UDMH, was established by using material sections cut from the palm as the standard for comparison. Nineteen of the 28 models resisted NO_2 permeation for the 90-min duration of the test. Four of the 28 resisted UDMH permeation for the 90 min.

It was found that, for the particular glove models chosen, all six neoprene-containing materials (three neoprene, three neoprene/natural rubber combinations), all four nitrile, all three butyl, and the single Viton-containing material resisted NO_2 permeation for 90 min. We conclude that these specific glove models should be among the first considered when exposure to liquid IRFNA is possible. It would be invalid to generalize that all glove models containing neoprene, nitrile, butyl, or Viton are resistant to liquid IRFNA since many factors, including thickness, the detailed composition, the manufacturing procedure, and the manufacturer's quality control, determine the performance potential of a commercial product.

The results of our tests involving glove sections made of natural rubber illustrate that it is invalid to generalize from specific test results to generic capabilities. Seven natural rubber glove materials (and three neoprene/natural rubber samples counted above among the neoprene group) were resistant for longer than 90 min, while two models reacted with liquid IRFNA and released SO_2 within 2 to 3 min. The models that reacted (10 and 11) were the thinnest natural rubber models tested. It is unknown whether the failure of these gloves was due to a difference in composition or manufacturing process, or simply that 0.2 ml of IRFNA was sufficient to consume 0.23 mm of natural rubber, but not 0.38 mm (the next thicker natural rubber). It was beyond the scope of this study to determine the failure mechanisms for gloves or suits that resisted permeation for less than 90 min.

The single PVA glove model, ~ 1.0 mm thick, was permeated almost instantly (0.1 - 0.2 min). This model is clearly incompatible with liquid IRFNA. The six PVC glove models were all permeated in less than 90 min. The breakthrough times increased with increasing thickness for the three Pioneer PVC gloves (20, 21, and 22), increasing from ~ 5 min for 0.25-mm material to ~ 40 min for 1.0-mm thickness. The three Edmond Wilson PVC models (23, 24, and 25), with thicknesses of ~ 0.9 - 1.2 mm, had breakthrough times of 26 to 50 min. The consistent permeation of all six PVC glove models in less than 90 min suggests that PVC should not be among the first materials to be considered when exposure to liquid IRFNA is possible. We return to a discussion of the compatibility of PVC with IRFNA while addressing the results of the suit material tests.

Only four of the 28 glove models included in our study resisted UDMH permeation following exposure to liquid UDMH for more than 90 min. All three butyl gloves, ranging in thickness from 0.3 to 0.8 mm, were resistant to UDMH for the full 90 min. Among the limited selection of materials and models we tested, butyl rubber is clearly the first choice (from the perspective of chemical protection) for consideration when exposure to liquid UDMH is possible. The "all" neoprene models (1, 26, and 27) afforded protection with breakthrough times increasing from 40 min for 0.46-mm material (1) to more than 90 min for 1.3 - 1.4-mm material (27). Note that 0.33-mm butyl permeation resistance is indistinguishable, within the scope of this test program, from that afforded by ~ 1.4-mm neoprene. The breakthrough times of the mixed neoprene/natural rubber glove palms (2, 3, and 4) were ~ 10 min for 0.4-mm-thick material in comparison with ~ 40 min for 0.46-mm "all" neoprene (1). The nitrile, natural rubber, PVA, and Viton samples tested had breakthrough times ranging from 4 to 15 min. These models should definitely not be among the first considered when exposure to liquid UDMH is possible. The PVC sample with thickness of 0.5 mm, comparable to the thickness of the nitrile, natural rubber, neoprene/natural rubber, nitrile, and Viton samples, had a comparable breakthrough time of 15 min. The thin sample, 0.25 mm, had t_B ~ 4 min; the thick samples, 0.9 to 1.2 mm, had breakthrough times from 20 to 40 min. Thus the PVC models tested performed no better than the comparable models of nitrile, natural rubber, or Viton against exposure to liquid UDMH.

The three butyl models tested clearly performed best against liquid UDMH (one thick neoprene model also resisted UDMH permeation for longer than 90 min). The other models offered less resistance to liquid UDMH and should be considered only when the superior chemical protection of the three butyl models is not the most important factor in the choice of a protective glove.

B. SUIT MATERIAL PERMEATION

We have established the relative resistance of the nine commercial suit materials toward permeation by NO_2 after exposure to liquid IRFNA and toward UDMH permeation after exposure to liquid UDMH. The results of the five replicate exposures provide preliminary data regarding the uniformity of each material's resistance to permeation. Permeation was observed in neither the five IRFNA nor the five UDMH tests of the chlorobutyl-coated Nomex material (fabric 1).

Fabric 1 was used in the Rocket Fuel Handler's Clothing Outfit (RFHCO) and exhibited the excellent permeation resistance demonstrated by other[16,17] chlorobutyl materials. Fabric 1 is DuPont material number 23219-41-1 and has been replaced by fabric number 23219-119-1, which is now being used in the RFHCO. The RFHCO chlorobutyl material is used in Air Force and NASA propellant transfer operations in which there is potential for exposure to hypergolic propellant liquid or concentrated vapor.

We observed no UDMH permeation in tests of the aluminized Mylar/nylon scrim/PVC, fabric 7. This material should be considered along with the chlorobutyl material, when exposure only to UDMH is considered a possibility. Its rapid (~ 2 min) permeation by NO_2 should preclude its use when exposure to liquid IRFNA is possible.

The chlorinated polyethylene, fabric 2, had t_H and t_L values of about 30 min after exposure to liquid IRFNA. Of the materials tested, this material would be a second choice to chlorobutyl where chemical resistance to both liquid IRFNA and UDMH is necessary.

Fabrics 3 and 5 (Winter Glo 20 and Gra-Lite 20) are the most interesting examples, in this study, of permeation resistance being a function of the detailed composition of the fabric. They also illustrate the danger in

extrapolating from the performance of one material to that of a "similar" material. Fabrics 3 and 5 are PVC-based materials of the same thickness (0.71 mm) made by the same manufacturer. Their permeation resistance differs significantly: 15 min versus 22 min against liquid IRFNA and 10 min versus 20 min against liquid UDMH. Winter Glo 20 (fabric 3) is intended for use in cold weather where enhanced flexibility is required. This is achieved by using a different plasticizer than that used in Gra-Lite 20 (fabric 5). This apparently accounts, at least in part, for their different resistances to permeation by IRFNA and UDMH. The four other PVC-based fabrics (4, 6, 8, and 9) had thicknesses ranging from 0.3 mm to 0.6 mm. They provided comparatively little protection against permeation by either NO_2 or UDMH, with breakthrough times ranging from 7 min to 0.3 min. All six PVC-based fabrics provided less protection against permeation than did the chlorobutyl SCAPE fabric (1) or the chlorinated polyethylene fabric (2).

C. THE INTERPRETATION OF OUR BREAKTHROUGH TIME MEASUREMENTS

Breakthrough times as defined in our experiments (NO_2 or UDMH permeation as detected by an electrochemical detector) may differ from times obtained by other techniques because of differences in the test parameters; those parameters are detection limits, the area of fabric exposed, and sensitivity to interferences created by fabric decomposition. Two gloves exhibited "negative" Ecolyzer responses, which were apparently caused by SO_2 production. It may be possible that other reactions produced compounds that cause a positive Ecolyzer response. Since it is unlikely that interference would exactly cancel out the detector response to NO_2 or UDMH, the "no-detectable-permeation" results indicate that NO_2 or UDMH truly failed to permeate within the 90-min test. The failure to permeate could indicate either fabric resistance to permeation by the hypergol or complete reaction of the hypergol with the material.

It is possible that exposure of protective materials to either IRFNA or UDMH may result in the generation of products more toxic than the original IRFNA or UDMH. These might go undetected in electrochemical detector-based studies. A definitive permeation study will require the use of a universal

detector such as a mass spectrometer to establish the identity of permeants as a function of time.

D. PERFORMANCE PREDICTION BASED UPON THESE RESULTS

It is invalid to extrapolate from our test results to a prediction of performance in actual use. If we consider that the suit fabric test pieces were cut from relatively new bolts of material, and that the glove pieces were cut from the thickest section of unused gloves and not repeatedly exposed to hypergolic material, sunlight, solvents, abrasion, or flexing before exposure, then we must conclude that the measured t_L and t_H values are best case results. The relative ordering might have been different had we studied samples repeatedly stressed for 6 months or a year. It is unlikely that the magnitude of the breakthrough or saturation times would be increased by such stress. The actual safety margin (between external exposure and internal breakthrough) afforded by the use of a given material that had a t_L value of 10, 20, 30, or even 90 min is thus unknown.

An alternative analysis, based upon the supposition that a person exposed to liquid IRFNA or UDMH would not keep a drop of liquid on one spot for any extended period, leads to a conclusion that these are worst case results. If one considers that the most likely exposure involves vapor rather than liquid, and that such exposures are less stressful than exposures involving liquid, then our results are worst case results.

The glove palm breakthrough times cannot be extrapolated to the performance of whole gloves, even under conditions identical to those of the tests. As illustrated by testing performed on gloves 12 and 27 (see the glove results section), the breakthrough times can depend strongly upon the portion of the glove that is exposed. Whole glove performance will likely depend upon the most easily permeated portion, which, in turn, may vary from glove to glove.

There is another type of limitation to the application of these test results to the prediction of performance: manufacturers of suit materials or gloves have been known to change the chemical composition of a fabric or glove, or its manufacturing process, without changing the product designation, such as model number or name, and without notifying users. Any change in the

composition or manufacturing process might significantly change the permeation resistance of a product—invalidating the results of even the most realistic performance testing.

The final caveat is that our test results might give no indication of the relative performance of other butyl, nitrile, or PVC-based products toward liquid IRFNA or UDMH, as the detailed composition, the manufacturer, and the quality control of the supplier can vary. Just as certainly, our breakthrough times should not be used in the definition of operational procedures.

V. SUMMARY AND CONCLUSIONS

The relative resistance of 40 items of protective equipment to permeation by NO_2 after exposure to liquid IRFNA and to permeation by UDMH after exposure to liquid UDMH was established. Our results are useful as a first screening of these specific protective materials. Palm sections of specific glove models made of butyl, neoprene, nitrile, natural rubber, and Viton resisted NO_2 permeation for the full 90-min duration of the tests. NO_2 permeation was observed for all the PVC samples, the single PVA sample, and two of the six natural rubber samples tested. The three butyl models and one of the six neoprene models were the only palm samples that resisted UDMH permeation for the full 90 min. In the other palm sections examined, permeation occurred between 0.1 min and ~ 80 min following application of liquid UDMH or IRFNA.

Of the nine suit fabrics examined, only chlorobutyl-coated Nomex resisted permeation by both NO_2 and UDMH for more than 90 min. The aluminized Mylar/nylon scrim/PVC material resisted UDMH permeation for more than 90 min; it was permeated by IRFNA in ~ 2 min. The chlorinated polyethylene fabric resisted NO_2 and UDMH permeation for ~ 30 min in each case. Six PVC materals were tested; permeation was observed to occur in each case, with breakthroughs occurring between 0.4 min and 22 min, depending upon the specific PVC fabric.

We must be circumspect and not generalize too broadly on the basis of this study. A limited selection of commercially available equipment was studied, the tests were static and limited to small samples, permeation was detected by reagent-specific monitors, glove tests were of palm sections, and quality assurance programs are not in place to protect the user from manufacturing changes that may alter the degree of chemical permeation protection afforded by a given material. It is certainly reasonable to suggest, however, that the butyl and the chlorobutyl rubbers be the first materials from our test group to be considered (from the perspective of permeation resistance) when exposure to <u>both</u> liquid IRFNA and UDMH is possible. Further, it is evident that no item of protective equipment should be adopted without specific chemical compatibility testing, that procedures are needed to ensure

quality control in adopted equipment and, finally, that the performance of a specific model of protective equipment cannot be predicted with certainty from the performance of other models made of similar materials, even when all are made by the same manufacturer.

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APPENDIX: CATEGORIES OF HAZARDS REQUIRING PROTECTIVE EQUIPMENT

The selection of protective equipment for a particular NASA or Air Force operation is based upon recognition of the hazards that are present or might be encountered. Consideration is given not only to the obvious dangers of exposure to the propellant, but also to the hazards associated with heat stress and reduced dexterity. Equipment must provide adequate protection from the propellant without eliminating the possibility of a self-rescue that could involve a 5-min egress from a servicing tower.

Three general categories are considered in the use of protective equipment: (1) potential exposure to pressurized propellant (the greatest hazard); (2) hand protection for operations in a "shirt sleeves" environment; and (3) high work load (potential heat stress), complex manipulation, limited work space, and the potential of exposure to low concentrations of vapor or limited quantities of propellant presenting hazards of comparable magnitude.

In the first category the Rocket Fuel Handler's Clothing Outfit (RFHCO) is used. It consists of a fitted, zipper-locked, full-body chlorobutyl-coated Nomex suit, a rigid helmet, boots, gloves, and a self-contained breathing apparatus backpack with a 1- to 2-hr air supply. The unit is maintained at a slight positive pressure, with air distributed throughout to minimize heat stress. The combination of bulky and heavy backpack, heavy suit, gloves, and positive pressurization limit the work load and dexterity associated with RFHCO use.

The second category requires maximum dexterity and resistance to permeation in the event of exposure to drops of propellant.

The requirements of the third category are the hardest to define, since an assessment of relative hazards might require more or less chemical protection in one operation than in another. Eight of the tested protective fabrics (fabrics 2-9, Table 2) are used or are being considered for adoption in category 3 working environments. In category 3 operations, a water washdown is required as soon as possible following contact with propellant. Our studies

indicate that some fabrics are almost instantly permeated by UDMH or IRFNA and that others might give less than 5 min of protection. The use of fabrics 2 through 9 imposes severe systems safety constraints on operations, since self-rescue and washdown must be feasible within the limited protection time that the materials provide following their contact with liquid hypergolic oxidizer or fuel.

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry aerodynamics and heat transfer, propulsion chemistry and fluid mechanics, structural mechanics, flight dynamics; high-temperature thermomechanics, gas kinetics and radiation; research in environmental chemistry and contamination; cw and pulsed chemical laser development including chemical kinetics, spectroscopy, optical resonators and beam pointing, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and bioenvironmental research and monitoring.

Electronics Research Laboratory: Microelectronics, GaAs low-noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter-wave and microwave technology.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; component failure analysis and reliability; fracture mechanics and stress corrosion; evaluation of materials in space environment; materials performance in space transportation systems; analysis of systems vulnerability and survivability in enemy-induced environments.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.