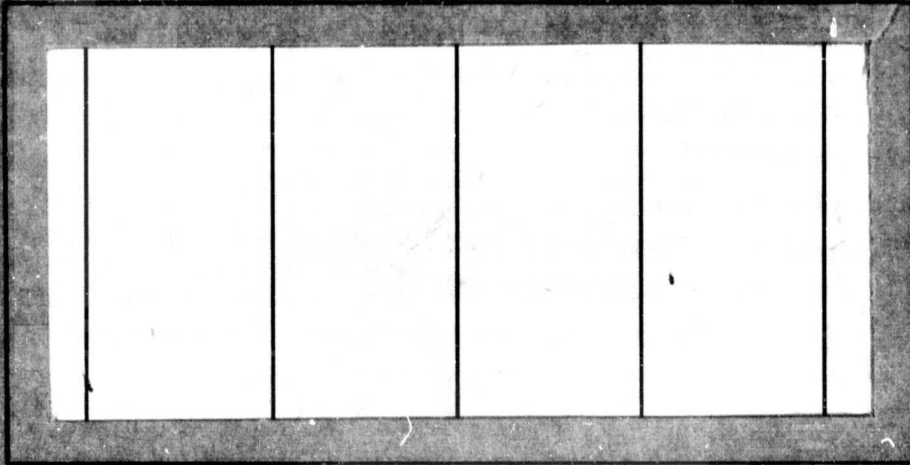


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SCIENCE APPLICATIONS INCORPORATED

(NASA-CR-151247) DEVELOPMENT OF FLAME RESISTANT TREATMENT FOR NOMEX FIBROCUS STRUCTURES Interim Technical Report, 3 Nov. 1975 - 31 Mar. 1977 (Science Applications, Inc.) 25 p HC A02/MF A01 N77-21236 Unclas 24332 CSCL 11E G3/27



DEVELOPMENT OF FLAME RESISTANT TREATMENT
FOR NOMEX FIBROUS STRUCTURES
INTERIM TECHNICAL REPORT

By:

Madeline S. Toy, Ph.D.
Principal Investigator

Prepared For:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lyndon B. Johnson Space Center
Houston, Texas 77058

Attention: Dr. F.S. Dawn, Mail Code EC

Contract NAS9-14827

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FOREWARD

This final technical report represents the results accomplished during the past year. The program on Development of Flame Resistant Treatment for Nomex Fibrous Structure was carried out at Science Applications, Incorporated for the National Aeronautics and Space Administration under Contract NAS9-14827.

The contract is administered by NASA Lyndon B. Johnson Space Center, with Dr. F. S. Dawn as technical monitor.

This report covers work conducted from November 3, 1975 to March 31, 1977. Personnel, who have contributed to the project, are Dr. M. S. Toy and Mr. R. S. Stringham. Mr. L. Fogg assisted in the laboratory and Mr. V. C. Sanford engineered the design of the prototype reactors.

ABSTRACT

The objective of this program is to develop new technology providing flame resistant fibrous materials for Space Shuttle application. The approach is through chemical modification of commercially available aromatic polyamide fibrous products.

The new surface treatment was achieved in the laboratory by ultraviolet activation of the fabric in the presence of fluoroolefin monomers and a diluent gas. The monomers grafted under these conditions provide the improved properties of the fabric in flame resistance, chemical inertness and nonwettability without the sacrifice of color nor physical properties. The addition of a diluent gas such as nitrogen to the active reagents was a major step forward of this program toward a practical industrial process.

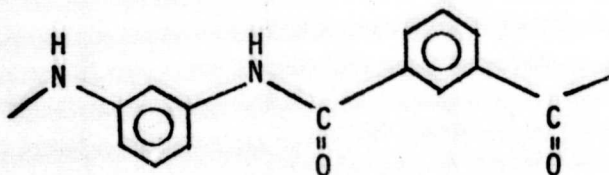
The laboratory reaction vessel was scaled-up to a batch continuous process, which treats ten yards of the commercial width textiles. The treated commercial width Nomex (HT-10-41) from the scaled-up reactor is self-extinguishing in an oxygen-enriched environment, water-repellent, soft, silky and improved in chemical resistance without the sacrifice of color nor its physical properties. Unlike most textile processes, the grafting unit operates under dry conditions and no chemical by-products have to be washed out of the finished product.

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1.0 INTRODUCTION AND SUMMARY

The objective of this program is to develop new technology providing flame resistant fibrous materials for Space Shuttle application. The approach is through chemical modification of commercially available aromatic polyamide fibrous products. Organic fibrous products, which possess a highly aromatic backbone, are known to exhibit outstanding fire resistance. An aromatic polyamide, poly(m-phenyleneisophthalamide), is sold by DuPont under the trademark Nomex:



Nomex

Nomex aramid fibrous structures are self-extinguishing in air under atmospheric pressure, but not in oxygen-enriched environment.

Previous work with Nomex fabric verifies that improvement of flame resistance is feasible through chemical modification such as phosphorylation and halogenation. However, these treatments change the color of the fibrous products to brown or black and exhibit degradation of the aromatic polyamides.

This program is based on our invention to photograft haloolefins onto the surface of Nomex fabric. This new surface grafting technique introduces a chemically bonded surface, which irreversibly modifies the Nomex fabric and upgrades the flame resistant properties in an oxygen enriched environment.

The improved surface treatment was achieved in the laboratory by ultraviolet activation of the fabric in the presence of

fluoroolefin monomers and a diluent gas. The monomers grafted under these conditions provide the improved properties of the fabric in flame resistance, chemical inertness and nonwettability without the sacrifice of color nor physical properties. The addition of a diluent gas such as nitrogen to the active reagents (i.e., the mixed fluoroolefins) was a major step forward in the program for a practical industrial process.

The laboratory treatment and reaction vessel were scaled up to a batch continuous process, which treats ten yards of the commercial width textile. The treated commercial width Nomex (HT-10-41) from the scaled up reactor is self-extinguishing in an oxygen-enriched environment, water-repellent, soft, silky and improved in chemical resistance without the sacrifice of color nor its physical properties. Unlike most textile processes, the grafting unit operates under dry conditions and no chemical by-products have to be washed out of the finished product.

2.0 RESULTS AND DISCUSSION

2.1 Prototype Reactor I

The design and construction of the prototype Reactor I were based on the state of the art developed under a previous Contract NAS9-14839. This task was started simultaneously with the advanced development and process optimization studies of the current project. At that time, the two major problems of the process were:

- (1) The formation of bulk polymer by-product.
- (2) The slow rate of the photolytic reaction.

Prototype Reactor I was constructed for the treatment of commercial width textile of ten yards, so the fabric progresses in the vertical position past the ultraviolet source as shown in Figure 1, which illustrates the interior portion of the fabric on the fabric rolling unit I before inserting into the aluminum vacuum chamber (28.5 cm id and 122 cm length). This is because in a conventional horizontal flow position, problem (1) will definitely be worsened causing nonuniformity and cloudy appearance of the fabric. Thus in an effort to partially resolve this serious problem, Reactor I operates in a vertical position. Figure 2 (Reactor 1) shows the cross section view of Reactor I and the flow of the fabric. The commercial ultraviolet lamps (122 cm in length and 20 mm od), which give out 50 watts at approximately 0.4 watt/cm, were used.

2.2 Advanced Technology Development

The improved process, which was invented under Contract NAS9-14827, not only completely eliminates the bulk polymer problem, but also increased the efficiency and decreases the cost of the process. The addition of a diluent gas such as nitrogen to the active reagents (i.e., the mixed fluoroolefins) is a major step forward for this program toward a practical industrial process.

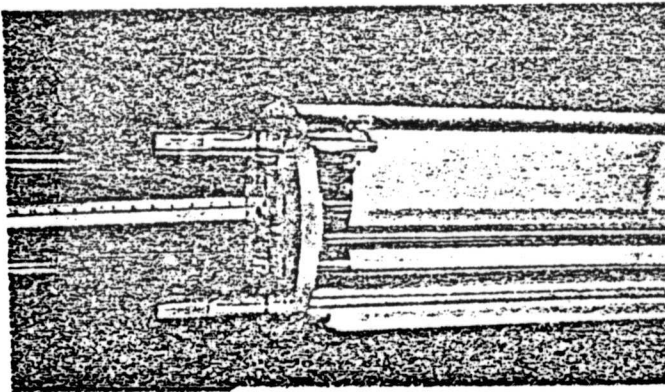
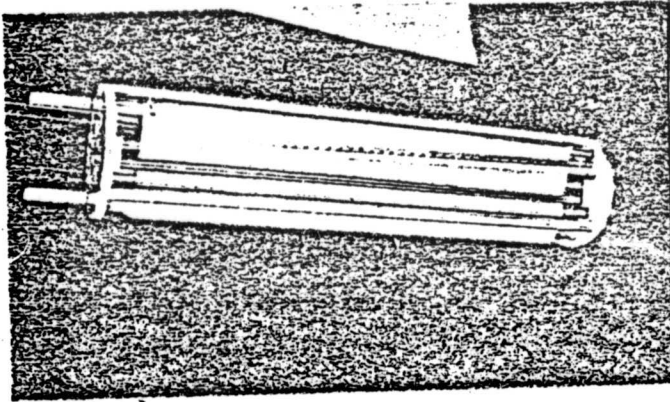
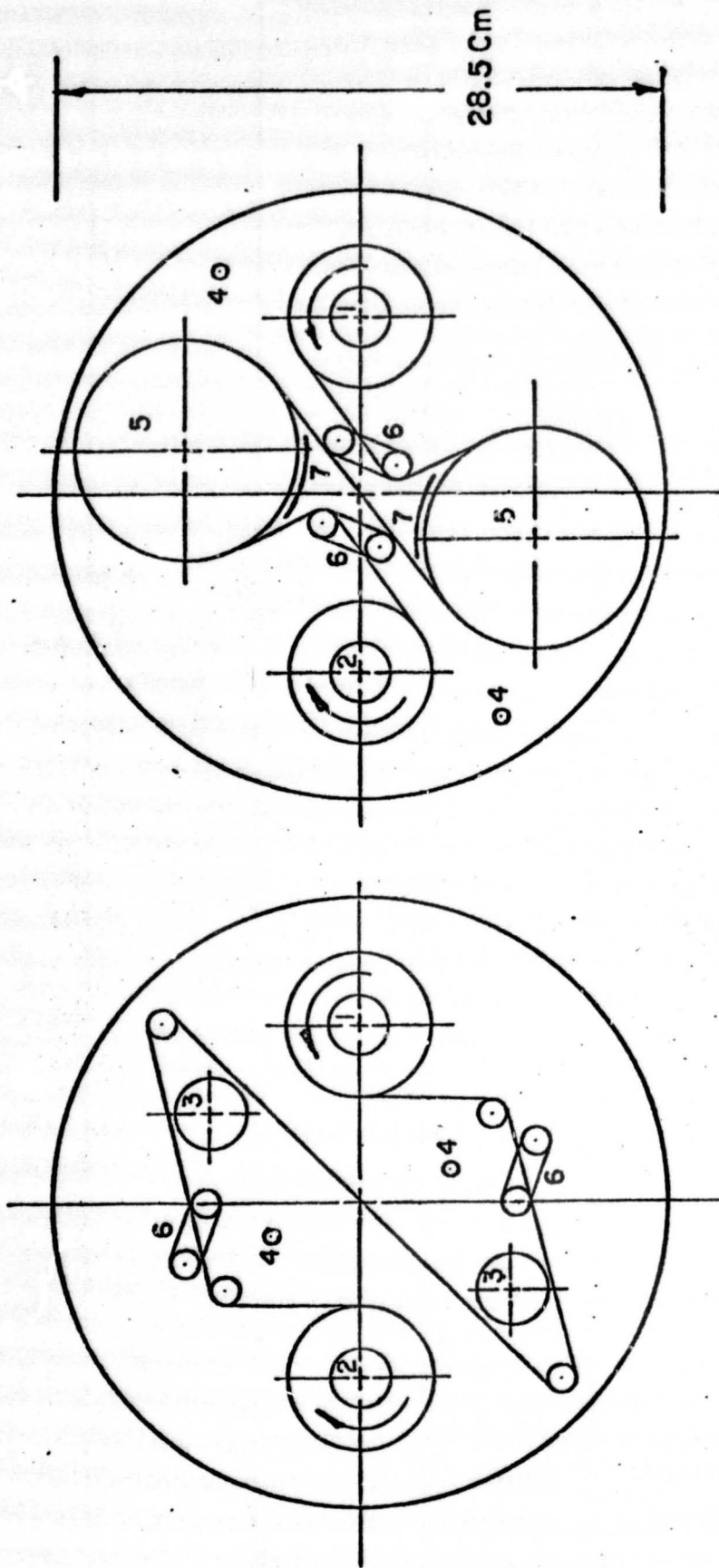


FIGURE 1 NOMEX FABRIC ON FABRIC ROLLING UNIT I
FOR PROTOTYPE REACTOR I



Reactor I (Vertical Flow)

Reactor II (Horizontal Flow)

FIGURE 2 CROSS SECTION OF PROTOTYPE REACTORS SHOWING FLOW OF FABRIC
 (1) Fabric supply, (2) Uptake, (3) Hollow quartz tube (2.6 cm od) and uv lamp,
 (4) Gas inlet, (5) Hollow quartz tube (11.0 cm od) and uv lamp, (6) Tension
 roller, (7) Metal reflector.

The chemistry and process parameters for the laboratory scale treatment, which includes the laboratory reactor, vapor composition, stoichiometry, pressure, temperature and irradiation exposure time and source, are described in Appendix 1. The methods of characterization of the treated fabric consist of water wettability, scanning electron microscope, x-ray analysis, infrared and ^{19}F NMR. Appendix 1 has been accepted for publication in Journal of Applied Polymer Science.

This new photografting technique for flame resistant treatment was also presented at Clemson University, Clemson, South Carolina. The two-day short course (May 25 and 26, 1976) was sponsored by NASA and the university for technology exchange between the textile industry and government. The invention was disclosed in NASA Case No. MSC-16074.

2.3 Process Scale-up and Optimization of Reactor I

The purpose for scaling-up the reaction parameters as described in Appendix 1 was for treating commercial width Nomex fabric (from Stern and Stern Textiles, HT-10-41, woven fabric, natural color, 41 inches width) in Reactor I (Figures 1 and 2). The process optimization includes the following:

- (1) The temperature was increased to 120°C .
- (2) The distance between the ultraviolet source and the fabric as shown in Figure 2 Reactor I was decreased to direct contact with the quartz tube (2.6 cm od) surface.
- (3) A lower cost vapor composition was used, which constitutes 5% of a premixed mixture of $\text{C}_2\text{F}_3\text{Br}$ and C_2F_4 at 60/40 ratio in 95% nitrogen to 635 mm Hg.

The strip of Nomex fabric thus treated in Reactor I became self-extinguishing in an oxygen-enriched environment (i.e., 31/69 O_2/N_2 at 10 psia).

2.4 Prototype Reactor II

Prototype Reactor II (Figure 2) was designed and constructed for the purpose of increasing the surface contact between the fabric and the quartz tubes in order to increase the fabric rolling rate. The same reactor body of Reactor I was used to decrease the added cost of Reactor II. However, the four end plates of the aluminum vacuum chamber of Reactor I had to be replaced, because the new end plates, which are in contact with the large quartz tubes (11.0 cm od), are required to hold and rotate the quartz tubes. The rotating design and seals attached between the end plates and the large quartz tubes were tested, modified and subsequently functioned properly for Reactor II.

The other new features of Reactor II are:

- (1) A gas circulating device was added to replace the propeller of Reactor I.
- (2) The quartz tube outlets were enclosed to replace the air surrounding the ultraviolet lamps with nitrogen in order to eliminate the ozone generation problem.
- (3) A long thin strip of metal reflector piece was placed length-wise along the surface of the quartz tube (Figure 2(7)), which is not in contact with the fabric, to reduce the ultraviolet light from directly shining through the gaseous mixture in the reactor.

2.5 Process Optimization of Reactor II

Optimization of the reaction parameters for Reactor II are the following for treatment of commercial width Nomex fabric (HT-10-41) on one side:

Vapor composition:	C ₂ F ₃ Br (4.5%)
	C ₂ F ₄ (0.5%)
	N ₂ (95.0%)
Total pressure:	630 mm Hg
Temperature:	160°C (between the quartz tube and the fabric)

The one-side treated commercial width Nomex fabric in Reactor II (Run 546RII17) by the above parameters was self-extinguishing in an oxygen-enriched environment (31/69 O₂/N₂ at 10 psia), water repellent, soft, silky and improved in chemical resistance (e.g. conc. H₂SO₄) without the sacrifice of color nor its physical properties.

The gas compositions in Reactor II during the treatment of one foot to a yard of commercial width fabric on one side or both sides were monitored by infrared spectroscopy and no variations in gas composition were detected. There was also no pressure decrease in Reactor II. These two factors suggest an economical process.

An accumulative treatment on one side by the same parameters as Run 546RII17 had been demonstrated to further improve the self-extinguishing property or flammability rating. However when the Nomex fabric was treated on both sides (Figure 2) using the parameters of Run 546RII17, a lower level flammability rating was achieved (Sample 546RII22). Samples 546RII17 and 546RII22 were mailed to NASA-JSC-ES5 and both samples were tested as acceptable for space shuttle applications.

2.6 Production Item

Due to the limited time and effort available, the ten yards of Nomex fabric (HT-10-41 at 41 inches width) were treated on one side by an accumulative treatment method. As the number of treatments increased the self-extinguishing property of the fabric increased and then decreased with extensive treatments.

Appendix 1

Paper Accepted for Journal of Applied Polymer Science.

PHOTOADDITION OF FLUOROOLEFINS ON AROMATIC POLYAMIDE

MADELINE S. TOY and ROGER S. STRINGHAM, Science Applications, Inc.
1257 Tasman Drive, Sunnyvale, California 94086, and FREDERIC S. DAWN,
National Aeronautics and Space Administration, Lyndon B. Johnson Space
Center, Houston, Texas 77058

SYNOPSIS

A photografting method has been developed to surface-treat aromatic polyamide fabrics in the presence of fluoroolefin vapors. The new fabrics are more flame-resistant in oxygen-enriched environment than untreated commercial aramid fabrics. The photoaddition reaction of haloolefins has been shown to irreversibly modify the fabrics, which were analyzed by water-wettability, scanning electron microscopy, x-ray analysis and F^{19} nuclear magnetic resonance spectroscopy.

INTRODUCTION

The objective of this work is to chemically modify commercial aromatic polyamide for providing flame-resistant fibrous materials in an oxygen-enriched environment. Such fibrous products are aimed for applications in space and deep-sea vehicles. Organic fibrous products, which possess highly aromatic backbone, are known to exhibit outstanding flame resistance.¹ Nomex, which is a high temperature aromatic polyamide manufactured by du Pont, is self-extinguishing in air but burns in atmospheres with an elevated partial pressure of oxygen (e.g., 31/69 O₂/N₂ at 10 psia).

Prior work with Nomex fabric shows that improvement of flame resistance is feasible through chemical modification as phosphorylation² and halogenation.³ However, such treatments strongly color the fibrous products and also degrade the aromatic polyamide.

This paper describes a photoaddition reaction of fluoroolefins to modify aromatic polyamide without the apparent change of physical properties and appearance of the fibrous material.

EXPERIMENTAL

Materials

Aromatic polyamide (Nomex HT-10-41, woven fabric, natural color) was purchased from Stern and Stern Textiles. Tetrafluoroethylene and bromotrifluoroethylene were obtained from PCR and nitrogen (99.999%), special gas mixture of 31% oxygen and 69% nitrogen and fluorotrichloromethane from Matheson Gas. The fabric and reagents were used as received. The vapors of fluoroolefins were checked by infrared analysis.

Apparatus

A copper vacuum manifold was used for transferring fluoroolefin vapors from the storage cylinder to a piece of fabric specimen hanging in a reaction vessel (Figure 1). The cylindrical Pyrex reaction vessel consists of a centered quartz sleeve for receiving a 11-inch Pen Ray mercury-arc lamp (Ultraviolet Products). Pressures were measured with Heise gauge and the reaction temperature was maintained by heating tape or infrared lamps.

Figure 2 shows the flammability test apparatus. The ignitor (Type B, Clenweld Products) was held in position by coiled Nichrome ignition wire (1ohm/in). The sample (2.5 x 5 inches) was mounted vertically between the stainless steel sample holders, leaving 2 x 5 inches of exposed surface. The vertical flame test⁴ uses a mixture of 31% oxygen and 69% nitrogen at 10 psia.

Analytical Instruments and Sample Preparations

For ir transmission analysis, a strip of fabric was ground into 40 mesh, mixed with KBr and pressed into a pellet. A fabric sample for attenuated total reflectance (ATR) ir used a Wilkes double-beam ATR attachment at a 45° angle of incidence in direct contact with a KRS-5 reflector plate (52.5 x 20 x 2mm). Both ir transmission and ATR spectra were recorded on a Perkin Elmer Model 467 spectrometer.

A Cambridge Mark IIA Stereoscan scanning electron microscope (SEM), equipped with an EDAX 505 energy dispersive x-ray probe, was used for the photomicrographs and x-ray analysis. The SEM fabric samples were chilled and cut in liquid nitrogen for a clearer end view at the interphase and were subsequently deposited with a thin layer of gold-palladium. An antistatic solution (Ernest F. Fullam, Inc.) was added on the SEM fabric

samples right before examination for improved resolution of the photomicrographs.

The F^{19} NMR spectrum was measured by a Varian XL-100 spectrometer operating at 94.1MHz. A piece of 4 x 9 inches (3.6g) treated Nomex fabric was shredded into individual fibers and dissolved in 4ml concentrated sulfuric acid with added deuterated water for the internal lock. The viscous solution was poured into a 12mm o.d. NMR tube. Fluorotrichloromethane was used as an external standard.

Procedure

The fabric sample was mounted around the centered quartz tube (at 0 to 1cm from the surface) in the photografting reaction vessel (Figure 1b). The side arm was attached to the copper manifold and evacuated. Measured amount of gaseous fluoroolefins as neat or premixed fluoroolefins at specified ratio was introduced alternately for improved mixing with anhydrous nitrogen to a specified pressure, temperature and photolysis time. Amount of volatile reagents were determined by P-V-T measurements assuming ideal gas behavior.

At the end of the irradiation time, the reaction vessel was evacuated and air was introduced. The photografted fabric sample was washed with fluorotrichloromethane and dried under vacuum.

RESULTS AND DISCUSSION

The vertical flame test (Figure 2) in a mixture of 31% oxygen and 69% nitrogen at 10 psia was used to show the difference of flammability characteristics of some photografted Nomex fabric, which were treated by varied fluoroolefin compositions in the presence of

nitrogen. Figure 3 summarizes the results using one exposure to a medium pressure Hg arc lamp (See under Apparatus). The photoaddition reaction of fluoroolefins chemically modified the aromatic polyamide surface and thus upgraded not only the flame resistant properties but also acid resistance.

An increase in light energy of the process shortens the fabric treatment time under photolysis, but high energy ultraviolet source darkens the Nomex fabric rapidly.

In Figure 3 all samples are photografted and water nonwetttable regardless of their flammability characteristics. The water-nonwettability characteristic readily distinguishes them from the untreated samples. However the ir spectroscopy (transmission and ATR) failed to show any significant difference between the treated and untreated samples. The absence of C-F bonds by ATR measurements for difluorocarbene modified fiber surfaces has been previously reported.⁵ The lack of ir absorption for C-F bonds suggests the mono-molecular-like character of the modified surface.

Figure 4 shows the edge views of treated Nomex fiber before (a) and after (b) soaking a 70% sulfuric acid for 80 sec. The SEM photomicrographs illustrate the ease of aromatic polyamide fiber to be strongly etched by the concentrated acid, while the surface of the treated fiber is affected at a substantially decreased rate.

The x-ray probe attached to the SEM is not a sensitive elemental analysis for the light elements,⁶ but the presence of bromine on the photografted fabric shows a strong signal. Thus several treated samples by varied ratios of tetrafluoroethylene and bromotrifluoroethylene were subjected to a gold evaporation process in the same vacuum chamber. Then the gold content of the various samples was assumed as identical and used as the standard. The higher the ratios of C_2F_3Br to C_2F_4 in

the premixed vapor composition shows a corresponding higher bromine content on the treated sample.

The F^{19} NMR spectrum shows the two major narrow absorptions ϕ 144 and 170ppm from $CFC1_3$ at the relative intensities of 2:1 ratio. The spectrum rules out any significant quantity of the homopolymer⁷ and confirms the presence of chemically bonded fluorocarbon-modified Nomex surface.

This work was supported by National Aeronautics and Space Administration under Contract NAS9-14827. The authors are indebted to Mr. B. Lan for preliminary exploration, Mr. L. Cary for F^{19} NMR and Mr. J. Terry for SEM and x-ray analysis.

REFERENCES

1. J. H. Ross and R. M. Stanton, "High Temperature and Flame-Resistant Fibers," ed. by J. Preston and J. Economy, John Wiley, New York, 1973, pp. 109-119.
2. C. E. Hathaway and C. L. Early, *ibid.*, pp. 101-108.
3. S. S. Hirsch (to Monsanto Company) U. S. Patent 3,549,307 (December 27, 1970) and 3,607,798 (September 21, 1971).
4. NASA Document NHB8060.1A, "Flammability, Odor and Offgassing Requirements and Test Procedures for Materials in Environments That Support Combustion," Office of Manned Space Flight, National Aeronautic and Space Administration, Washington, D. C. (February, 1974).
5. D. A. Olsen and A. J. Osteraas, *J. Appl. Polymer Sci.*, 13, 1523 (1969).
6. O. Johari and A. V. Samudra, "Characterization of Solid Surface," ed. by P. F. Kane and G. B. Larrabee, Plenum Press, New York, 1974, p. 118.
7. C. W. Wilson, *J. Polymer Sci.*, 56, 163 (1962).

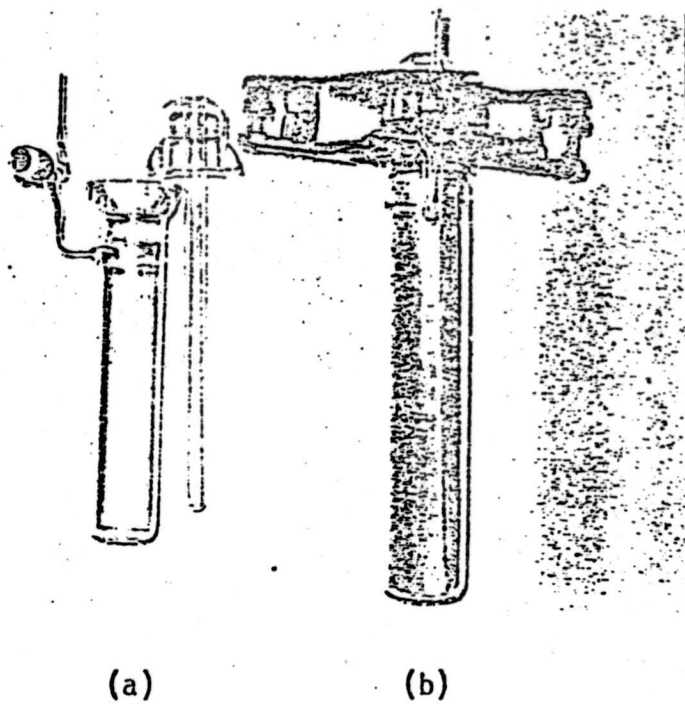


FIG. 1. Reaction vessel (a) an opened cylindrical Pyrex reactor with side arm and valve for attachment to the manifold (to the left) and quartz sleeve (to the right); (b) a closed reaction vessel with the fabric mounted around the centered quartz tube.

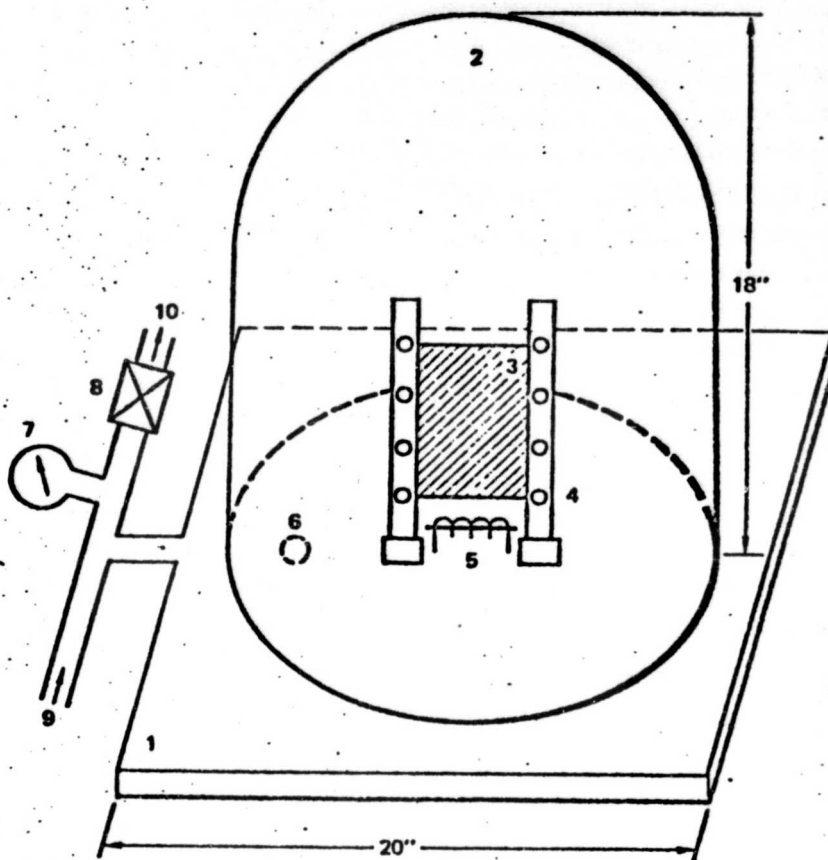


FIG. 2 Flammability Test Apparatus.

1. Metal Base Plate
2. Bell Jar (2 cu ft)
3. Sample
4. Sample Holders
5. Ignition Wire and Ignitor
6. Vacuum and Gas Inlet
7. Vacuum Gauge
8. Valve to Vacuum
9. Gas Inlet
10. To Vacuum Pump

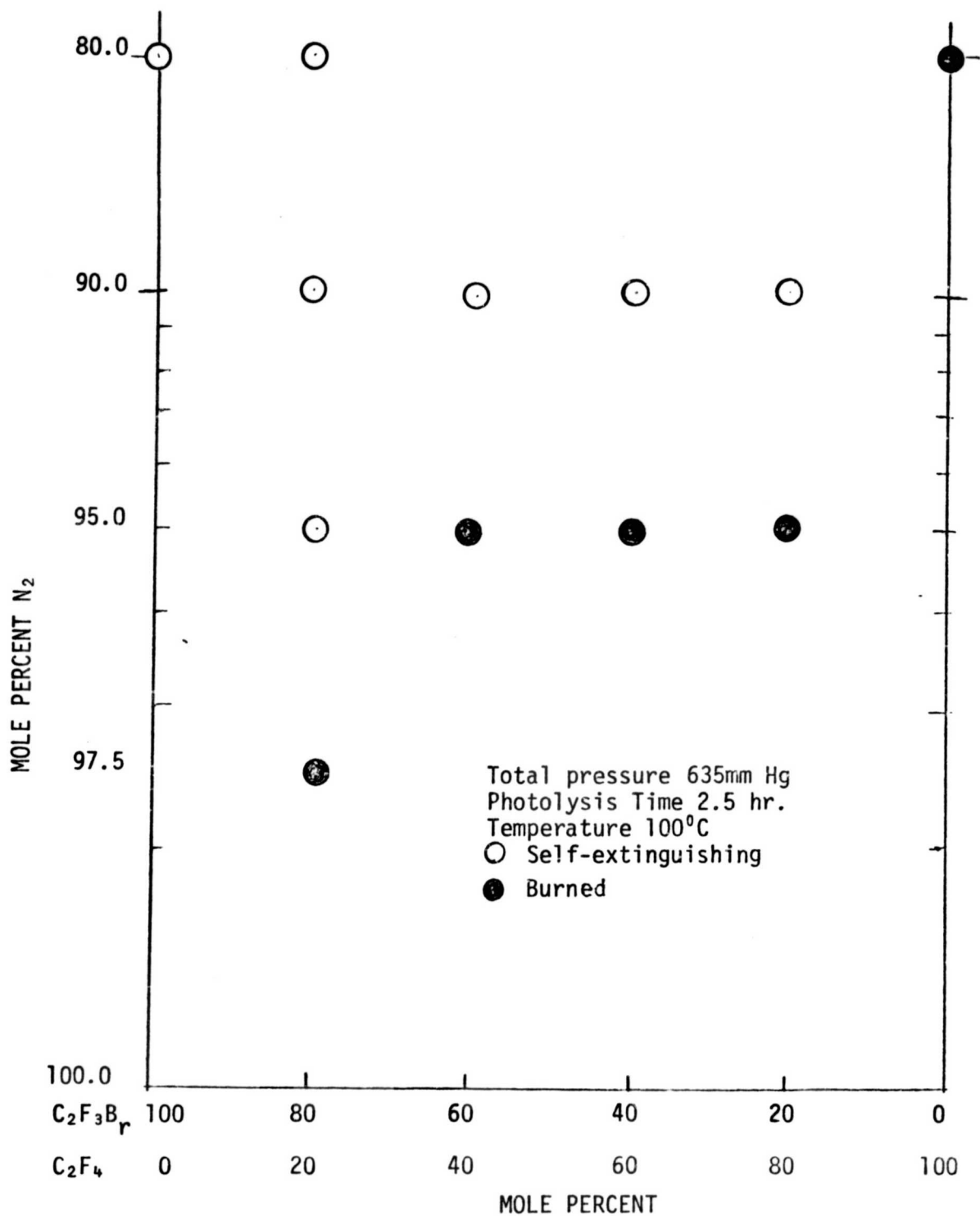
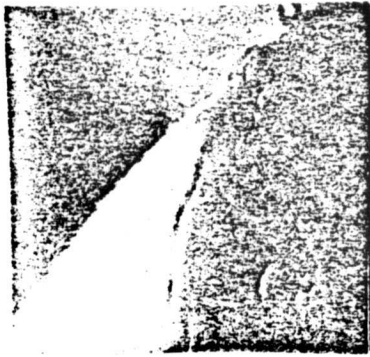
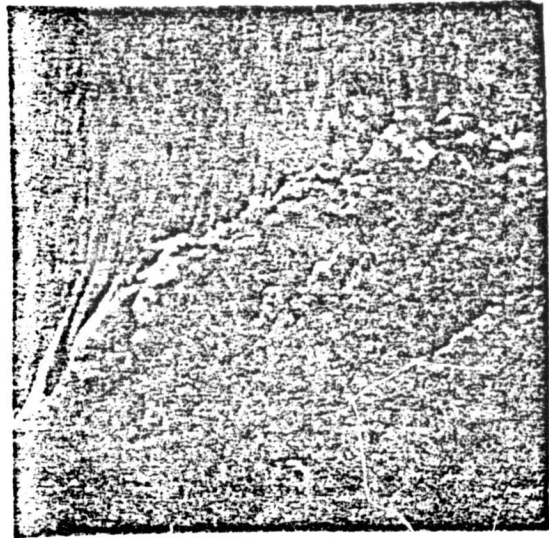


FIG. 3 The effect of fluoroolefin composition on flammability characteristics of photografted Nomex fabrics.



(a)



(b)

FIG. 4 Edge views (cut in liquid nitrogen) of treated Nomex fibers (a) 12,000 X, angle 75, Kv20 (b) after soaking in 70% H_2SO_4 for 80 sec., 11,000 X, angle 30, Kv20.