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Important Experimental Parameters for the
Nitrogen Dioxide Permeation Testing of the
Propellant Handler's Ensemble Coverall Material

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20030121129

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-83-C-0086 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. P. Thompson, Jr., Director, Aerophysics Laboratory.

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SD-TR-86-14	2. GOVT ACCESSION NO. AD-A166719	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) IMPORTANT EXPERIMENTAL PARAMETERS FOR THE NITROGEN DIOXIDE PERMEATION TESTING OF THE PROPELLANT HANDLER'S ENSEMBLE COVERALL MATERIAL		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) Robert N. Abernathy		6. PERFORMING ORG. REPORT NUMBER TR-0086 (6452-30)-1
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		8. CONTRACT OR GRANT NUMBER(s) F04701-85-C-0086
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Los Angeles Air Force Station Los Angeles, Calif. 90009-2960		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 7 April 1986
		13. NUMBER OF PAGES 74
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemturion Dinitrogen tetroxide Chlorinated polyethylene Hydrazine Chlorobutyl MMH Cloropel Nitrogen dioxide Concentration dependence Nitrogen tetroxide		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We reviewed a NASA and an Air Force permeation test procedure and found them to be inadequate for their intended purpose of being standards for inter-laboratory comparison of the permeation resistance of material samples. In order to evaluate the importance of the various experimental parameters that were neither defined nor controlled by these earlier test specifications, we developed a new permeation test apparatus and procedure and applied them to the evaluation of the experimental parameters and several coverall materials.		

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19. KEY WORDS (Continued)

Permeation
PHE
Propellant Handler's Ensemble
Propellants
RFHCO
Rocket Fuel Handler's Clothing Outfit

Rubber
Temperature dependence
Testing

20. ABSTRACT (Continued)

In this report we describe a test apparatus and detailed procedure for carrying out reproducible conditioning of material samples by controlled exposure to known volumes of liquid hypergols at a well-defined temperature as well as subsequent quantitative permeation testing of the conditioned samples under conditions of controlled temperature, absolute pressure, differential pressure, and equivalent concentration of dinitrogen tetroxide vapor (N_2O_4). We applied this apparatus to the nitrogen dioxide (NO_2) permeation testing of three materials: the E. I. du Pont de Nemours chlorobutyl material currently used in the construction of the Rocket Fuel Handler's Clothing Outfit (RFHCO), the du Pont chlorobutyl material proposed for use in the Propellant Handler's Ensemble (PHE), and the ILC Dover chlorinated polyethylene material currently used in the Chemtursion (CHEM) protective ensemble. The CHEM material is also known as Cloropel.

Our results for samples of the PHE coverall material indicate that the NO_2 breakthrough occurs faster when the temperature at which the permeation test is performed is reduced for a fixed " N_2O_4 concentration," or when the " N_2O_4 concentration" is increased for a fixed permeation test temperature. The " N_2O_4 concentration" is the concentration of N_2O_4 that would exist if there were no dissociation into NO_2 . Therefore, these experimental parameters, which were not defined in the earlier NASA and Air Force permeation test procedures, should be defined and controlled in future tests.

Both the RFHCO and PHE coverall materials resisted NO_2 permeation for more than 60 min under all test conditions that were investigated. Therefore, they exhibited satisfactory resistance to NO_2 permeation according to the NASA specification for the PHE coverall material. On the other hand, the CHEM coverall material deteriorated severely during the conditioning and thus could not be evaluated according to the NASA qualification test procedure.

PREFACE

I would like to acknowledge the great laboratory skills of Sunne Genova, who performed most of the laboratory work associated with this and the preceding permeation test programs. I would also like to thank Eric Fournier for his assistance and effort-saving ideas, Doug Schulthess for his occasional assistance when someone became ill, and Alan Knowles for the design of our solenoid valve controller. Ronald Rianda and Ronald Cohen also provided helpful suggestions during this and the preceding permeation test programs. I would also like to thank Sherwin Lewis and Roberta Gleiter for their continued interest and support throughout this test program. Last, but not least, I would like to acknowledge the U.S. Air Force for its support.

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I. INTRODUCTION

A. PROBLEM AND PURPOSE

The NO₂ permeation test procedures that have been used to evaluate the new Propellant Handler's Ensemble (PHE) coverall material did not adequately define the important experimental parameters. Therefore, in this report we critically review these permeation test procedures and describe a new permeation test apparatus and procedure that is intended to allow for interlaboratory comparison of NO₂ permeation results in future tests.

We have applied this test procedure and apparatus to three coverall materials in order to determine their permeation resistance under various experimental conditions and to establish the importance of the various experimental variables.

Our results have provided an important data base that established the need for improvements in the referenced military specifications for coverall materials. From our data we were able to make several recommendations for the new military specification when it was reviewed in 1984.

B. ORGANIZATION

This report is organized to allow rapid access to the various topics that are discussed. The introduction is broken into three sections. The purpose of this report is briefly defined in the above section. A background to the problem is given in the next section.

Section II of this report provides a detailed description of the earlier permeation test procedure and explains why it is inadequate.

Section III briefly describes the new test apparatus, the coverall materials, chemicals, and calibration techniques, and briefly outlines the main components of the new conditioning and NO₂ permeation testing procedures. The NO₂ breakthrough time is defined in this section. A more detailed description of the apparatus is provided in Appendix A. A more detailed description of the conditioning and permeation test procedures is provided in Appendix B.

Section IV presents the results and discussion of our NO₂ permeation tests. The discussion is broken into sections that refer to particular sets of data in order to establish the effect of each of the experimental parameters upon the time to attain NO₂ breakthrough (as defined in Section III).

The main experimental results and their implications for future permeation test procedures are summarized in Section V.

C. BACKGROUND

Personnel carrying out hypergolic propellant transfer operations for the Space Shuttle and for expendable launch vehicles such as Titan, Agena, and Scout require protective equipment to prevent their being exposed to toxic and hazardous vapors and liquids. NASA was the lead federal agency responsible for developing a new self-contained atmospheric protective ensemble called the Propellant Handler's Ensemble (PHE), designed for use in hypergolic transfer operations involving the following propellants: dinitrogen tetroxide (N₂O₄), hydrazine (HY), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The Air Force Systems Command's Space Division also participated in that development effort and contracted with ILC Dover to purchase PHEs to replace existing protective equipment.

As a result of the satisfactory performance of chlorobutyl materials used in the construction of earlier protective ensembles worn in hypergolic environments, ILC Dover selected a chlorobutyl material prepared by E. I. du Pont de Nemours and Co., Inc. (du Pont) for the construction of the PHE coverall. Since the specification of a generic material was not enough to ensure that its permeation resistance would be comparable with earlier formulations,¹⁻³ specific permeation testing of the proposed material was necessary. The NASA specification⁴ for the PHE specified a permeation test procedure and an acceptable permeation rate that are to be used to determine whether or not the du Pont material qualifies for use in the PHE.

Three laboratories carried out NO₂/N₂O₄ permeation tests on the PHE coverall material to determine its resistance to permeation by NO₂ and reported the following results:

1. A. D. Little, Inc. (ADL)⁵ reported that the PHE coverall material failed their NO₂ permeation test (NO₂ permeated the PHE coverall material after 30 min).
2. The Martin Marietta Corporation (MMC)⁶ reported that the PHE coverall material passed the military specification⁷ for permeation resistance but was permeated by the NO₂ after approximately 45 min.
3. The NASA Materials Testing Section (NASA-MTS)⁸ reported that the PHE coverall material resisted NO₂ permeation for more than 2 hr, indicating superior permeation resistance.

Because of the apparent conflict between the results reported by the three laboratories (which used three different permeation test procedures), the Air Force Systems Command's Space Division has continued to review the PHE program independently. Therefore, the Mission Assurance Directorate requested that we review the three permeation tests to evaluate the NO₂ permeation resistance of the du Pont chlorobutyl coverall material.

The Aerospace Corporation has reviewed the permeation tests in detail⁹ and enumerated the potentially significant deviations from the Qualification¹⁰ and Military Specification⁷ Test Procedures, which were evident upon close examination of the test procedures reported by ADL,⁵ MMC,⁶ and NASA-MTS.⁸ Since neither the Qualification nor the Military Specification Test Procedures were followed in the reported permeation tests, there are no reliable data that can be used to qualify the du Pont material for use in the PHE.

In response to the Program Office's request for guidance regarding the capability of the PHE chlorobutyl material to resist NO₂ permeation, we carried out a preliminary head-to-head comparison of the PHE material with two other chlorobutyl materials. Since the du Pont chlorobutyl material used in the Rocket Fuel Handler's Clothing Outfit (RFHCO) had previously been tested by MMC¹¹ and was found to have excellent resistance to hypergol permeation, we ranked the permeation resistance of the PHE material against the RFHCO material by using a N₂O₄ splash permeation test procedure that we had previously used to evaluate the relative resistance of 40 materials to permeation by NO₂.¹⁻³ By performing similar tests on the RFHCO material and the proposed PHE material, we ranked the permeation resistance of the two materials on a relative basis. If the PHE material had demonstrated NO₂ permeation

resistance equal or superior to that of the RFHCO material, then its permeation resistance would have been considered adequate for use. However, the results of our permeation tests¹² indicated that the PHE coverall material's NO₂ permeation resistance is inferior to that of the two other commercially available chlorobutyl materials included in our tests. Therefore, it was necessary to test the PHE material according to the Qualification Test Procedure and compare its permeation resistance to the acceptance criteria of the NASA specification.

A detailed examination of the Qualification and Military Specification Test Procedures revealed that these procedures lack experimental details concerning material conditioning, design criteria for the experimental apparatus, and control mechanisms for potentially important experimental parameters. Therefore, we concluded that these procedures are inadequate for their intended purpose of being standards for quantitative permeation testing and interlaboratory comparison.

In order to quantitate the PHE permeation resistance, we have developed a detailed test procedure and an improved test facility that allow control of all experimental parameters, including the following that had not previously been defined or controlled: the absolute temperature of the liquid hypergols and the permeation test apparatus, the absolute pressure during the permeation test, and the concentration of the N₂O₄ vapor during the permeation test. We applied this apparatus to the NO₂ permeation testing of three materials: the du Pont chlorobutyl material that is currently used in the construction of the Rocket Fuel Handler's Clothing Outfit (RFHCO), the du Pont chlorobutyl material proposed for use in the Propellant Handler's Ensemble (PHE), and the ILC Dover chlorinated polyethylene material that is currently used in the Chemtursion (CHEM) protective ensemble.

In this report we critically review the Qualification Test Procedure, describe our new test apparatus, and report our permeation test results. Our results not only provide a relative ranking of the NO₂ permeation resistance of the three coverall materials that were conditioned and tested under

identical experimental conditions, but also determine the effects of the various experimental parameters upon the NO₂ breakthrough time of the PHE coverall material. We conclude this report with recommendations for future permeation test procedures.

II. REVIEW OF THE QUALIFICATION TEST PROCEDURE

A. PHE QUALIFICATION TEST PROGRAM SPECIFICATIONS

The NASA specification for acceptance of a coverall material for use in the PHE requires NO_2 permeation testing according to a procedure that was developed by the Martin Marietta Corporation.⁴ This MMC test procedure, T79-80A, appeared in the Qualification Test Plan for Propellant Handler's Ensemble with Detailed Test Procedures.¹⁰

There are two parts to MMC test procedure T79-80A: (1) conditioning of the material by alternating exposures to liquid N_2O_4 and monomethylhydrazine (MMH), and (2) NO_2 permeation testing of the conditioned material. In the conditioning sequence the outside of the fabric is sequentially exposed to hypergols while the inside and edges are protected from direct exposure. The conditioning sequence in T79-80A consists of two cycles of the following: a 1-min exposure to liquid N_2O_4 , a 1-min water rinse, a 24-hr period of air drying, then a 1-min exposure to liquid MMH, a 1-min water rinse, and a 24-hr period of air drying.

The permeation test is carried out in a test cell that allows exposure of the conditioned side of the material to saturated $\text{N}_2\text{O}_4/\text{NO}_2$ vapor (at room temperature and atmospheric pressure) while simultaneously monitoring the concentration of NO_2 in the sweep gas that flows across the unexposed side of the material. Throughout the permeation test, the pressure on the unexposed side of the material is required to be 75 Pascals (0.3 in. of water) higher than on the exposed side.

Further, the test procedure specifies that the NO_2 concentration on the unexposed side of the material be monitored with an Ecolyzer NO_2 detector (an electrochemical detector) until either a sharp increase in NO_2 concentration occurs in the sweep gas or 2 hr have elapsed since the initiation of exposure. No pass or fail criteria are defined in the MMC T79-80A test procedure. The NASA specification⁴ for the PHE indicated that the results should be evaluated according to the requirements of an earlier Military Specification⁷ for other

chlorobutyl materials, wherein acceptable cumulative NO_2 permeation during the first hour of $\text{N}_2\text{O}_4/\text{NO}_2$ vapor exposure is specified to be 1.54×10^{-3} mg NO_2 cm^{-2} . For comparison this would be equivalent to an average of 0.17 ppm of NO_2 throughout the first hour, given the 2-l/min sweep air flow and the 24.6-cm^2 area of fabric used in our tests.

B. ADDITIONAL SPECIFICATIONS AND REQUIREMENTS

In the Qualification and Military Specification Test protocols, several potentially significant parameters were left to the choice of the experimenter or the control of ambient laboratory conditions. For the conditioning phase of the experiment, the uncontrolled parameters included (1) the volume of the liquid hypergol applied to the material and (2) the temperature of the liquid hypergol and the fabric. Since variations in these parameters could cause scatter in the test results, we designed a conditioning apparatus that allowed control and therefore specification of these parameters.

In the permeation test procedure, the experiment is carried out at ambient pressure [e.g. 101,000 Pascals (1 atmosphere) at sea level to 82,160 Pascals (0.811 atmosphere) in Denver]. Likewise, the temperature of the apparatus (this includes the temperature of the material) was unspecified. The vapor pressure and consequently the vapor concentration of N_2O_4 depend upon both ambient pressure and temperature. Since experiments^{13,14} have demonstrated that the permeation rate of compounds through fabrics has a complex dependence on the vapor-phase concentration of the substance to which the fabric is exposed, it is apparent that the absolute pressure, the permeation test temperature, and the concentration of the gases and vapors should be controlled and defined. Therefore, we designed a permeation test apparatus that allows control of these important experimental parameters.

In addition to the undefined and uncontrolled experimental parameters discussed in the above paragraphs, we have also addressed an earlier criticism regarding the conditioning of the material. NASA's Material Testing Section (NASA-MTS) has suggested⁸ that there may be preferential decay of the material at the sealing edge during conditioning as a result of incomplete rinsing of the hypergol, and that this could result in premature breakthrough during the

permeation testing. In order to eliminate this concern, NASA-MTS used Krytox grease on the Teflon gasket material in their conditioning cell and performed a second water rinse (which was not documented in their report) after the material was removed from the conditioning apparatus.

In order to avoid not only the potential effects of the proposed preferential decay of the fabric at the gasket seal but also the introduction of potential interferences caused by the use of Krytox grease and solvents, we decided to condition a larger section of the material (8.9 cm by 8.9 cm) than required by the 5.6-cm (inner diameter, or i.d.) permeation test cell. Therefore, the surface of the material marred by the conditioning cell is not included in the section that is evaluated in the permeation test. In addition, we have also included a second water rinse after the material is removed from the conditioning apparatus, in order to ensure that the entire surface of the material is rinsed.

III. EXPERIMENTAL

A. APPARATUS

Separate experimental facilities were used to accomplish the liquid N_2O_4 conditioning, the liquid MMH conditioning, and the NO_2 permeation testing. These apparatus are illustrated schematically in Figs. 1, 2, and 3, respectively, and are briefly described in the following paragraphs.

1. CONDITIONING APPARATUS

The liquid N_2O_4 (Fig. 1) and liquid MMH (Fig. 2) conditioning apparatus were composed of the following components: the hypergol reservoir, an air purge system, a water rinse system, a waste reservoir, a temperature control system, and the test stand. A brief description of the system is given in the following paragraphs, and a more detailed description is included in Appendix A.

A square section of the test material, 10 cm by 10 cm, was sandwiched in the conditioning block (Fig. 4) between the stainless-steel baseplate and the Teflon block, with the "outside" of the test material facing up. The conditioning block was positioned in the horizontal position ($\theta = 180^\circ$ in Figs. 1, 2, and 4) prior to and during the hypergol exposure, and was lowered by means of a block and tackle (which, for the sake of clarity, is not shown in the figures) to an inclined position ($\theta = 115^\circ$) during the water rinse and the air purge. The chilled liquid hypergol was introduced through a 0.64-cm i.d. hole in the top of the Teflon block (see Fig. 4). As illustrated in Figs. 1 and 2, the stainless-steel baseplate and the Teflon block were cooled with the same water that was circulated through the hypergol reservoir. The water and air purge were accomplished within the conditioning apparatus by switching valves and lowering the conditioning block.

2. NO_2 PERMEATION APPARATUS

The NO_2 permeation apparatus (Fig. 3) is composed of the following systems: the test chamber, the temperature control system, the N_2O_4 vapor generator, the pressure monitoring and control system, the waste reservoir,

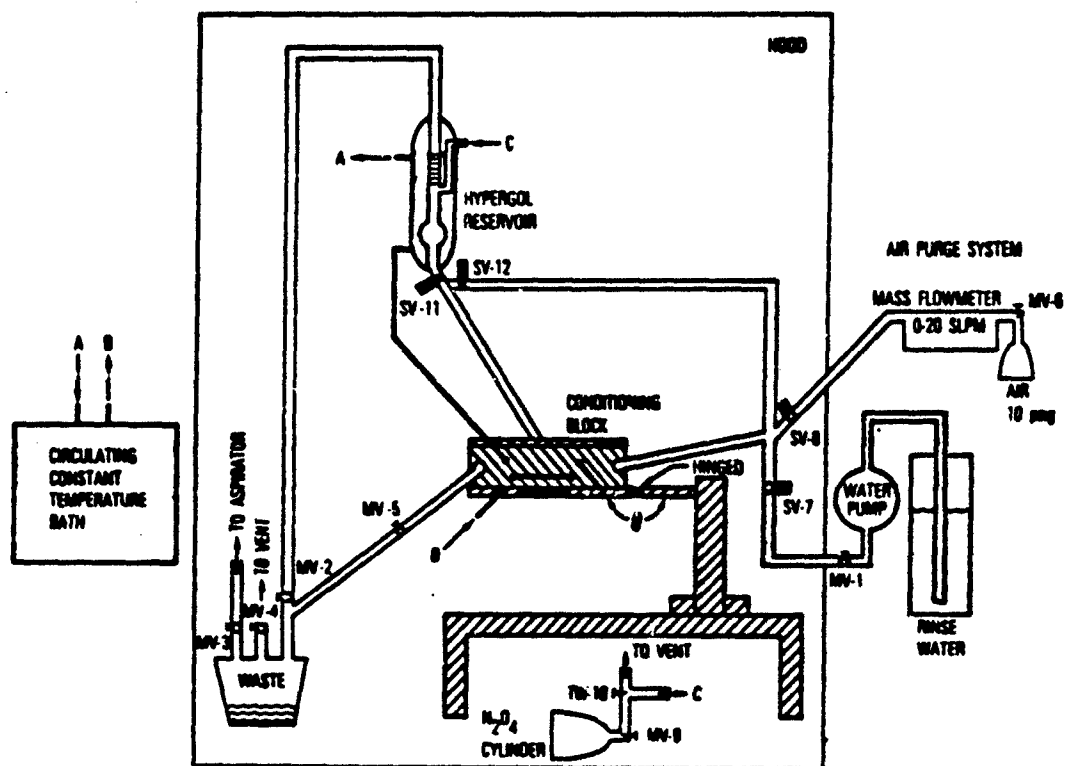


Fig. 1. Liquid N₂O₄ Conditioning Apparatus. Manual valves are identified by "MV" and solenoid valves by "SV".

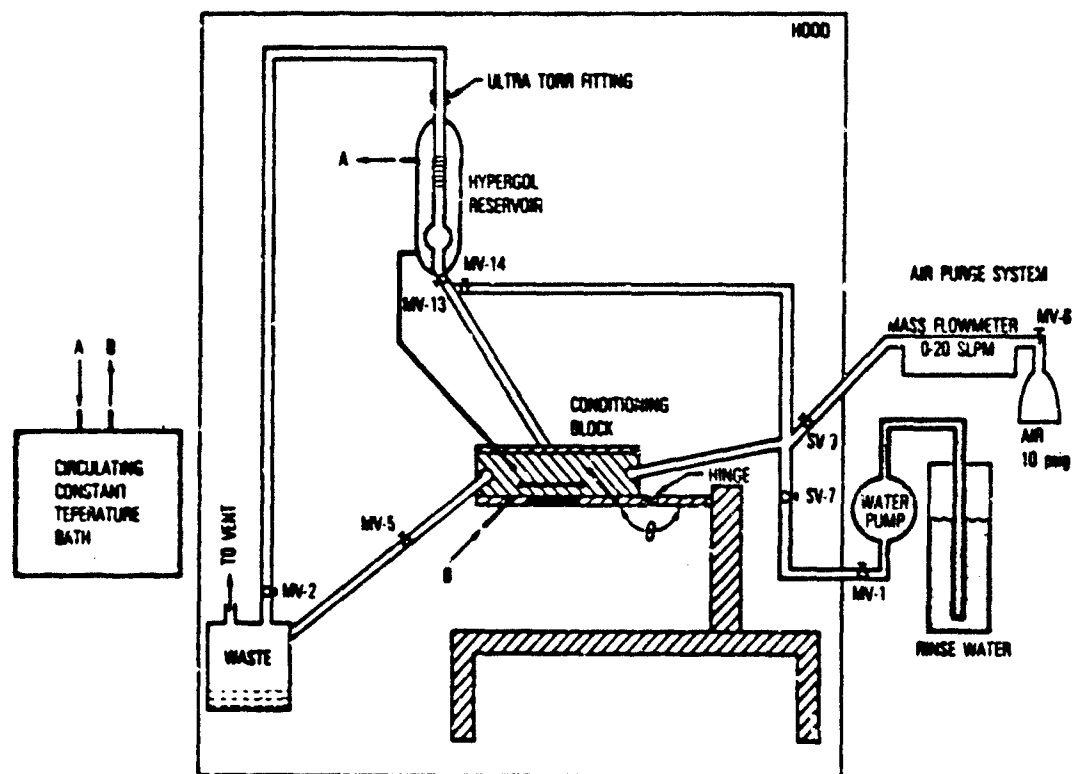


Fig. 2. Liquid-MPH Conditioning Apparatus. Manual valves are identified by "MV" and solenoid valves by "SV".

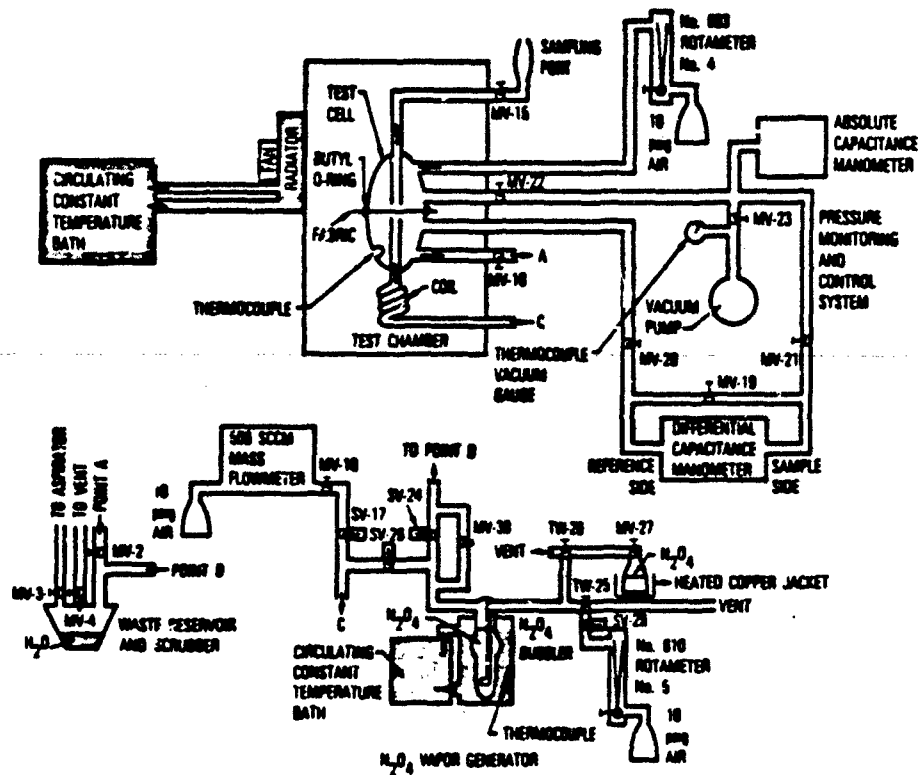


Fig. 3. NO₂ Vapor Permeation Apparatus. Manual valves are identified by "MV" and solenoid valves by "SV". This apparatus allows separate control of the temperatures of the permeation test chamber and the N₂O₄ bubbler, and thus the concentration of the "N₂O₄" vapor. The absolute pressure in the test cell and the differential pressure across the test fabric are also controlled.

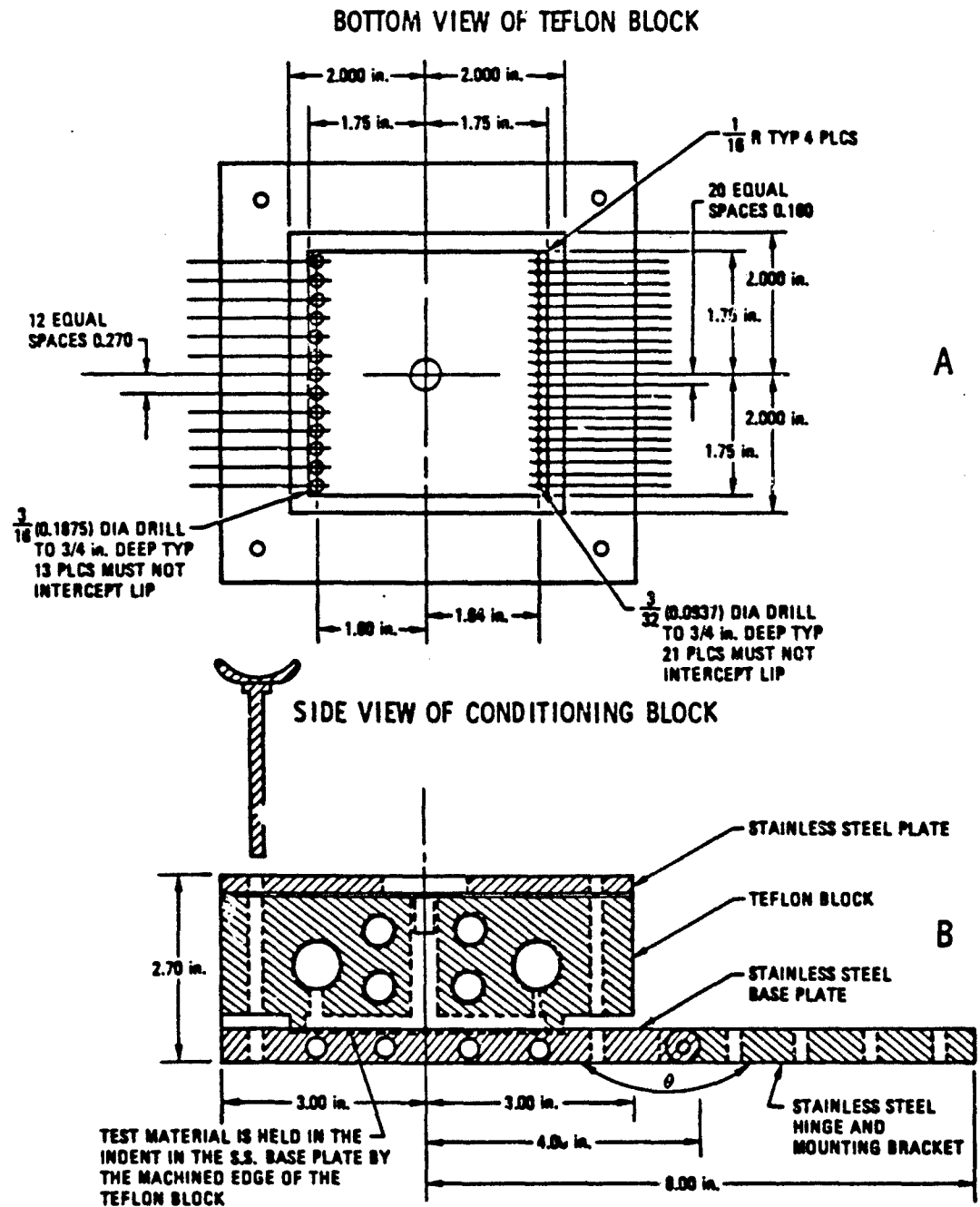


Fig. 4. (a) Bottom View of the Teflon Conditioning Block, and (b) Side View of the Assembled Conditioning Block.

and compressed air supplies. A brief description of the system is given in the following paragraphs, and a more detailed description is included in Appendix A.

The test cell, which was contained within the test chamber, was made from two modified glass joints. A butyl rubber O-ring was used to form an air-tight seal between the unexposed side of the test material and the upper half of the test cell. Direct contact with the rim of the bottom Pyrex joint was found to provide an adequate seal with the exposed side of the fabric.

The temperature of the test cell was regulated by means of a Plexiglas housing, a fan, a radiator, and a circulating constant-temperature bath. The temperature could be maintained to within ± 0.5 K of the selected temperature throughout the permeation test.

Capacitance manometers were used to monitor the absolute pressure in the test cell and the differential pressure across the material. The absolute and differential pressures were adjusted by restricting the sweep air flow from the top of the test cell by means of manual valve MV-15 in Fig. 3 and by restricting the oxidizer flow from the bottom of the test cell by means of manual valve MV-16. A mechanical vacuum pump was used to zero the absolute capacitance manometer before each experiment and to evacuate the manometers following each experiment.

A special gas manifold was designed and constructed out of Teflon tubing (Cole-Parmer) and Teflon solenoid valves (Fluorocarbon Co.) in order to establish the correct differential pressure prior to the start of hypergol exposure and to minimize the time required for the initiation of the exposure. A calculated flow of ~ 2.4 moles of N_2O_4 /min was generated by means of a small flow of air (i.e., 5 ml/min for the 293.2-K bubbler temperature) through a water-jacketed bubbler that contained liquid N_2O_4 . The flow is expressed in the number of moles of N_2O_4 , which is the number of moles that would exist if there were no dissociation to NO_2 . The bubbler was maintained at a constant temperature by means of a circulating water bath. The oxidizer vapor was vented through solenoid valve SV-24 prior to the start of the experiment. The differential pressure across the test material was

established by means of a 77-ml/min air flow through manual valve MV-18 and solenoid valve SV-17 prior to the start of exposure. The exposure was initiated by simultaneously shutting Teflon solenoid valves SV-17 (i.e., stopping the air flow to the bottom of the cell) and SV-24 (closing the vent for the N_2O_4/NO_2 vapor) while opening Teflon solenoid valve SV-26. In this way the flow of N_2O_4/NO_2 vapor was diverted into the bottom of the test cell so as to contact the test material.

The permeation of NO_2 was monitored by an Energetics Science, Inc. (ESI) 7000 series Ecolyzer, which is an electrochemical detector. The Ecolyzer sampled the 2-l/min sweep air flow at a rate of 0.71 l/min as it vented through the sampling port.

B. MATERIALS

E.I. du Pont de Nemours and Co., Inc. (du Pont) has produced a variety of chlorobutyl materials that have been used in various versions of self-contained atmospheric protective ensembles (SCAPEs). The chlorobutyl material that was originally used by Arrowhead Products Division of Federal Mogul Corporation in the manufacture of a SCAPE some 20 years ago contained a fire retardant. Since the fire retardant was determined to be a carcinogen in animal studies, du Pont has investigated several different chlorobutyl formulations in the interim.

A du Pont chlorobutyl material (#23219-119-1, also designated as YX-1002) is currently used by Arrowhead in the manufacture of the RFHCO. Material 23219-119-1 is a blue and tan, two-tone material. We obtained samples of the RFHCO material from Arrowhead Products Division of Federal Mogul Corporation, Los Alamitos, California. Since the material was delivered in the form of large sheets containing several square feet of material, all RFHCO material tests reported in this report were carried out on samples cut from one sheet of prospective material.

The gray and tan, two-tone du Pont chlorobutyl material (#23219-93-1) proposed for use in the PHE was obtained in two shipments from ILC Dover, Inc., Frederica, Delaware. In order to determine if there were significant differences between the two shipments received from ILC Dover, the first

shipment is designated as PHE and was used in the preliminary splash tests and in 13 other tests that are discussed in this report. Samples from the second shipment (identified as lot 001, fabricated in the spring of 1982) are designated as PHE' in Table 1. Since the samples were delivered in the form of several square sections measuring 18 cm on a side, only one test sample could be cut from each section of the PHE material.

The Cloropel material used in the ILC Chemtursion (hereafter CHEM) protective suit is a chlorinated polyethylene. We received samples of this blue material from ILC Dover. The Cloropel material is also used in the category VI SCAPE at NASA's Kennedy Space Center (NASA/KSC) for selected hydrazine fueling operations. NASA is currently considering this ensemble for additional hypergol operations. The CHEM samples were cut from the same sheet of Cloropel material in order to minimize sample-to-sample variability.

C. CHEMICALS

Dinitrogen tetroxide (N_2O_4) of 99.5% stated minimum purity was purchased from Matheson Gas Products. It was used without further purification in the initial 18 tests. In order to assess the effects due to impurities, it was purified by fractional distillation and the 294.2-K fraction was used for tests 19 through 24. The purified oxidizer was used within a week of its distillation and was stored in a dry air atmosphere at reduced temperature.

Methylhydrazine with a stated purity of 98% was purchased in 100-g bottles from Aldrich and was used without further purification. In order to minimize the potential for oxidation, the bottles were purged with dry nitrogen before being recapped and were stored in a refrigerator.

The calibration gas, 93 parts per million (ppm) NO_2 in air, was supplied by Matheson Gas Products, who had verified its concentration. Air Products breathing air was used as the sweep and dilution gas. It contains less than 1000 ppm CO_2 and has a dew point below 70 K. Air Products extra-dry nitrogen was used to purge the monomethylhydrazine bottles before they were recapped.

Table 1. Nitrogen Dioxide Permeation Test Results

Exp. #	Fabric	Thickness, mm	Cond., cycled	$T_{\text{cond.}}$, K	$T_{\text{bubb.}}$, K	H_2O_2 (1), % Purity	Purge Air Flow, ml/min	H_2O_2 Flow, ml/min ($\times 10^{-3}$)	$P_{\text{H}_2\text{O}_2}$, atm	$P_{\text{H}_2\text{O}_2}$, atm	$P_{\text{diff.}}$, Pa	$T_{\text{cell.}}$, K	$t=0.09$, min	$t=3.0$, min
1	PME	0.505	1	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	146	-175°C
2	PME	0.488	1	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	123	-151
3	PME	0.485	2	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	91	123
4	PME	0.488	2	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	85	121
5	PME	0.490	0	na ^a	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	172	-208
6	PME	0.490	0	na	293.2	99.5	5.0	2.65	0.40	0.68	75	308.2	>464 ^b	>464
7	PME	0.508	2	288.2	293.2	99.5	5.0	2.65	0.40	0.68	75	298.2	79	106
8	EPNCO	0.488	2	288.2	293.2	99.5	5.0	2.65	0.30	0.68	250	298.2	152	189
9	PME	0.490	0	na	293.2	99.5	5.0	2.65	0.30	0.68	250	298.2	184	215
10	PME	0.518	0	na	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	142	163
11	PME	0.505	0	na	293.2	99.5	5.0	2.65	0.34	0.67	75	303.2	287	347
12	EPNCO	0.488	2	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	161	204
13	PME	0.531	0	na	293.2	99.5	5.0	2.65	0.30	0.68	-250	298.2	166	195
14	CP/2A	0.528	1	288.2	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	66	68
15	PME	0.523	0	na	293.2	99.5	5.0	2.65	0.27	0.68	75	294.2	68	75
16	PME	0.505	0	na	293.2	99.5	5.0	2.65	0.30	0.68	75	298.2	122	140
17	PME	0.503	0	na	288.2	99.5	5.0	0.49	0.27	0.53	75	298.2	522	>565
18	PME	0.500	0	na	291.2	99.5	11.5	2.34	0.28	0.52	75	298.2	222	248
19	PME	0.511	2	288.2	293.2	distilled	5.0	2.65	0.30	0.68	75	298.2	93	113
20	PME	0.516	2	288.2	293.2	distilled	5.0	2.65	0.30	0.68	75	298.2	67	90
21	PME	0.513	2	293.2	293.2	distilled	5.0	2.65	0.30	0.68	75	298.2	100	134
22	EPNCO	0.521	0	na	293.2	distilled	5.0	2.65	0.30	0.68	75	298.2	293	333
23	CEEA	0.511	0	na	293.2	distilled	5.0	2.65	0.30	0.68	75	298.2	46	47
24	PME	0.511	2	182.2	291.2	distilled	5.0	2.65	0.30	0.68	75	298.2	116	144
25	PME	0.495	0	na	291.2	99.5	11.5	2.34	0.28	0.62	75	298.2	275	334
26	PME	0.495	0	na	288.2	99.5	20.3	2.00	0.27	0.53	75	298.2	529	>601
27	PME	0.498	0	na	291.2	99.5	2.8	0.57	0.28	0.62	75	298.2	282	332
28	PME	0.505	0	na	288.2	99.5	20.3	2.00	0.22	0.53	75	289.2	190	216
29	PME	0.505	0	na	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	62	70
30	EPNCO	0.483	0	na	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	93	104
31	EPNCO	0.483	0	na	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	85	91
32	PME	0.500	2	288.2	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	103	115
33	PME	0.500	2	288.2	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	100	115
34	EPNCO	0.495	2	288.2	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	65	76
35	PME	0.496	2	288.2	294.5	99.5	0.5	5.41	0.29	0.73	75	308.2	172	232
36	EPNCO	0.490	0	na	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	155	173
37	EPNCO	0.490	0	na	294.5	99.5	0.5	5.41	0.29	0.73	75	295.5	332	385

Not applicable

^a (greater than) = no breakthrough at this time
^c small extrapolation off edge of chart paper

The deionized water was produced with a Millipore Milli-Q Water Purification System that consisted of four in-line cartridges (prefilter, super-C carbon, and two-ion exchange) followed by a twin 90 filter. The resistivity was always above 16 MΩ.

D. CALIBRATION

The ESI 7000 series Ecolyzer NO₂ detector was calibrated on a daily basis by means of Matheson-certified 93-ppm NO₂ in air, a simple dilution apparatus, and calibrated rotameters. The span of the Ecolyzer was typically adjusted to have twice the sensitivity intended by the manufacturer when it was challenged with a 3.0-ppm concentration of NO₂ in air. The rotameters and mass flow meters were calibrated by means of a wet-test meter or the bubble displacement method, depending upon the flow rate. The calibration of the capacitance manometers was verified by the Aerospace instrument center.

E. TEST PROCEDURE

Our experiments can be considered extensions of the Martin Marietta Corporation test procedure MMC T79-80A. Our test procedure consists of the following two stages: (1) one side of the material sample is "conditioned" by a series of alternating, 1-min exposures to 50 ml of liquid N₂O₄ and 50 ml of liquid monomethylhydrazine (MMH) that are separated by water rinses and air drying; and (2) the material's resistance to permeation by NO₂ is then determined by means of a second test apparatus that allows 24.6 cm² of the conditioned side of the test material to be exposed to N₂O₄/NO₂ vapor while the concentration of NO₂ in a 2-l/min flow of sweep air is monitored on the other side of the material. Two characteristic times were recorded for each test. The breakthrough time ($t = 0.09$) was defined as the time elapsed between the initiation of exposure to concentrated N₂O₄/NO₂ vapor and the attainment of 0.09 ppm of NO₂ in the sweep air. The second characteristic time ($t = 3.0$) was the time elapsed between the initiation of exposure to concentrated N₂O₄/NO₂ vapor and the attainment of 3.0 ppm of NO₂ in the sweep air. Since the experimental parameters and conditions were carefully controlled, the breakthrough times were used to rank the permeation resistance of different materials.

We found that a step-by-step, check-it-off-as-you-go procedure was required in order to ensure that the experimental apparatus and procedures were reproducible. Once the detailed test procedure was established, it was then possible to evaluate the effects of the various individual experimental parameters on the NO₂ breakthrough times for the PHE coverall material without excessive scatter caused by procedural inconsistencies. The detailed test procedure is available upon request, and is briefly summarized in Appendix B.

IV. RESULTS AND DISCUSSION

The results of the NO_2 permeation testing of the three coverall materials are listed in Table 1 in the chronological order in which the tests were performed. The experiment number, the type of material, and the thickness of the material in millimeters (mm) are indicated in columns 1, 2, and 3, respectively. The following abbreviations were used for the materials: PHE and PEI' for the first and second shipments of the Propellant Handler's Ensemble that were received from ILC Dover, RPHCO for the Rocket Fuel Handler's Clothing Outfit, and CHEM for the Chemtursion Cloropel material. These materials were previously described in the experimental section of this report.

In our discussions and in column 4 of Table 1, we define a cycle of conditioning (abbreviated as "Cond., cycles") as an exposure to liquid oxidizer [i.e., dinitrogen tetroxide (N_2O_4)] on one day, followed by an exposure to liquid fuel [i.e., monomethylhydrazine (MMH)] on the next day (the exposures being separated by water rinses and air drying). Therefore, zero cycles of conditioning would indicate that the material was tested after an initial water rinse and air drying. On the other hand, one or two cycles of conditioning would indicate that the fabric had been subjected to two days or four days, respectively, of conditioning with alternating exposures to liquid oxidizer and liquid fuel.

Several temperatures are also indicated in Table 1. The conditioning temperature (abbreviated as " T_{cond} " in column 5) is the temperature of the liquid hypergol, of the conditioning block, and of the material sample during the conditioning exposures. The temperature of the bubbler that contains liquid N_2O_4 and that determines the " N_2O_4 " equivalent vapor concentration is listed in column 6 as " T_{bubb} ". We define the " N_2O_4 " equivalent vapor concentration as the concentration of N_2O_4 that would exist if there were no dissociation to NO_2 . The temperature of the permeation test cell (i.e., the temperature of the $\text{N}_2\text{O}_4/\text{NO}_2$ /air mixture in the permeation test cell and of the test sample) is listed in column 13 as " T_{cell} ".

The purity of the liquid N_2O_4 that was used as the source of $\text{N}_2\text{O}_4/\text{NO}_2$ vapor is indicated in column 7. The partial pressure (in atmospheres) of the NO_2 and the N_2O_4 vapors in the permeation test cell are abbreviated as P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ in columns 10 and 11, respectively, in Table 1. These partial pressures were calculated as a function of the temperature of the bubbler, the total pressure in the test cell, and the temperature of the permeation test cell. We maintained a total pressure of 770 mm Hg (i.e., 102,600 Pa or 1.013 atmospheres) in the test cell in all of our experiments.

In these calculations it was assumed that the equilibrium vapor pressure of $\text{N}_2\text{O}_4/\text{NO}_2$ was attained in the small flow of purge air that passed through the liquid N_2O_4 at the bubbler temperature. The partial pressures of the NO_2 and N_2O_4 in the test cell were a function of both the total " N_2O_4 " equivalent concentration in the test cell (as determined by the temperature of the bubbler) and the temperature of the test cell. These calculations took into account the equilibrium's dependence upon both temperature and the total " N_2O_4 " equivalent concentration.

It should be noted that the actual vapor pressure would be equal to or less than the concentration calculated in this manner, depending upon the purity of the liquid N_2O_4 in the bubbler and the extent of equilibrium. As discussed in Sections IV.E and IV.G, below, it appears that 99.5% liquid N_2O_4 is of adequate purity for the purposes of these studies. As will be discussed in Section IV.H, it appears that the equilibrium assumption is also valid for our bubbler design and purge-air flow rates.

The calculated molar " N_2O_4 " equivalent flow (abbreviated as " N_2O_4 " Flow) of the resulting $\text{N}_2\text{O}_4/\text{NO}_2$ /air mixture is listed in moles " N_2O_4 "/min in column 9 of Table 1. We use moles of " N_2O_4 " to indicate the number of moles of N_2O_4 that would exist if there were no dissociation to NO_2 . The molar " N_2O_4 " equivalent flow was calculated from the vapor pressure of N_2O_4 at the bubbler temperature and the purge-air flow through the bubbler. As long as the total pressure in the test cell remains above the vapor pressure of the oxidizer at the bubbler and test cell temperatures, the molar flow is independent of both the total pressure and the test cell temperature.

The differential pressure (abbreviated as " P_{diff} " in column 12) across the material during the permeation test may be converted to its equivalent pressure in inches of water by dividing by 250. A positive differential pressure was defined as a higher pressure on the unexposed side of the material.

In all of our experiments the absolute pressure on the unexposed side of the material was maintained at 770 mm Hg (i.e., 102,600 Pa or 1.013 atmospheres) during the permeation tests.

The permeation results are summarized in Table 1 as the time ($t = 0.09$ in column 14) required to attain an NO_2 concentration of 0.09 ppm and the time ($t = 3.0$ in column 15) required to attain an NO_2 concentration of 3.0 ppm in the 2-l/min flow of sweep air after the initiation of exposure to the N_2O_4/NO_2 vapor. The first time ($t = 0.09$) will be called "breakthrough time" and serves as a useful indicator of the relative permeation resistance of the various materials under the same test conditions, or of the relative protection provided by a given material under various conditioning and test conditions.

A. PRECISION OF DETERMINATIONS

Since we obtained two shipments of Propellant Handler's Ensemble coverall material, we could not be certain that they were cut from the same lots of material. Therefore, we have given them different designations in Table 1. Within the scatter of our determinations, there is no discernible difference in the permeation resistance of the two shipments of Propellant Handler's Ensemble coverall material and, therefore, we have not differentiated between the two shipments in any of the figures.

If we assume that the two shipments of material were cut from the same lot, then the scatter in our determinations represents the combined uncertainty that is due to small fluctuations in experimental parameters and sample-to-sample variability in the PHE (and PHE') coverall materials. The scatter in our data indicates that the average breakthrough time determined with even a very elaborate permeation test apparatus will have a relative standard deviation of 10 to 20%.

B. EFFECT OF CONDITIONING

In order to illustrate the effect of conditioning on the three overall materials, the breakthrough times ($t = 0.09$ in Table 1) for the various materials are plotted as a function of the number of conditioning cycles in Fig. 5. The RFHCO data (experiments 8, 12, and 22) are plotted as circles, the CHEM data (experiments 14 and 23) are plotted as squares, and selected PHE (and PHE') data (experiments 1 through 5, 7, 10, 16, 19, and 20) are plotted as diamonds. In these experiments, all other experimental parameters were identical except for the number of cycles of conditioning. In Fig. 5, we have included lines between the RFHCO data points as well as between the CHEM data points. The line that is drawn between the combined PHE and PHE' data points represents the least-squares linear regression fit to those data.

As illustrated in Fig. 5, the breakthrough times (i.e., the permeation resistance) for the RFHCO and both shipments of the Propellant Handler's Ensemble (PHE and PHE') decreased following initial exposure (i.e., conditioning) to the liquid hypergols. It should be noted that these chlorobutyl materials were tacky immediately after exposure but did not remain tacky when they dried. The surface of the chlorobutyl materials became roughened, and their thickness increased (typically reaching 0.6 to 0.7 mm after several exposures) during the conditioning. However, the chlorobutyl materials did remain pliable throughout the conditioning.

As indicated in Fig. 5, the two data points for the CHEM overall material (Cloropel) suggest that, in contrast to the results for the chlorobutyl materials, Cloropel's permeation resistance may increase slightly following initial exposure (i.e., conditioning) to the liquid hypergols. This trend is of limited interest, since the Cloropel is severely attacked by the liquid hypergol and is discolored, curls, and becomes stiff after drying. The physical deformation of the material, which accompanies the apparent increase in permeation resistance, made it difficult to install it into the MMH conditioning apparatus after its first exposure to liquid N_2O_4 , and precluded the completion of two cycles of conditioning. It is unlikely that such badly distorted and discolored Cloropel would be reused after being exposed to liquid hypergol or its concentrated vapors.

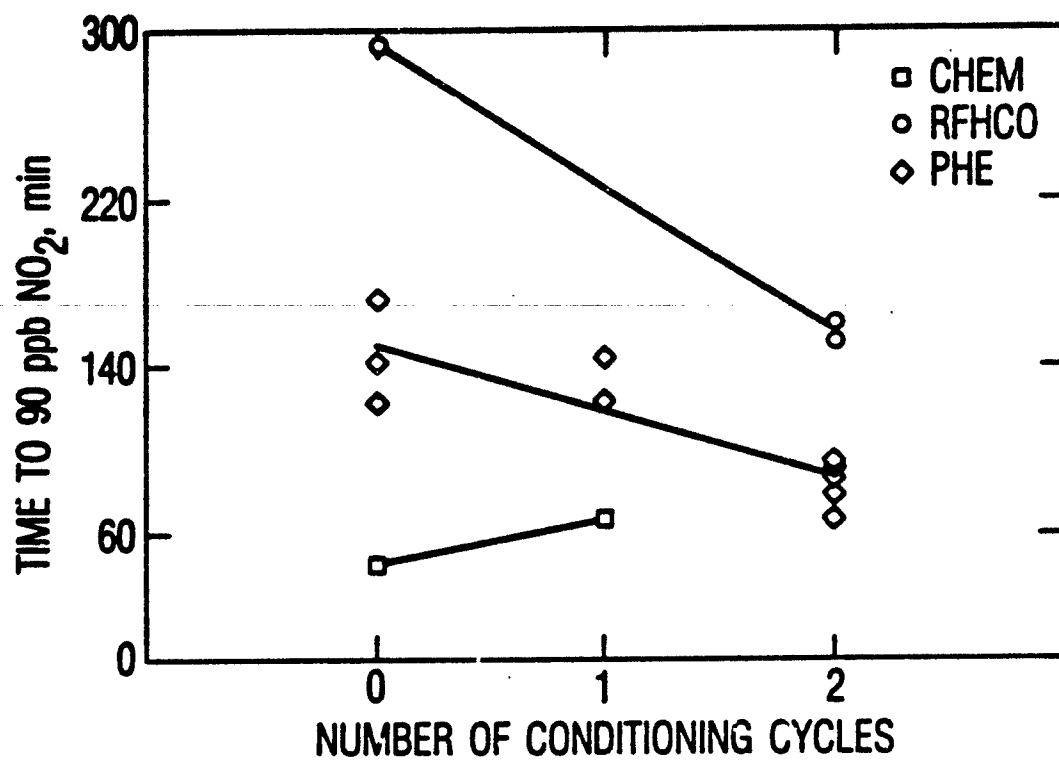


Fig. 5. Comparison of Coverall Materials. The NO₂ breakthrough times for the CHEM (□), RFHCO (○), and both batches of the Propellant Handler's Ensemble (◇) are plotted against the number of cycles of preconditioning.

It should be noted that the effect of conditioning is not very great under these test conditions, and may depend on the conditioning and permeation test conditions as well as on the age of the test material. This is discussed in more detail in Section IV.L.

C. RELATIVE RANKING OF THE THREE MATERIALS

The data in Fig. 5 indicate a relative ranking of the three coverall materials under one set of experimental conditions, so that $\text{RFHCO} > \text{PHE} > \text{CHEM}$ in order of their decreasing resistance to permeation by NO_2 . The average relative ranking was not significantly affected by the number of conditioning cycles that were investigated for these experimental conditions.

The Martin Marietta Corporation (MMC) carried out permeation tests on both the PHE and RFHCO coverall materials.^{6,11} They reported that conditioned PHE material was permeated by NO_2 in less than 45 min in three out of four tests, while conditioned RFHCC material resisted permeation for more than 60 min in four similar tests. As discussed in an earlier section of this paper, the MMC test procedure lacked control of key experimental parameters, and therefore a quantitative comparison of their results with ours is not warranted.

Likewise, the same relative ranking of the NO_2 permeation resistance was obtained for unconditioned RFHCO, PHE, and CHEM coverall materials by means of our preliminary splash test procedure.^{1-3,12} These preliminary tests employed a 25-ml splash with liquid N_2O_4 , followed by exposure to saturated oxidizer vapor. The temperature, the absolute pressure, and therefore the oxidizer vapor pressure were determined by ambient conditions. Consequently, because of the procedural differences, the smaller exposed area (8 cm^2) of the material, and the uncontrolled experimental parameters, the absolute values of these breakthrough times cannot be compared to our results obtained with the new test procedure.

As discussed above, the three sets of tests carried out under a variety of experimental conditions indicate that the NO_2 permeation resistance of the PHE material is inferior to that of the RFHCO material. In addition, data obtained through two different experimental procedures indicate that the

resistance of the PHE material to NO_2 permeation is superior to that of the CHEM material. As discussed in Section IV.L, the relative ranking may depend on the conditioning and permeation test conditions as well as on the age of the test sample.

D. EFFECT OF CONDITIONING TEMPERATURE

The effect of the conditioning temperature, which includes the temperature of the liquid hypergol, the conditioning block, and the test material, on the breakthrough times for the PHE (and PHE') coverall material was investigated in experiments 19, 20, 21, and 24 (plotted as diamonds in Fig. 6). In these experiments the samples of the coverall material were subjected to 2 cycles of conditioning. Distilled N_2O_4 was used for both conditioning oxidizer exposures as well as in the permeation test bubbler. As seen in Fig. 6, the breakthrough times for the PHE (and PHE') coverall material were not strongly dependent upon the conditioning temperature over the range investigated. The temperature range was determined by the cooling capacity of the circulating constant-temperature bath on the low end, and by the normal boiling point (294 K) of N_2O_4 on the high end.

If the above data points are treated as one data set, they have a mean value of 94 min with a standard deviation of 21 min (or a 22% relative deviation). Therefore, if the NO_2 breakthrough time for the PHE' material does depend upon the conditioning temperature over the range investigated, it is a weak dependence that would require many more experiments to confirm.

E. EFFECT OF IMPURITIES IN THE OXIDIZER

In order to evaluate the potential effect of the impurities present in the 99.5% liquid N_2O_4 purchased from Matheson, the results of three additional PHE tests were also plotted in Fig. 6. In experiments 3, 4, and 7 (plotted as circles in Fig. 6), the oxidizer used in the conditioning as well as in the permeation testing was taken directly from the Matheson cylinder (99.5% liquid N_2O_4), whereas in experiments 19, 20, 21, and 24 (plotted as diamonds), the 294.2-K fraction of the distilled oxidizer was used in both the conditioning and in the permeation test.

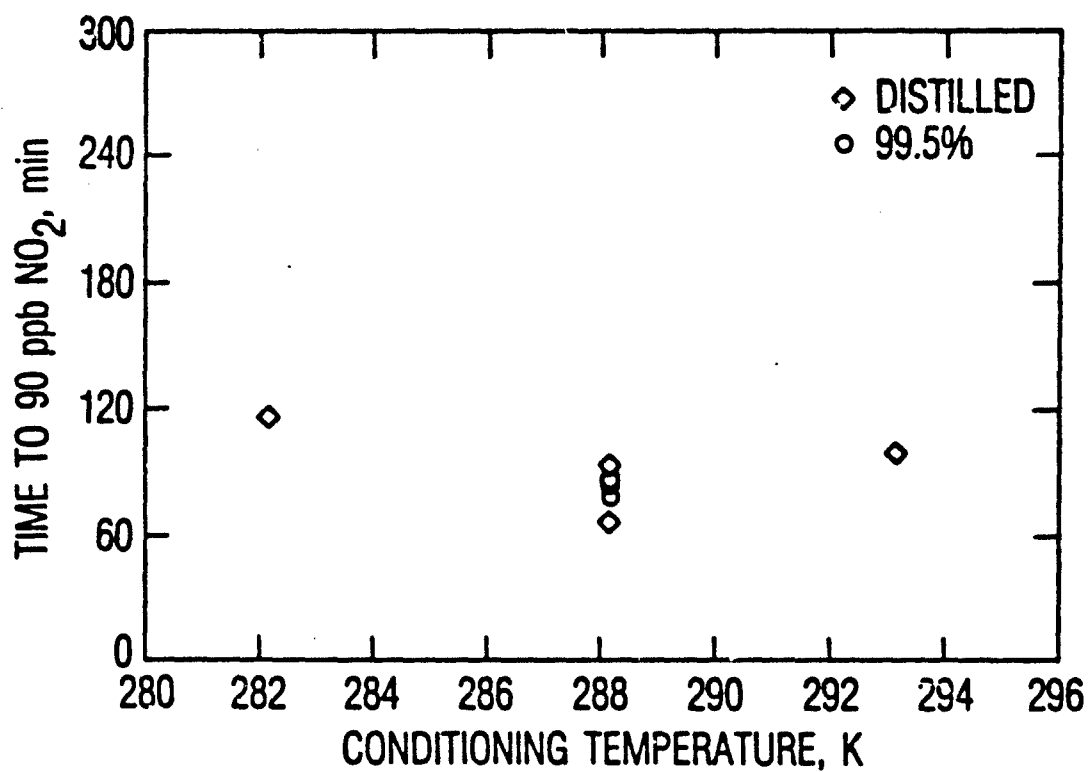


Fig. 6. Conditioned PHE, Showing the Effect of Conditioning Temperature and Purity of the Liquid N_2O_4 . The NO_2 breakthrough times obtained using distilled (◇) and 99.5% (○) liquid oxidizer are plotted against the conditioning temperature.

As illustrated in Fig. 6, the breakthrough times for the PHE which were obtained with the 99.5% oxidizer (as received from Matheson) fell in-between the breakthrough times obtained with the further-distilled oxidizer. We interpret this to mean that any effect due to impurities in the military specification (99.5%) oxidizer is smaller than the sample-to-sample variability of the PHE and PHE' materials. We also interpret this to mean that it was reasonable to use the vapor pressure of neat N_2O_4 liquid in the calculation of the partial pressure of NO_2 (column 10 in Table 1), the partial pressure of N_2O_4 (column 11 in Table 1), and the molar " N_2O_4 " equivalent flow (column 9 in Table 1) for the purities used in these experiments.

F. SELECTIVITY OF THE DETECTOR

Impurities in the oxidizer or by-products of the reaction of oxidizer with the material can produce either positive or negative interference with the detection system. We had observed such effects in our earlier studies of NO_2 permeation of protective materials.¹⁻³ In those studies SO_2 and N_2O were produced by the reaction of NO_2 with several natural-rubber materials. By causing a negative response, the SO_2 interfered with the detection of NO_2 by the 7000 series Ecolyzer.

Since it is unlikely that an interference would produce a response that would exactly cancel the response due to NO_2 , the breakthrough times reported here indicate that either NO_2 or a positive interference permeated the material at the recorded times. Since any interference with the method of detection can result in an error in determining the breakthrough time, the selectivity of the detector is a critical factor.

A universal selective detector that allows identification of permeants as a function of time would provide for the detection of reaction by-products produced during the reaction of the hypergol with the material. Since these by-products could be as toxic or more toxic than the hypergols themselves, this would be an important capability that is not currently provided by the electrochemical and colorimetric methods. A mass spectrometric detection system would provide such capabilities and could be applied to a variety of chemicals.

G. EFFECT OF THE BUBBLER TEMPERATURE

The effect of the temperature of the bubbler that contains the liquid N_2O_4 upon the NO_2 breakthrough times for the PHE materials was investigated in experiments 5, 10, 16, 18, 25, and 26 for calculated " N_2O_4 "-equivalent flows of ~ 2.4 moles of " N_2O_4 "/min (see Table 1, column 9, for the calculated flows). The data are plotted in Fig. 7 as diamonds. As mentioned previously, the moles of " N_2O_4 " equivalent are the number of moles of N_2O_4 that would be present if there were no dissociation into NO_2 . As is apparent from Fig. 7, the breakthrough times of the PHE coverall materials are extremely sensitive to the temperature of the bubbler. This is because changes in the temperature of the liquid oxidizer create changes in the partial pressures of the nitrogen oxides in the vapor phase.

In order to illustrate the effect of the bubbler temperature on both the N_2O_4 pressure and consequently on the breakthrough times, the above breakthrough times are plotted in Fig. 8 against the partial pressure of the N_2O_4 ($P_{N_2O_4}$) which is calculated from the bubbler temperature and the permeation cell temperature. It is apparent after examination of Fig. 8 that the breakthrough times decrease rapidly for small increases in the partial pressure of N_2O_4 . It should be noted that the partial pressure of NO_2 (P_{NO_2}) also increased when the temperature of the bubbler was increased. Since the ratio of $P_{N_2O_4}/P_{NO_2}$ also increases with increasing bubbler temperature (for a constant permeation test-cell temperature), the major effect of the bubbler temperature is on $P_{N_2O_4}$.

The curves in Figs. 7 and 8 represent second-order polynomial least-squares fits to the data. Since the bubbler temperature (and hence the partial pressures of NO_2 and N_2O_4) was the only experimental variable in the above experiments, it is apparent that the N_2O_4 concentration is an important experimental parameter.

Since the partial pressure of the nitrogen oxides which is actually achieved in the test cell depends upon the purity of the N_2O_4 used in the bubbler and the residence time (i.e., the degree of equilibrium between liquid and vapor) of the purge air in the bubbler, the calculated values of P_{NO_2} and

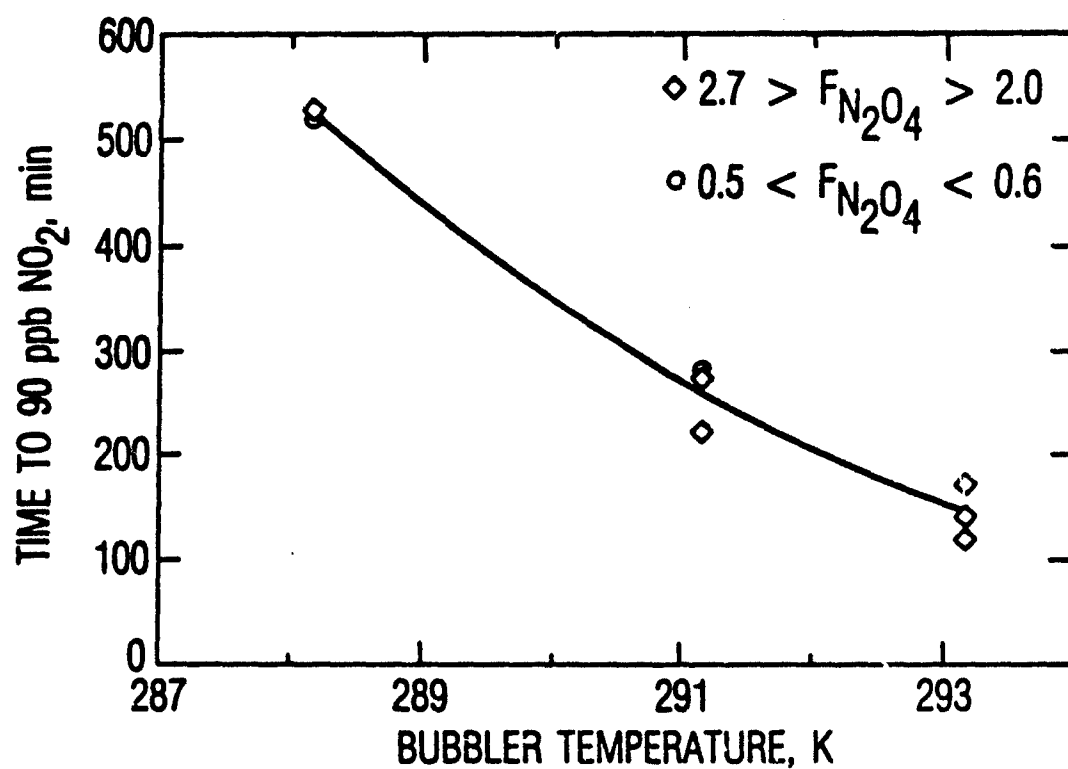


Fig. 7. Unconditioned PHE, Showing the Effect of the Temperature of the Bubbler and the Molar Flow of " N_2O_4 " ($F_{N_2O_4}$) in Moles of " N_2O_4 " Equivalent/Min. The NO_2 breakthrough times for oxidizer vapor flows of ~ 0.5 moles " N_2O_4 " /min ($\circ$) and ~ 2.4 moles " N_2O_4 " /min ($\diamond$) are plotted against the temperature of the bubbler.

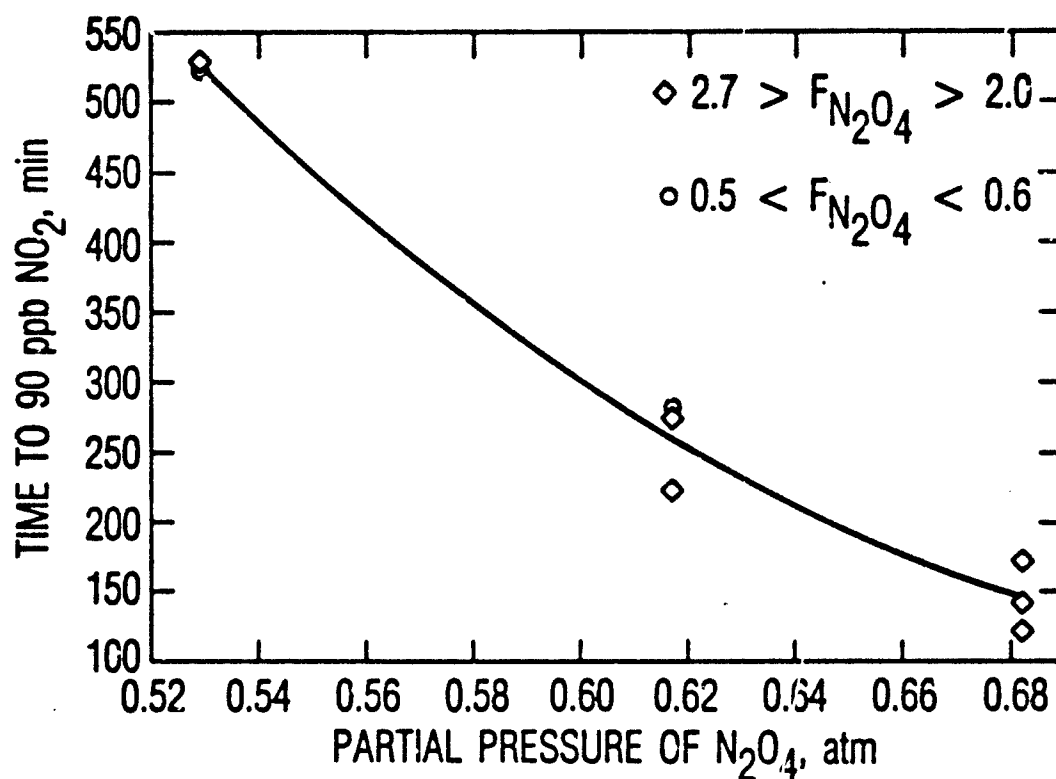


Fig. 8. Unconditioned PHE, Showing the Effect of the Partial Pressure of N_2O_4 ($P_{N_2O_4}$) and the Molar Flow of " N_2O_4 " ($F_{N_2O_4}$) in Moles of " N_2O_4 " Equivalent/Min. The NO_2 breakthrough times for oxidizer flows of ~ 0.5 moles " N_2O_4 "/min ($\circ$) and ~ 2.4 moles " N_2O_4 "/min ($\diamond$) are plotted against the partial pressure of N_2O_4 (as calculated from the temperature of the bubbler and the temperature of the test cell).

$P_{N_2O_4}$ (columns 10 and 11 in Table 1) represent an upper limit to the actual partial pressures. Since there was no significant effect of impurities in the 99.5% liquid oxidizer (see Section IV.E) upon the breakthrough times, we believe that we are justified in using the vapor pressure of neat N_2O_4 in our calculation of the partial pressures of the oxidizer vapors generated by the bubbler. However, the data that evaluated the effects of impurities in the 99.5% liquid oxidizer cannot be used to evaluate the degree of equilibrium that was obtained in those experiments.

One would expect that the degree of equilibrium would be determined by the bubbler design, the bubbler temperature, and purge air flow. We have qualitatively evaluated the degree of equilibrium for our bubbler in the following section by investigating the effect of purge air flow for two bubbler temperatures.

H. EFFECT OF THE FLOW OF OXIDIZER VAPOR

The effect of the flow of the oxidizer vapor on the breakthrough times for the PHE' material was investigated in experiments 17 and 27. In these experiments, the oxidizer flow was reduced from the calculated ~2.4 moles of " N_2O_4 "/min used in experiments 5, 10, 16, 18, 25, and 26 (the diamonds in Figs. 7 and 8) to a calculated ~0.55 moles of " N_2O_4 "/min (plotted as circles in Figs. 7 and 8) by reducing the purge air flow. There is no apparent effect of oxidizer flow on the breakthrough times for the PHE' material in Figs. 7 or 8; therefore, the breakthrough times appear to be independent of the flow of the oxidizer vapor over the range investigated.

If the N_2O_4 liquid in the bubbler was not in equilibrium with the purge air flow through the bubbler, one would expect a change in purge air flow to affect the degree of equilibrium by changing the residence time of the air in the liquid oxidizer. This would affect an important experimental parameter (i.e., the oxidizer concentration) and, therefore, the breakthrough times for a nonequilibrium situation. Since there was no apparent effect of the factor-of-4 change in air purge rate, it appears that the equilibrium assumption is valid for the air purge rates investigated and for the bubbler used in these studies.

In addition to evaluating the degree of equilibrium, this set of experiments also evaluated the importance of the total mass flow of N_2O_4 vapor through the permeation cell. If the permeation rate was limited by the rate of diffusion of oxidizer to the surface of the fabric or by losses of oxidizer on the surfaces of the test apparatus, then it would have shown a dependence upon the change in oxidizer/air mixture flow. At the high concentrations of oxidizer used in these experiments, it is unlikely that either of these cases would apply. It is also unlikely that the effects of the change in purge air flow upon the degree of equilibrium, upon the diffusion rate, and upon the oxidizer losses would have been able to cancel exactly if any of these parameters were important for the given test conditions.

Therefore, we conclude that the oxidizer is at equilibrium at the purge air flows that we used, and that there is sufficient mass flow of oxidizer vapor to compensate for losses due to permeation through the material and adsorption on the surfaces of the test apparatus.

I. EFFECT OF PERMEATION TEST CHAMBER TEMPERATURE

The effect of the permeation test chamber temperature upon the breakthrough time of the PHE material is illustrated in Fig. 9, where the results of experiments 5, 6, 10, 11, 15, and 16 are plotted as diamonds. These experiments were carried out on unconditioned samples of the PHE material under the same experimental conditions, except for the temperature of the permeation test chamber. The curve in Fig. 9 represents a second-order polynomial least-squares fit to the experimental data (using a value of 464 min for the 308.2-K experiment).

Upon examination of Fig. 9, it is apparent that the NO_2 permeation occurs much more rapidly at the lower temperatures than at the higher temperatures. In fact, NO_2 breakthrough did not occur during the 464 min of the 308.2-K experiment (experiment 6), which was stopped because the bubbler's oxidizer was nearly exhausted. The lowest permeation test cell temperature that could be investigated under the specified test conditions was 294.2 K, which is 1 K warmer than the temperature of the bubbler that was used in all of the experiments included in Fig. 9.

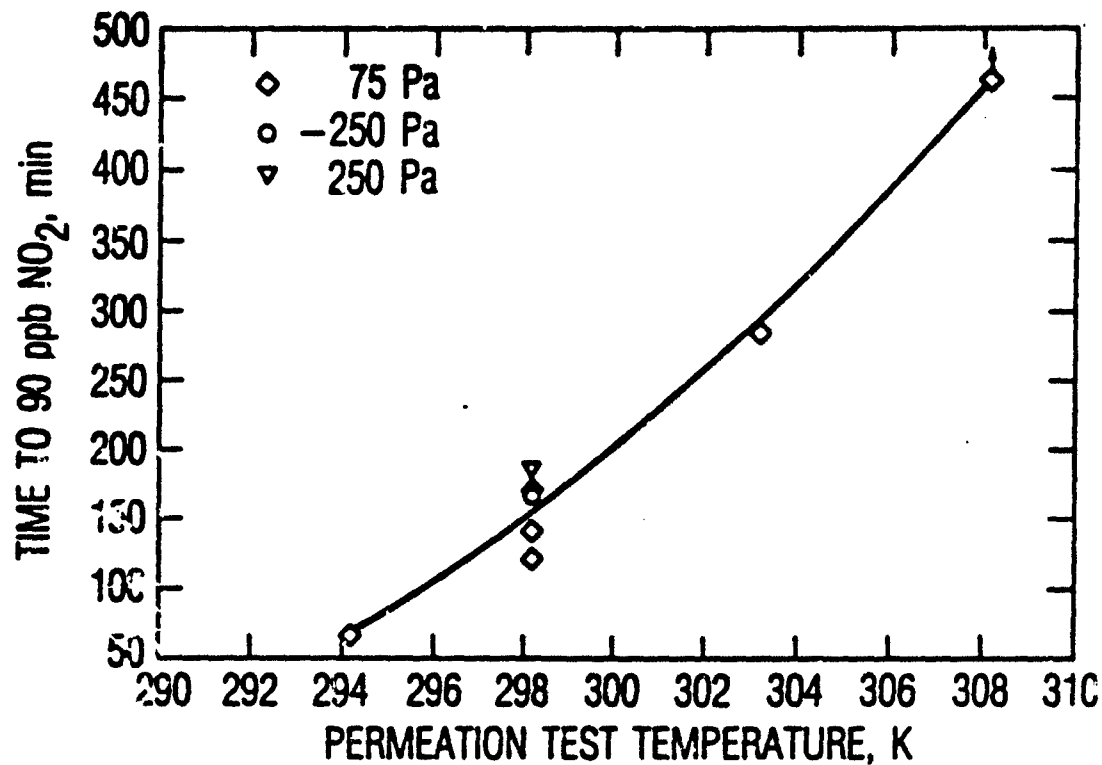


Fig. 9. Unconditioned PHE, Showing the Effect of the Permeation Test Chamber Temperature and the Differential Pressure across the Test Fabric. The NO₂ breakthrough times for 75 Pa (◇), -250 Pa (○), and 250 Pa (▽) differential pressures are plotted against the permeation test chamber temperature. The highest temperature data point represents a minimum value, since no breakthrough occurred during the 464 min of the monitoring.

If we assume, for the sake of illustration, that the inverse of the breakthrough time (t_B^{-1}) is roughly proportional to the rate of breakthrough, then a plot of the $\ln(1/t_B)$ versus $1/T_{\text{cell}}$ would have a slope equal to the activation energy divided by the gas constant R (1.987 calories K^{-1} mole $^{-1}$) for an Arrhenius-type reaction. As seen in Fig. 10, we obtained a positive slope of 13000, which would correspond to an activation energy of -26 kcal/mole. Therefore, the breakthrough times for the PHE coverall material exhibit anti-Arrhenius behavior. This is consistent with a mechanism for breakthrough which is limited by exothermic steps, e.g. association, condensation, and, potentially, the mixing of N_2O_4 with the chlorobutyl material. Thus the observed temperature dependence could be a result of any one or a combination of all of the above processes.

In order to investigate the potential importance of the temperature dependence of association of NO_2 to N_2O_4 upon the observed effect of the permeation test cell temperature, the same data discussed above for Figs. 9 and 10 were included in Fig. 11, where the breakthrough time was plotted against the ratio of $P_{N_2O_4}/P_{NO_2}$. It appears that the breakthrough time decreases as the ratio $P_{N_2O_4}/P_{NO_2}$ increases. Therefore, the association of NO_2 into N_2O_4 has a temperature dependence similar to that observed for the breakthrough times.

If the observed dependence of the breakthrough times upon permeation test cell temperature is mainly a result of the temperature dependence of the dinitrogen tetroxide/nitrogen dioxide equilibrium, then the data of Fig. 7 and 9 (i.e., the effect of T_{bubb} and T_{cell}) should be indistinguishable when plotted against an expression that accounts for the effect of both the bubbler and permeation temperatures. Since $P_{N_2O_4}$ was strongly influenced by T_{bubb} (see the discussion for Figs. 7 and 8) and the ratio $P_{N_2O_4}/P_{NO_2}$ was strongly influenced by T_{cell} , the breakthrough times for all of the experiments that were included in Figs. 7 and 9 were plotted against the product of $P_{N_2O_4}$ times $P_{N_2O_4}/P_{NO_2}$ in Fig. 12. This product was expressed as $(P_{N_2O_4})^2/P_{NO_2}$ in Fig. 12.

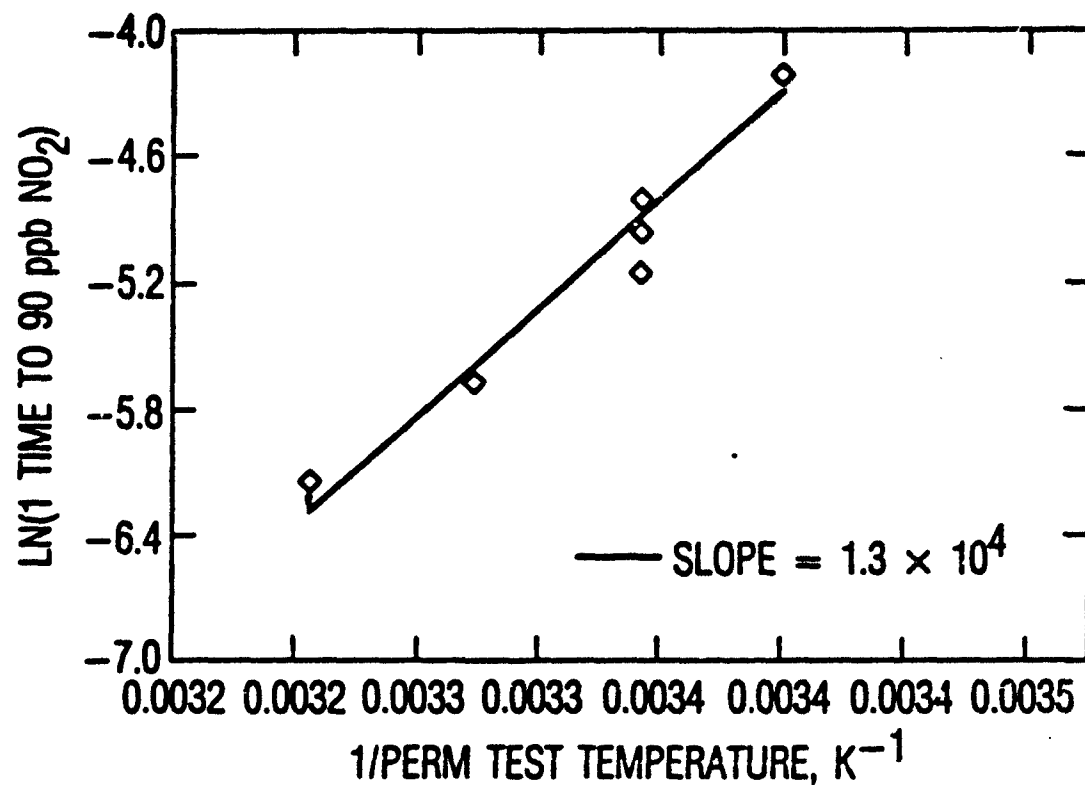


Fig. 10. Unconditioned PHE, Showing the Effect of the Permeation Test Chamber Temperature. The natural logarithms of the inverse of the NO₂ breakthrough times are plotted against the inverse of the permeation test chamber temperature. The slope yields a calculated "activation energy" of -26 kcal/mole (slope/R).

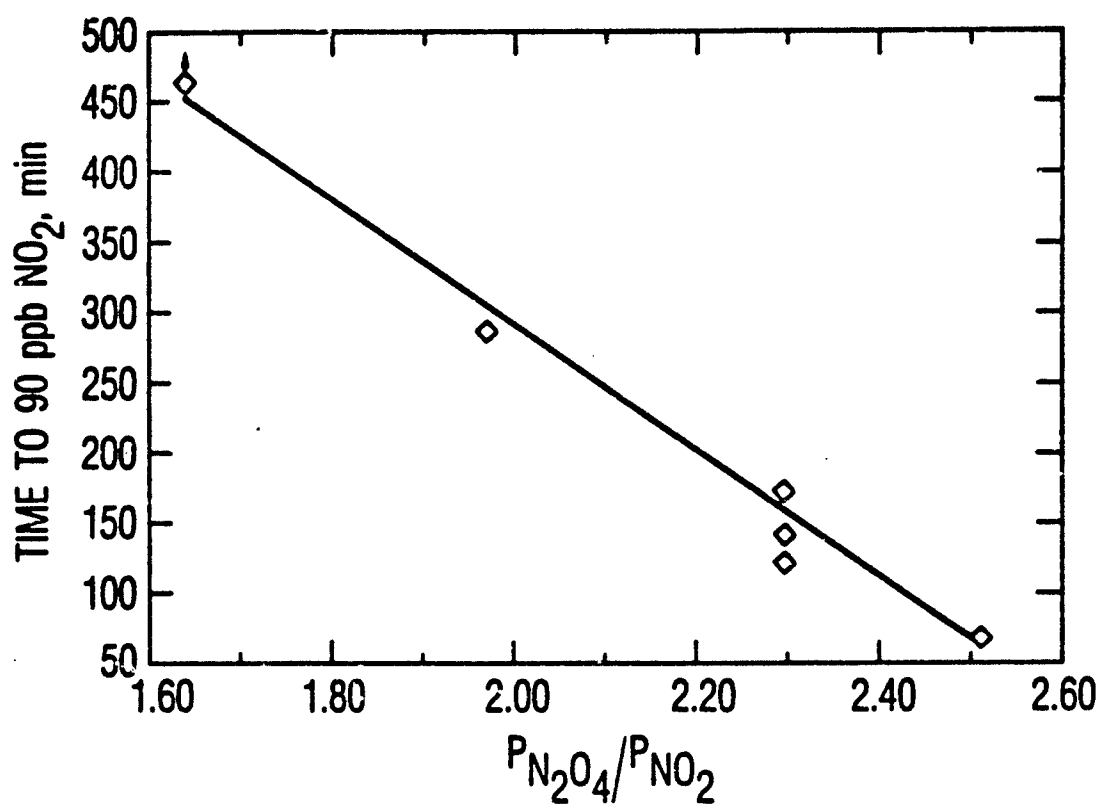


Fig. 11. Unconditioned ZHE, Showing the Effect of the Permeation Test Chamber Temperature. The breakthrough times are plotted against the ratio of the partial pressures of N_2O_4 and NO_2 . This ratio decreases as the permeation test chamber temperature is increased. The lowest ratio data point represents a minimum value, since no breakthrough occurred during the 464 min of the monitoring.

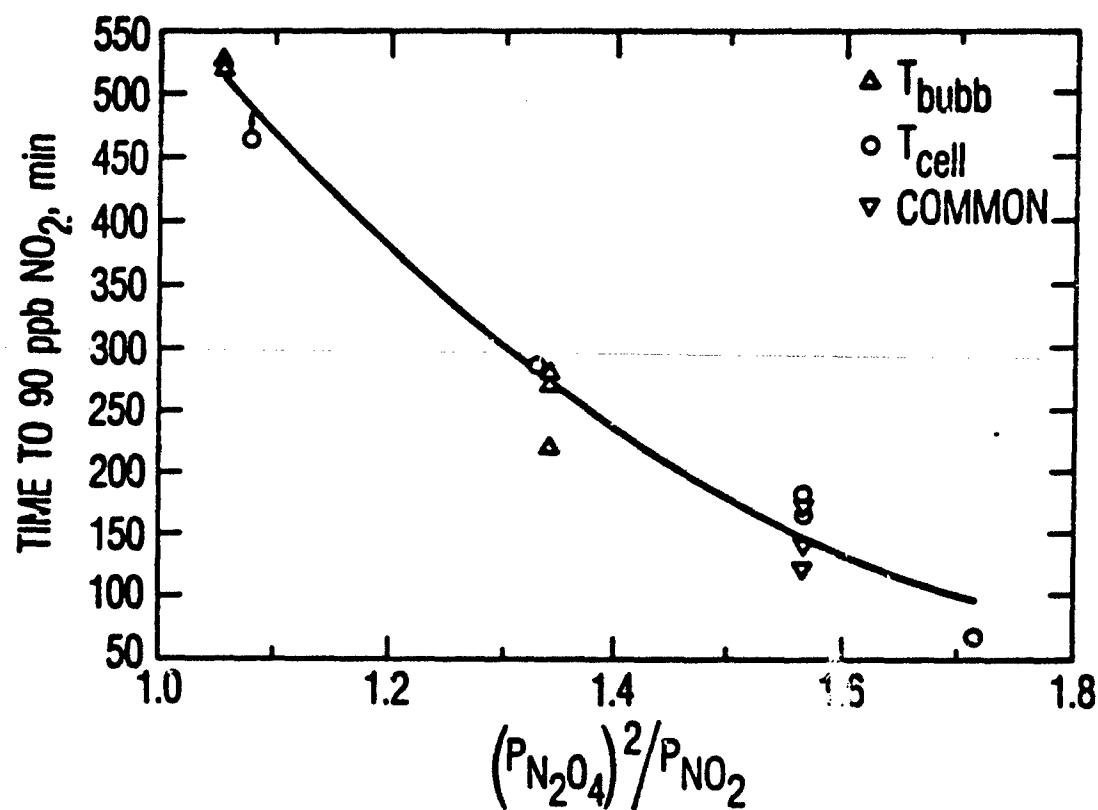


Fig. 12. Unconditioned PHE, Showing the Combined Effect of the Temperatures of Both the Bubbler (T_{bubb}) and the Permeation Test Chamber (T_{cell}). The common data are the data used in Figs. 7 and 9 (T_{bubb} and T_{cell} plots). The breakthrough times are plotted against the product of the partial pressure of N_2O_4 (which is strongly influenced by T_{bubb}) times the ratio of the partial pressures of N_2O_4 to NO_2 (which is strongly influenced by T_{cell}).

The data are symbolically labeled in Fig. 12 as follows: triangles represent the experiments that investigated the effect of T_{bubb} , circles represent the experiments that investigated the effect of T_{cell} , and upside-down triangles represent the experiments common to both investigations. Since we had previously concluded that the experiments that investigated the effect of molar flow of " N_2O_4 " were indistinguishable from the T_{bubb} data, they were also included (as triangles) in Fig. 12. Likewise, the experiments that investigated the effect of differential pressure were included (as circles) with the T_{cell} data.

It is apparent that the breakthrough times for all of the experiments included in Fig. 12 appear to have the same complicated dependence upon the partial pressures of the oxides of nitrogen. Therefore, at least part of the observed dependence of the breakthrough times upon the permeation test cell temperature (T_{cell}) may be due to the temperature dependence of the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium. This does not, however, rule out the potential importance of condensation and possibly solubility upon the observed dependence of breakthrough time on permeation test cell temperature.

Consequently, these data indicate that the temperature of the permeation test chamber (i.e., the temperature of the oxidizer/air mixture and the test material) is an important experimental parameter. Since the permeation test cell temperature was not controlled in earlier test procedures, the variation in laboratory temperatures probably contributed to the inconsistent results reported by ADL, NASA, and MMC.

J. EFFECT OF THE DIFFERENTIAL PRESSURE

A discussion of the 298.2-K data in Fig. 9 is helpful in evaluating the potential effect on breakthrough time of the differential pressure across the fabric during the permeation test for the unconditioned PHE (and PHE') material. The following data were included in this comparison: experiments 5, 10, and 16 (represented as diamonds) were performed at a differential pressure of 75 Pa across the PHE (and PHE') material; experiment 9 (represented as an inverted triangle) was performed at a differential pressure of 250 Pa across

the PHE material; and experiment 13 (represented as a circle) was performed at a differential pressure of -250 Pa across the PHE material.

Upon examination of the above data in Fig. 9, it appears that any effect that the differential pressure across the material might have on the NO₂ breakthrough time of the Propellant Handler's Ensemble coverall material is overshadowed by the scatter in the determination of the breakthrough times. Therefore, over the range of -250 to 250 Pa (-1 to +1 inches of water) differential pressure, the scatter in the breakthrough time which results from material variation appears to be greater than any effect due to the changes in differential pressure.

K. RATE OF DETERIORATION

In the previous sections, the breakthrough time was used as an indicator of the permeation resistance of the materials under various test conditions. Once "breakthrough" has occurred, the rate of deterioration of the permeation resistance of the fabric can be represented by the time required for the oxidizer concentration in the sweep gas to increase from the breakthrough concentration of 0.09 ppm (column 14 in Table 1) to 3.0 ppm (column 15 in Table 1). We will refer to this difference in time as Δt and have plotted Δt versus the breakthrough time in Fig. 13 for most of our experiments; the PHE data are represented as diamonds, the RPHCO data as circles, and the CHEM data as squares. In experiments 1, 2, 5, 6, 17, and 26, the value in column 15 of Table 1 was either approximate (being obtained from a small extrapolation on the strip chart recording) or was undetermined. Therefore, Δt could not be determined for these tests and is not represented for them in Fig. 13. The line in Fig. 13 represents a first-order least-squares fit to all of the included experimental data.

It is apparent from examination of Fig. 13 that both the breakthrough time and Δt are useful indicators of the rate of deterioration of the materials following exposure to the oxidizer; the data indicate that early breakthrough is usually accompanied by a relatively short Δt .

A short Δt presents a special danger from an operational point of view, since it indicates that the propellant handler would have very little time

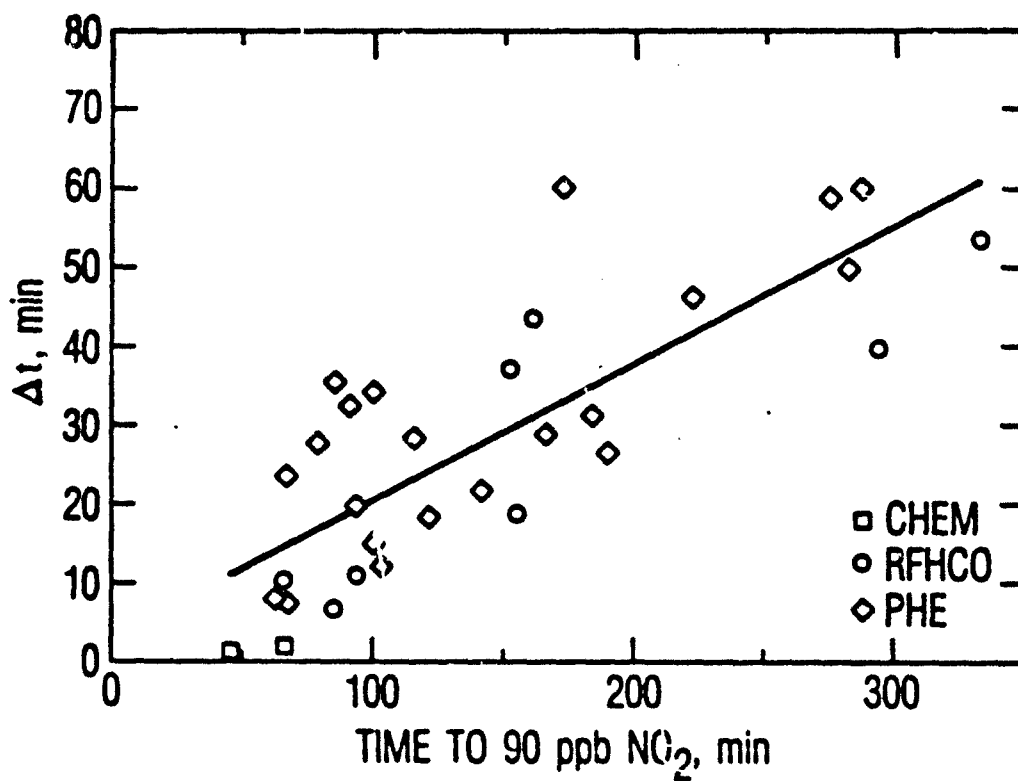


Fig. 13. Rate of Deterioration. Δt is defined as the difference in time between obtaining breakthrough (NO_2 concentration = 0.09 ppm in the sweep air) and obtaining an NO_2 concentration of 3.0 ppm in the sweep air. Δt values for the CHEM ($\square$), RFHCO ($\circ$), and both batches of the Propellant Handler's Ensemble ($\diamond$) are plotted against the breakthrough times for each experiment.

between first detecting breakthrough (by his nose, for example) and having dangerous concentrations within the ensemble. It should be noted that the CHEM results (squares in Fig. 13) represent an extreme case of early breakthrough followed by catastrophic failure of the material within 1 to 2 min. On the other hand, both the RFHCO and PHE samples provided Δt 's of more than 6.6 min, even under worst-case test conditions.

Therefore, the chlorobutyl materials (i.e., PHE and RFHCO) not only provide better permeation resistance (i.e., have longer breakthrough times for the same test conditions) but also deteriorate more slowly (i.e., have larger Δt 's for the same breakthrough times) than the CHEM (chlorinated polyethylene) material.

L. WORST-CASE CONDITIONS

Since the Qualification Test Procedure did not define or specify the value of many of the experimental parameters that we investigated, it is difficult to determine when enough data have been taken. If one assumes that the material must meet the Qualification requirements under worst-case conditions, then enough data must be collected to define those conditions. We identified the worst-case conditions for the unconditioned samples and then tested the conditioned samples under these "worst-case" conditions.

1. FOR UNCONDITIONED SAMPLES

As indicated in our previous discussions of the test results, the breakthrough time depends most strongly upon the temperature of the permeation test cell (see Figs. 9 through 11) and upon the temperature of the bubbler (see Figs. 7 and 8). Since N_2O_4/NO_2 vapor would condense in the test cell if the temperature of the permeation test cell became cooler than the temperature of the N_2O_4 bubbler, the worst-case condition for noncondensable vapor exposures would be either (case A) a low permeation test cell temperature at a reduced bubbler temperature or (case B) a high bubbler temperature at slightly elevated permeation test cell temperature.

We investigated case A in experiment 28. For this experiment we simultaneously reduced the temperature of both the permeation test cell

and the N_2O_4 bubbler by 5 K from the test conditions used in experiment 15, which showed the fastest breakthrough time (Fig. 9). Since the breakthrough time for experiment 28 was 2.8 times slower than that for experiment 15, the most important experimental parameter appears to be the bubbler temperature and hence the $P_{N_2O_4}$ to which the material is exposed.

We investigated case B in order to confirm the above conclusion. In experiment 29 we simultaneously increased both the temperature of the permeation test cell and the bubbler temperature by 1.3 K from the test conditions used in experiment 15. As predicted in the above paragraph, the breakthrough occurred sooner in experiment 29 (at 62 min) than for any other PHE sample tested under any of the previous test conditions. The RFHCO coverall samples tested in experiments 30 and 31 under these same conditions had shorter breakthrough times (93 and 85 min, respectively) than for any other RFHCO sample tested under any previous test condition. It should be noted that the unconditioned RFHCO coverall samples had 44% longer breakthrough times than did the unconditioned sample of PHE' under worst-case conditions; therefore, the relative ranking is the same as that established in all earlier tests.

Thus the worst-case permeation test conditions for the unconditioned PHE material are a 288.2-K conditioning temperature, a 295.5-K permeation test temperature, and a 294.5-K bubbler temperature. It should be noted that an operationally reasonable worst-case condition could involve cold PHE material and a warm source of oxidizer; under these conditions N_2O_4 might condense onto the fabric. Consequently, one would expect that the breakthrough times for condensed N_2O_4 vapor would approach those obtained for an initial exposure to liquid N_2O_4 .

2. FOR CONDITIONED SAMPLES

The permeation resistances of conditioned samples of PHE' (experiments 32 and 33) and a conditioned sample of RFHCO (experiment 34) were determined under the worst-case permeation test conditions that applied to unconditioned PHE'. These tests were carried out 3 to 4 months after experiments 29 through 31 (on the unconditioned samples) in a different building at The Aerospace Corporation.

On the basis of the effects of conditioning chlorobutyl materials in the experiments discussed previously (see Section IV.B), we would have predicted that the conditioned chlorobutyl experiments (32, 33, and 34) would have had shorter breakthrough times than the unconditioned chlorobutyl experiments (29, 30, and 31) for the worst-case test conditions. This was the case for the RFHCO samples but not for the PHE' coverall samples. The breakthrough times for the conditioned PHE' samples were 66% longer than the breakthrough time for the unconditioned PHE' when tested under the worst-case conditions that were determined for unconditioned samples. Since all experimental parameters were set to the worst-case conditions, the greater permeation resistance of these conditioned samples must be attributed to a greater inherent permeation resistance of the aged samples (see discussion below), a different effect of conditioning for the worst-case test conditions, or a combination of both these factors.

3. EFFECT OF SAMPLE AGING

In order to evaluate the effect of aging upon the permeation resistance of the RFHCO coverall material, two additional permeation tests were carried out on unconditioned RFHCO coverall samples (experiments 36 and 37) at the same worst-case conditions used 4 months earlier for experiments 30 and 31. It is apparent that the older RFHCO samples had much greater permeation resistance when tested under the same permeation test conditions. Therefore, it appears that the permeation resistance of samples of chlorobutyl materials will change upon storage at room temperature in an office environment.

4. EFFECT OF PERMEATION TEST TEMPERATURE REVISITED

The effect of the permeation test chamber temperature upon the breakthrough time was evaluated for unconditioned samples of the PHE coverall and was discussed in Section IV.I. Comparison of the results of experiments 32 and 33 with the result of experiment 35 indicates that a 12.7-K increase in permeation test chamber temperature resulted in a 66% increase in breakthrough time for conditioned PHE' samples that were challenged with the highest concentration of oxidizer. On the other hand, a 14-K increase in permeation test temperature resulted in a 582% increase in breakthrough time for

unconditioned PHE' samples that were challenged with the same concentrations of oxidizer vapor in a series of tests performed several months earlier.

Therefore, the breakthrough time is a function of the permeation test cell temperature for both conditioned and unconditioned samples of material. The magnitude of the sensitivity to the permeation test temperature appears to depend upon one or more of the following: the age of the sample; the exposure history (i.e., cycles of conditioning); the permeation test conditions; and the sample-to-sample variability of the materials.

5. RELATIVE RANKING REVISITED

In all previous experiments, samples of the RFHCO coverall material exhibited longer NO₂ breakthrough times than the samples of the PHE coverall material tested under identical experimental conditions. The results of experiments 34 (RFHCO) and experiments 32 and 33 (PHE) represent an exception to this ranking. All three of these tests were performed in the same time period under identical experimental conditions, yet the breakthrough time of the RFHCO sample was only 65 min compared with the 103 and 100 min for the PHE samples. These data indicate that the relative ranking of these materials depends upon the same parameters that were listed in the previous paragraph.

M. QUALIFICATION OF THE MATERIALS

As discussed in Section II, the Qualification Test Procedure specified that the NO₂ concentration on the unexposed side of the material be monitored with an Ecolyzer NO₂ detector until either a sharp increase in NO₂ concentration occurs in the sweep gas or 2 hr have elapsed since the initiation of exposure. Since no pass or fail criteria were defined in the MMC T79-80A test procedure, the NASA specification⁴ for the PHE indicated that the results should be evaluated according to the requirements of an earlier military specification⁷ for other chlorobutyl materials in which an acceptable cumulative NO₂ permeation during the first hour of N₂O₄ vapor exposure is specified to be 1.54×10^{-3} mg NO₂/cm². For comparison this would be equivalent to an average of 0.17 ppm of NO₂ throughout the first hour in the 2-l/min sweep air flow and for the 24.6 cm² area of fabric that were used in our tests.

Therefore, the concentration (0.09 ppm NO₂) that we defined as "breakthrough" in our experiments is one half of this characteristic concentration.

Both the RFHCO and PHE coverall materials resisted permeation by NO₂ vapor for more than 60 min under all experimental conditions investigated, and therefore met the requirements of the NASA specification.

Under the conditions of experiment 23, unconditioned CHEM coverall material (Cloropel) was permeated by NO₂ within 46 min, and the concentration of NO₂ vapor in the sweep air increased beyond the range of the detector (>3.0 ppm) within a minute of the breakthrough. Even had the concentration remained at 3.0 ppm for the remaining 13 min of the hour, the cumulative NO₂ permeation during the first hour would have been 0.006 mg NO₂/cm², which is approximately 4 times the maximum acceptable by the NASA specification. Since it is more likely that the NO₂ concentration would have continued to increase after it exceeded the scale of the Ecolyzer, the actual cumulative NO₂ permeation was probably much higher than this estimate.

As previously discussed, the CHEM material was severely attacked during the first cycle of conditioning and was so badly curled that it could not be installed into the conditioning apparatus for the second cycle of conditioning. Therefore, the permeation resistance of the unconditioned CHEM coverall material is not only inadequate according to the acceptance criteria of the military specification, but also is so badly attacked by the liquid hypergols that it would not likely be reused following such an exposure.

V. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

In order to provide for future interlaboratory comparison of permeation test results, our experiments have established the need for a more detailed NO_2 permeation test procedure than those previously used by NASA and the Air Force.

We have described a test apparatus and a procedure for carrying out reproducible conditioning of material samples by controlled exposure to known volumes of liquid hypergols at a well-defined temperature, as well as for conducting subsequent quantitative permeation tests of the conditioned samples under conditions of controlled temperature, absolute pressure, differential pressure, and concentration of the dinitrogen tetroxide vapor.

We carried out $\text{N}_2\text{O}_4/\text{NO}_2$ permeation testing on three coverall materials and have thereby ranked their resistance to permeation by NO_2 as RFHCO > PHE > CHEM in decreasing order of their breakthrough times under most, but not all, experimental conditions. Under most test conditions, samples of the RFHCO coverall material (the E. I. du Pont chlorobutyl material currently used in the construction of the Rocket Fuel Handler's Clothing Outfit) typically resisted permeation by NO_2 by ~1.4 times as long as similarly conditioned samples of the PHE coverall material (the du Pont chlorobutyl material used in the new Propellant Handler's Ensemble) and approximately 4 times as long as similarly conditioned samples of the CHEM coverall material [the ILC Dover chlorinated polyethylene (Cloropel) material currently used in the Chemtursion protective ensemble]. This relative ranking is consistent with the permeation data reported by the Martin Marietta Corporation^{6,11} as well as with our earlier test results.^{1-3,12} It should be noted, however, that samples of the PHE coverall material provided longer breakthrough times than did a sample of similarly conditioned and tested RFHCO coverall material under one set of the experimental conditions we investigated. Therefore, the relative ranking of PHE and RFHCO samples may depend upon one or more of the following: the age of the sample; the exposure history (i.e., cycles of conditioning); the permeation test conditions; and the sample-to-sample variability of the materials.

Our results also indicate that the samples of both the PHE and the RFHCO coverall materials that we tested according to the NASA specification procedures met the criteria for acceptance for use in the Propellant Handler's Ensemble even under worst-case conditions. The failure of the PHE coverall material during the Arthur D. Little test may have resulted from several differences that could include the following: the temperature of the liquid N_2O_4 and the permeation test cell, the volume of hypergol used in the conditioning, and quite likely the age of the samples. Our data suggest that the permeation resistance of the PHE and RFHCO materials may increase with storage in ambient air.

An unconditioned CHEM (Cloropel) sample was permeated by NO_2 vapor after 46 min of exposure to the oxidizer vapor, and therefore appears to have an unacceptable permeation resistance even before it was conditioned. In addition, the Cloropel material became so badly distorted following its exposure to the liquid hypergols that it could not be installed into the conditioning apparatus for the second set of conditioning hypergol exposures. Therefore, it is unlikely that an ensemble made out of the Cloropel material would be considered for reuse after such liquid hypergol exposures.

We used our test apparatus to investigate the importance of various experimental parameters and have demonstrated the importance of defining and controlling the following: the temperature of the permeation test chamber (i.e., the material and the vapor) and the temperature of the liquid N_2O_4 used as the source of oxidizer vapor to which the material is exposed. The conditioning temperature and the differential pressure across the fabric during the permeation test were also investigated and appeared to have little, if any, effect on the breakthrough time of the PHE material over the ranges investigated.

We feel that it would require an enormous effort to investigate all possible experimental conditions for every material. Therefore, convenient or reasonable values of most of the experimental parameters should be consistently defined in future test procedures. We suggest that unconditioned

candidate materials be screened using 308 and 294-K permeation test cell temperatures and 294.5 and 288.2-K bubbler temperatures. The results of these four tests would establish the trends in breakthrough times for the candidate materials in the minimum of time, since each test would require only one day to perform. In addition, the permeation resistance of the materials would be ranked by these tests; thus only the best material would then be subjected to the conditioning and subsequently be tested under the "worst-case conditions" determined for its unconditioned samples.

It is apparent that interlaboratory comparison and batch-to-batch monitoring can only be accomplished by using a permeation test procedure that provides detailed step-by-step protocols and completely defines all of the experimental conditions. We found our test procedure to be adequate for this task and have recommended that the military specification test procedures be updated to include definition and control of the additional experimental parameters that were identified in this report.

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APPENDIX A: EXTENDED DESCRIPTION OF THE APPARATUS

Separate experimental facilities were used to accomplish the liquid N_2O_4 conditioning, the liquid MMH conditioning, and the NO_2 permeation testing. These apparatus are illustrated schematically in the text in Figs. 1, 2, and 3, respectively, and are described in the following paragraphs.

A. LIQUID N_2O_4 CONDITIONING APPARATUS

The liquid N_2O_4 conditioning apparatus (Fig. 1) was composed of the following components: the hypergol reservoir, an air purge system, a water rinse system, a waste reservoir, a temperature control system, and the test stand. Each of these systems will be briefly described in the following paragraphs.

In experiments 1 through 4, 7, 8, 12, 14, and 32 through 35, a water-jacketed, calibrated, Pyrex hypergol reservoir was used to condense 50 ml of liquid N_2O_4 from a N_2O_4 cylinder. The hypergol reservoir was maintained at the same temperature as the conditioning block (normally set at 288.2 K). The N_2O_4 cylinder was maintained at 298.2 K by using an electrically heated copper jacket.

In experiments 19, 20, 21, and 24, the same water-jacketed Pyrex reservoir was used to chill 50 ml of liquid N_2O_4 after the N_2O_4 was transferred from a distillation flask. The liquid N_2O_4 was previously purified by fractional distillation in a second hood in order to evaluate the effects of potential impurities on the permeation test results. The low-temperature (<294.2 K) fraction, which formed blue crystals in the liquid nitrogen trap, was not retained. We collected the 294.2-K (i.e., the normal boiling point of N_2O_4) fraction, which formed white crystals when trapped at liquid nitrogen temperatures. This fraction was stored at reduced temperature under constant dry-air purge until it was used in either the conditioning or permeation tests. The distillation was performed on a weekly basis.

As indicated in Fig. 1, the hypergol reservoir was positioned above the conditioning block, and therefore gravity caused the hypergol to flow onto the

test fabric when the Teflon solenoid valve (SV-11) at the bottom of the reservoir was opened.

The liquid N_2O_4 test stand consisted of a steel platform, a low-profile magnetic mount, a hinged stainless-steel baseplate, and a Teflon block. Additional details of the hinged stainless-steel baseplate and the Teflon block, which were both specifically designed for this program, are illustrated in Fig. 4.

The conditioning block was positioned in the horizontal position ($\theta = 180^\circ$ in Fig. 1) prior to and during the hypergol exposure, and was lowered to an inclined position ($\theta = 115^\circ$) during the water rinse and the air purge; a block and tackle were used which, for the sake of clarity, are not shown in Fig. 1. As illustrated in that same figure, the stainless-steel baseplate and the Teflon block (both detailed in Fig. 4) were cooled with the same water that was circulated through the hypergol reservoir.

A square section of the test material, 10 cm by 10 cm, was sandwiched in the conditioning block (see Fig. 4) between the stainless-steel baseplate and the Teflon block, with the "outside" of the test material facing up. The Teflon block and the stainless-steel baseplate were machined so that the Teflon formed a 0.64-cm-wide seal on the edge of the sample, therefore leaving a 8.9 cm by 8.9 cm surface of one side of the material that would be exposed to the liquid hypergol. The chilled liquid hypergol was introduced through a 0.64-cm-i.d. hole in the top of the Teflon block (see Fig. 4).

The water and air purge systems were used to carry out a 1.5 l/min water rinse of the material after the hypergol exposure and to blow the excess water from the system after the water rinse, respectively. Teflon solenoid valves were used to control the water and air flows. The water was directed into the top of the conditioning block through a Teflon solenoid valve (SV-12), as well as across the material through a series of holes along the hinged side of the conditioning block (see Fig. 4). The conditioning block was lowered ($\theta = 115^\circ$) during the water rinse so that gravity would facilitate drainage. The hypergol and contaminated rinse water drained from the block through a series of holes along the lower edge of the material (furthest from the

hinge). Therefore, the clean water entered along the upper edge of the material, and the contaminated rinse water drained into the waste reservoir from the lower edge of the material. A block and tackle were used to raise and lower the conditioning block remotely during the water rinse and air purge of the system. Therefore, the hypergol exposure and the water rinse were accomplished in one apparatus through remote switching of Teflon solenoid valves and manipulation of the angle of incline of the conditioning block by means of a block and tackle.

The stainless-steel waste reservoir, used as a trap for liquid discharge, was vented to the hood. This allowed the hypergol exposure to be performed at ambient atmospheric pressure. The reservoir was also connected to a water aspirator that was used during the cleanup.

Teflon valves and fittings (Fluorocarbon Co.) were used on the conditioning apparatus in order to prevent contamination of the hypergol and rinse water. FEP Teflon-lined polyethylene tubing (Dixon Industries) was used where there would be direct exposure to the liquid hypergol prior to the use of the conditioning block; it was replaced after each experiment. Poly Flo polyethylene tubing (Imperial-Eastman) was used in the water and air rinse systems and in the wastewater drain. The hypergol-contaminated polyethylene tubing was replaced after each experiment. Stainless-steel valves were used on the N_2O_4 cylinder and on the stainless-steel waste reservoir. Because of corrosion, the waste reservoir valves were replaced periodically.

The apparatus was thoroughly washed and dried prior to each use. In order to verify a positive seal around the edge of the material, the conditioning block was tested for leaks prior to each conditioning.

B. LIQUID MMH CONDITIONING APPARATUS

The liquid MMH conditioning apparatus (Fig. 2) was composed of the following components: the hypergol reservoir, an air purge system, a water rinse system, a waste reservoir, a temperature control system, and the test stand. The same air purge system, water rinse system, and test stand were used in both the MMH and N_2O_4 conditioning apparatus (see above description).

Since liquid MMH was poured directly into the water-jacketed Pyrex hypergol reservoir (after a Teflon fitting was removed), a different design was used for the MMH hypergol reservoir than for the oxidizer reservoir. In order to avoid any contact of the fuel with metals or other sources of ignition, the following changes were made: the Teflon solenoid valves SV-11 and SV-12 of the oxidizer-conditioning apparatus were replaced with manual Teflon valves MV-13 and MV-14, respectively, and a polyethylene waste reservoir replaced the stainless-steel waste reservoir used in the oxidizer apparatus.

The materials used in the MMH conditioning apparatus were the same as those described in the next to last paragraph of Section A of Appendix A, except that a manual Teflon valve (MV-2 in Fig. 2) was used between the MMH waste reservoir and the top of the MMH hypergol reservoir.

The apparatus was thoroughly washed and dried prior to each use. In order to verify a positive seal around the edge of the material, the conditioning block was leak tested prior to each conditioning.

C. NO₂ PERMEATION APPARATUS

The NO₂ permeation apparatus (Fig. 3) is composed of the following systems: the test chamber, the temperature control system, the N₂O₄ vapor generator, the pressure monitoring and control system, the waste reservoir, and compressed air supplies.

The test cell, which was contained within the test chamber, was made from two modified glass joints (Kontes of California, K671750 connector) that had stems that were 50 mm i.d. by 54 mm o.d. A size 2-229, butyl rubber O-ring (Absco Industries, B-591-80) was used to form an air-tight seal between the unexposed side of the test material and the upper half of the test cell; a new O-ring was used in every experiment. In order to avoid problems resulting from reactivity of the O-ring material with the concentrated oxidizer vapor, no O-ring was used on the conditioned side ("outside") of the fabric which faces the lower half of the test cell; direct contact with the rim of the bottom Pyrex joint was found to provide an adequate seal with the fabric.

The temperature in the test cell was monitored with a YSI model 425C tele-thermometer thermocouple that was inserted into a dimple in the wall of the test cell. The temperature of the test cell was regulated with a Plexiglas housing, a fan, a radiator, and a circulating constant-temperature bath (either a Lauda RC-3T-2 or a Neslab LT-50). The temperature could be maintained to within ± 0.5 K of the selected temperature throughout the permeation test.

A 1000-Torr range, absolute-capacitance manometer (MKS Baratron 370HS-1000 head, 170M-6C power supply, and 170M-27E digital readout) was used to monitor the absolute pressure in the test cell. The differential pressure across the material was monitored with a 10-in.-of-water range, differential capacitance manometer (MKS Baratron 400-10 head and a PDR-5B readout). The absolute and differential pressures were adjusted by restricting the sweep air flow from the top of the test cell using stainless-steel, Nupro manual valve MV-15 (Fig. 3) and by restricting the oxidizer flow from the bottom of the test cell using stainless-steel, Nupro manual valve MV-16. The differential pressure required constant monitoring throughout the experiment in order to keep it within 12 Pa (0.5 in. of water pressure) of the specified value. The sweep air flow was adjusted to 2 l/min by means of the metering valve on the rotameter (no. 603 from Matheson). A mechanical pump (Welch Duo-Seal model 1402B-01 vacuum pump) was used to zero the absolute capacitance manometer before each experiment and to pump out the manometers following each experiment.

A special gas manifold was designed and constructed out of Teflon tubing (Cole-Parmer) and Teflon solenoid valves (Fluorocarbon Co.) in order to establish the correct differential pressure prior to the start of hypergol exposure, and to minimize the time required for the initiation of the exposure. Initially the test cell pressures were established with an air flow through both the top and the bottom of the test cell. The flow through the bottom of the test cell was adjusted by manual valve MV-18 (Nupro stainless steel). The flow was monitored by a 500-ccm nitrogen mass flow meter (Tylan FM360) with a digital display (Matheson model 8143); the meter was calibrated in our laboratory for air. The air flow through the bottom of the test cell

could be switched on and off by Teflon solenoid valve SV-17 (Fluorocarbon Co.).

A calculated flow of ~2.4 moles of " N_2O_4 "/min was generated by means of a small flow of air (5 ml/min for the 293-K bubbler temperature) through a water-jacketed bubbler that contained liquid N_2O_4 . The moles of " N_2O_4 " are the moles that would exist if there were no dissociation into NO_2 . The bubbler was maintained at a constant temperature by means of a circulating water bath (Lauda RC-3B2 or Neslab LT-50). The oxidizer vapor was vented through Teflon solenoid valve SV-24 prior to the start of the experiment. The differential pressure across the test material was established by means of a 77-ml/min air flow through the bottom of the test cell. This flow was controlled by manual valve MV-18. The exposure was initiated by simultaneously shutting Teflon solenoid valves SV-17 (which stops the air flow to the bottom of the test cell) and SV-24 (which closes the vent for the oxidizer vapor) while opening Teflon solenoid valve SV-26. In this way the oxidizer vapor was diverted into the bottom of the test cell and the exposure of the material was initiated.

The same stainless-steel waste reservoir used in the oxidizer conditioning apparatus was used in the permeation test apparatus. The aspirator was used during clean-up procedures. During the permeation test, all of the waste oxidizer vapors were vented to the hood through the waste reservoir that contained approximately 100 ml of water. The waste oxidizer vapor passed over and not through this water.

Teflon valves and fittings (Fluorocarbon Co.) were used on the oxidizer vapor manifold. FEP Teflon-lined polyethylene tubing (Dixon Industries) was used where there would be direct exposure to the oxidizer vapor, whereas Teflon tubing (Cole-Parmer) was used where there would be direct contact with liquid oxidizer. The FEP Teflon-lined polyethylene tubing was replaced after each experiment. Poly Flo polyethylene tubing (Imperial-Eastman) was used for air flow and for the waste vapor. Oxidizer-contaminated Poly Flo tubing was replaced after each experiment. Stainless-steel valves were used on the N_2O_4 cylinder, on the stainless-steel waste reservoir, and for the flow restrictor

valves from the test cell. These valves were replaced periodically. Stainless-steel bellows valves were used in the capacitance manometer manifold and were pumped out after each use.

The apparatus was thoroughly purged with dry air after each use. Any tubing that could outgas oxidizer onto the fabric prior to the start of the oxidizer vapor exposure was replaced before each experiment. All oxidizer-contaminated polyethylene and Teflon-lined polyethylene tubing was replaced before each experiment. The permeation test cell was washed and oven-dried prior to each experiment.

APPENDIX B: EXTENDED DESCRIPTION OF THE PROCEDURES

Our experiments can be considered extensions of the Martin Marietta Corporation test procedure MMC T79-80A. Our experimental procedure consists of the following two stages: (1) one side of the material sample is "conditioned" by a series of alternating, 1-min exposures to 50 ml of liquid N_2O_4 and 50 ml of liquid monomethylhydrazine (MMH) which are separated by water rinses and air drying; (2) the material's resistance to permeation by NO_2 is then determined by a second test apparatus that allows the conditioned side of the test material to be exposed to N_2O_4/NO_2 vapor while the concentration of NO_2 in a 2-l/min flow of sweep air is monitored on the other side of the material. The "breakthrough time" of the material is defined as the time required for the NO_2 concentration in the sweep air to reach 0.09 parts per million NO_2 as determined by the Ecolyzer electrochemical detector. Since the experimental parameters and conditions were carefully controlled, the breakthrough times were used to rank the permeation resistance of different materials.

In order to evaluate the effects of the conditioning temperature, eliminate any problems with preferential decay of the material at the edge of the conditioning cell, avoid the potential effects due to the depth of the liquid hypergol on the material, and reduce the safety concerns in implementing the initial water rinse, we designed the special conditioning apparatus described in Section III and in Appendix A. These apparatus allow the temperature of the hypergol reservoir and conditioning block to be controlled, provide for conditioning larger areas of the material than are required in the permeation test cell, reproducibly deliver 50 ml of chilled liquid hypergol onto the material, and provide for remote control of the water rinse and the air purge of the system.

In order to evaluate the effects of the temperature during the permeation test, of the differential pressure across the fabric, and of the concentration of the oxidizer on the NO_2 breakthrough times for the PHE material, we designed the special permeation test apparatus described in Section III and in

Appendix A. It should be noted that the absolute pressure, the NO_2 concentration, and the temperature of the permeation test were not previously controlled or defined in the MMC T79-80A test procedure.

We found that a step-by-step, check-it-off-as-you-go procedure was required in order to ensure that the experimental apparatus and procedures were reproducible. Once the detailed test procedure was established, it was then possible to evaluate the effects of the various individual experimental parameters on the NO_2 breakthrough times for the PHE coverall material, without excessive scatter caused by procedural inconsistencies. The detailed test procedure is available upon request; it is briefly summarized in the following paragraphs.

A. MATERIAL PREPARATION AND CONDITIONING

The material samples were visually examined to ensure that they had no flaws. Their thickness was measured to within ± 0.002 mm by a digital micrometer (Fowler) and recorded. In order to avoid contamination of the samples, they were manipulated by their edges with tweezers. The material was rinsed with deionized water to remove any particulates or foreign materials, then was hung by its edge to dry in the room air for at least 8 hr, or as long as a weekend.

The material was installed in the clean, dry conditioning apparatus in the morning that the conditioning was to be performed. The temperature of the conditioning block was set to the specified temperature before the material was inserted, and was maintained at the specified temperature throughout the course of the conditioning. The leveled ($\theta = 180^\circ$ in Figs. 1 and 2) conditioning block was leak-tested by being pressurized with air to a gage pressure of 2500 Pa (10 in. of water), after which the rate of decay in the pressure was monitored when the air flow was turned off.

The hypergol was introduced into the hypergol reservoir and allowed to come to thermal equilibrium at the specified conditioning temperature. To initiate hypergol exposure, the valve at the bottom of the hypergol reservoir was opened, allowing the 50 ml of hypergol to drain onto the material.

After 55 s of exposure to the liquid hypergol, the test cell was lowered ($\theta = 115^\circ$), and at 60 s after the start of the hypergol exposure the water rinse was initiated. The test cell was slowly raised and lowered during the 50 s of water flow (1.5 l/min), in order to ensure that the entire surface of the fabric was rinsed. The water was then purged from the system for 5 min with dry air (15 l/min).

The material was then removed from the conditioning chamber and sequentially immersed into three beakers of the deionized water for 15, 15, and 30 s, respectively, to ensure uniform rinsing of the surface. The material was then hung in a corner of the hood to air-dry overnight.

Although the above description of the conditioning applies to both the fuel and the oxidizer, different detailed test procedures were required to take into account the differences in the experimental apparatus as well as in the waste disposal requirements.

B. THE PERMEATION TEST PROCEDURE

During the permeation test, the test cell temperature, the oxidizer bubbler temperature, the air flows, the absolute pressure (102,700 Pa = 1.013 atmospheres = 770 mm Hg) in the top side of the test cell, and the differential pressure across the material were carefully controlled. The test materials were clamped in the Pyrex test cell and a butyl rubber O-ring was used to ensure an airtight seal on the sweep-air side of the sample. The exposed area of material was 24.6 cm^2 (i.e., the i.d. was 5.6 cm).

Permeation of NO_2 was monitored by an Energetics Science, Inc. (ESI) 7000 series Ecolyzer, which is an electrochemical detector. Air Products breathing air was swept over the unexposed side of the test material at a rate of 2 l/min and sampled by the ESI detector at 0.71 l/min. The excess sweep gas was vented into the duct of the hood in which the entire apparatus was situated.

After the above experimental parameters were established with air flowing through the bottom of the test cell, the hypergol exposure was initiated by simultaneously switching three solenoid valves that stopped the air flow into

the bottom of the test cell while diverting the ~ 2.4 moles of " N_2O_4 "/min (calculated) flow into the bottom of the test cell. A regulated source of " N_2O_4 " vapor was provided by purging a liquid N_2O_4 bubbler with a few ml/min (5 ml/min for the 293.2-K bubbler temperature) of breathing-quality air. We use moles of " N_2O_4 " to mean the moles that would exist if there were no dissociation to NO_2 .

Two characteristic times were recorded for each test. The breakthrough time ($t = 0.09$) was defined as the time elapsed between the initiation of hypergol exposure and the attainment of 0.09 ppm of NO_2 in the sweep air. The second characteristic time ($t = 3.0$) was the time elapsed between the initiation of hypergol exposure and the attainment of 3.0 ppm of NO_2 in the sweep air.

LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security projects, specializing in advanced military space systems. Providing research support, the corporation's Laboratory Operations conducts experimental and theoretical investigations that focus on the application of scientific and technical advances to such systems. Vital to the success of these investigations is the technical staff's wide-ranging expertise and its ability to stay current with new developments. This expertise is enhanced by a research program aimed at dealing with the many problems associated with rapidly evolving space systems. Contributing their capabilities to the research effort are these individual laboratories:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, chemical dynamics, environmental chemistry, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed chemical and excimer laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, sensor out-of-field-of-view rejection, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photo-sensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, micro-electronics applications, communication protocols, and computer security.

Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices; atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; non-destructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.