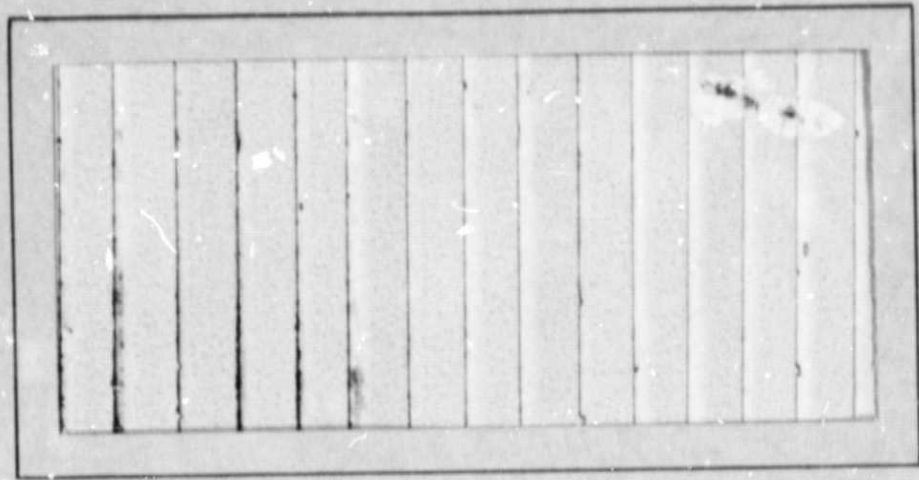


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SCIENCE Applications INCORPORATED



(NASA-CR-151834) DEVELOPMENT OF FLAME RESISTANT TREATMENT FOR NOMEX FIBROUS STRUCTURES Annual Report (Science Applications, Inc., Sunnyvale, Calif.) 40 p HC A03/MF A01 N79-10149 Unclas CSCL 11D G3/24 36873

DEVELOPMENT OF FLAME RESISTANT TREATMENT
FOR NOMEX FIBROUS STRUCTURES
ANNUAL REPORT

By
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Attention: Dr. F.S. Dawn, Mail Code EC
Contract NAS9-14827
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FOREWORD

The work described in this annual report was performed at Science Applications, Incorporated (Sunnyvale, California) under Contract NAS9-14827. The contract was administered by NASA Lyndon B. Johnson Space Center with Dr. F.S. Dawn as technical monitor.

The report covers work conducted from August 1, 1977 to July 31, 1978 and was prepared by Dr. M.S. Toy, the Principal Investigator. Dr. M.S. Toy, Mr. R.S. Stringham and Mr. L.C. Fogg were the major contributors to the program. Mr. V.C. Sanford engineered the design of the prototype reactor.

ABSTRACT

The goal of this program is to further develop the new technology, which renders aramid fibrous structures flame resistant through chemical modification. This project has scaled up the new flame resistant treatment from laboratory fabric swatches of a few inches to efficiently producing ten yards of commercial width (41 inches) aromatic polyamide. The radiation intensity problem of the previous processor was resolved. Further improvement of the processor cooling system has been recommended for two reasons:

(1) To advance current technology of flame-proofing Nomex fabric to higher oxygen-enriched atmospheres.

(2) To adapt the processor for direct applicability to low cost commercial fabrics.

The first significant accomplishment was meeting the program goal in treating ten yards of Nomex fabric with flame-proofing properties in an oxygen-enriched environment without sacrificing color or physical properties; while the untreated Nomex burned in this environment.

The second significant accomplishment was the nature of the treated products, which were irreversibly modified with fluorocarbon grafts, became water-repellent, soft, silky and improved in flame and chemical resistances. The treated fabric was also tested by the Department of Dermatology, Baylor College of Medicine, and found to be non-irritant and non-allergenic.

The third significant accomplishment was to identify the broad applicability of this technology. It was found potentially feasible to surface-graft almost all textiles at varied exposure times and temperatures. Unlike most textile processes, this grafting processor operates under dry conditions and no chemical by-products have to be washed out of the finished products.

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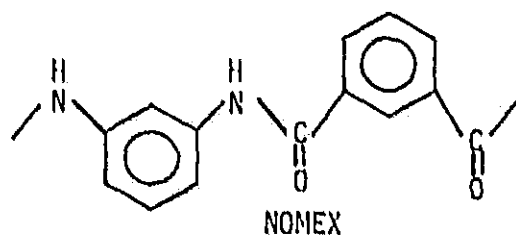
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INTRODUCTION

The new flame resistant treatment developed for Nomex fabric in Phases I and II of previous Contract NAS9-14827 requires improvement. The technology of the previous processor¹ was limited by the intensity of its ultraviolet lamp (122 cm in length and 20 mm od), which had an output of 50 watts at approximately 1 watt per inch. This ultraviolet source was too weak in developing into an efficient process. In other words, the fabric rolling rate would be too slow to be a practical industrial process.

This project has scaled up the new flame resistant treatment from small laboratory fabric swatches of a few inches to efficiently producing ten yards of commercial width (41 inches) Nomex fabric in meeting the flame-proofing goal in an oxygen-enriched environment without the sacrifice of color or physical properties. Such fibrous products have applications in space and deep-sea vehicles, where such environments are encountered.

This program is based on our invention to impart fluorocarbon grafts onto the surface of Nomex fabric.² Organic fibrous products, which possess highly aromatic backbone, are known to exhibit outstanding flame resistance.³ An aromatic polyamide, poly(m-phenyleneisophthalamide), sold by du Pont under the trademark Nomex:



is self-extinguishing in air, but burns in atmospheres with high percentage of oxygen (e.g., 27/73 O₂/N₂ at 10 psia).

Previous work on chemical modification of Nomex fabric by phosphorylation⁴ and halogenation⁵ have shown improved flame resistant property. However these treatments resulted in gold-to-brown-to-black fibrous products and exhibited degradation of the aromatic polyamide.

This new surface grafting technique introduces a chemically bonded surface, which irreversibly modifies the Nomex fabric with fluorocarbon grafts, upgrades the flame resistance properties in an oxygen-enriched environment and also enhances chemical resistance (e.g. acid). See Appendix A. The treated fabric became water-repellent, soft and silky. In addition, it had passed the skin patch test with guinea pigs and human volunteers as non-irritant and non-allergenic.⁷

2.0 RESULTS AND DISCUSSION

For the past year, a new ultraviolet lamp of the same previous dimension, but with a 200-fold increase in output (~9750 watts) was installed in the processor. Several modifications were necessary to accommodate the heat generated by the new lamp. A cooling jacket with circulating coolant around the new lamp and a new vacuum seal became essential requirements.

2.1 The Processor

Figure 1 shows the conceptual design of the processor. For vacuum sealing and insulating the outer quartz tube, aluminum seals with Viton O-rings were used. The new ultraviolet lamp (122 cm in length and 20 mm od) with an output about 9750 watts was purchased from Illumination Industries (Sunnyvale, CA). The temperature parameters of the new lamp are as follows:

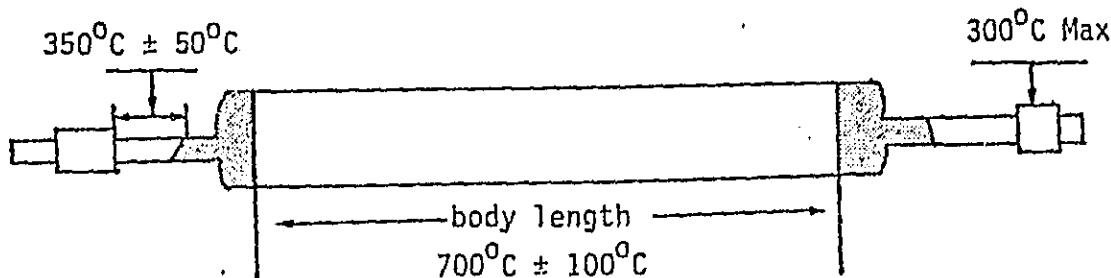
Base 300°C Max.

Necked down portion of lamp 350°C ± 50°C.

Body 700°C ± 100°C.

Note: Over Heating = Quartz Failure

Over Cooling = Internal Lamp Failure



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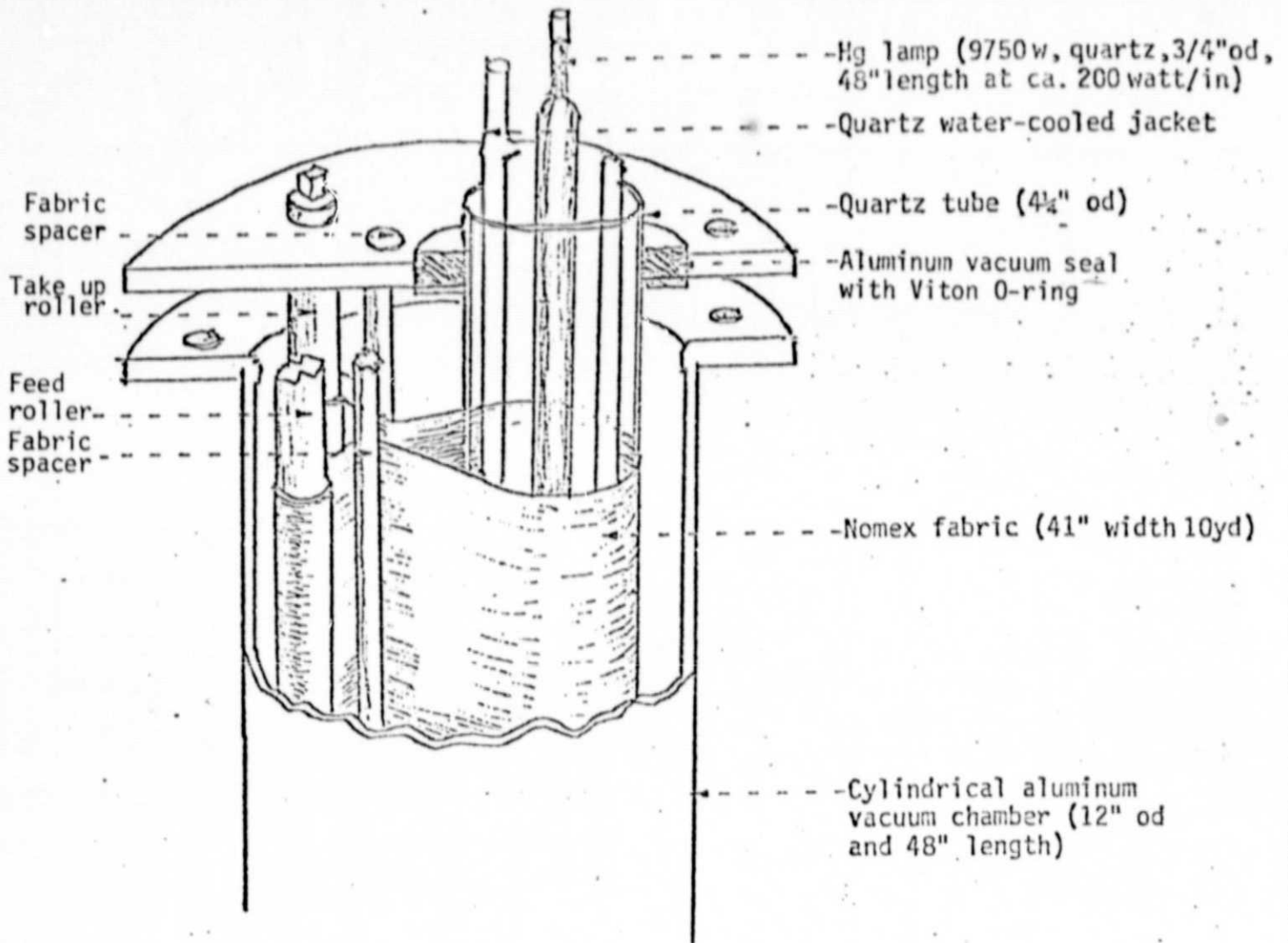


Figure 1. Conceptual Plan of the Processor

A new power supply was purchased from Hanovia for the new mercury lamp. The data for the power supply are:

	<u>Main Power</u>	<u>Control Power</u>	<u>Output</u>
Volts	220 ± 10%	120	
Amperes	56		
Hertz	60	60	60
Phase	single		
Volt-amps	12320		
Secondary Open Circuit V			1960 to 2160
Secondary Short Circuit I			10.5

Figure 2 shows the relative spectral radiance of the new ultraviolet lamp between 220 to 580 nm. For an optimum processing condition, an ideal filtering solution for this lamp is required in reducing the heat generated in the processor. It should be a liquid circulating in the quartz cooling jacket around the lamp and should absorb the total infrared and visible range with transparency (<300 nm) in the ultraviolet region. The spectral radiance of the ultraviolet lamp in the effective ultraviolet region should be determined by an ultraviolet spectrophotometer. The present Blak-Ray Model J-225 (Ultraviolet Products, San Gabriel, CA) for crudely measuring between 230 to 270 nm is inadequate.

Figure 3 shows the cross section of the ultraviolet portion of the processor. The long strip of Sauereisen No. 33 coat (Sauereisen Cement Co., Pittsburgh, PA), was painted on the opposite side of the quartz tube, where the fabric was not in direct contact leaving an unshielded area. The Sauereisen coat shielded the light through that area. Otherwise, the shining light may possibly cause some cyclization and polymerization of the monomers in the processor. Sauereisen is a porcelain-like coating commonly used as an electrical insulator. It adheres to quartz, withstands high temperature (to 2000°F) and functions superbly for the purpose.

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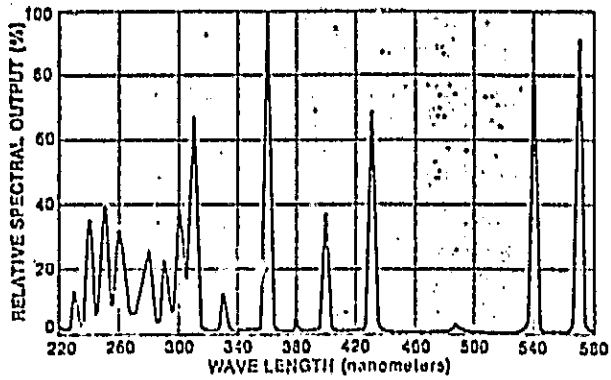


Figure 2 Relative Spectral Radiance of the Ultraviolet Lamp of
The Processor.

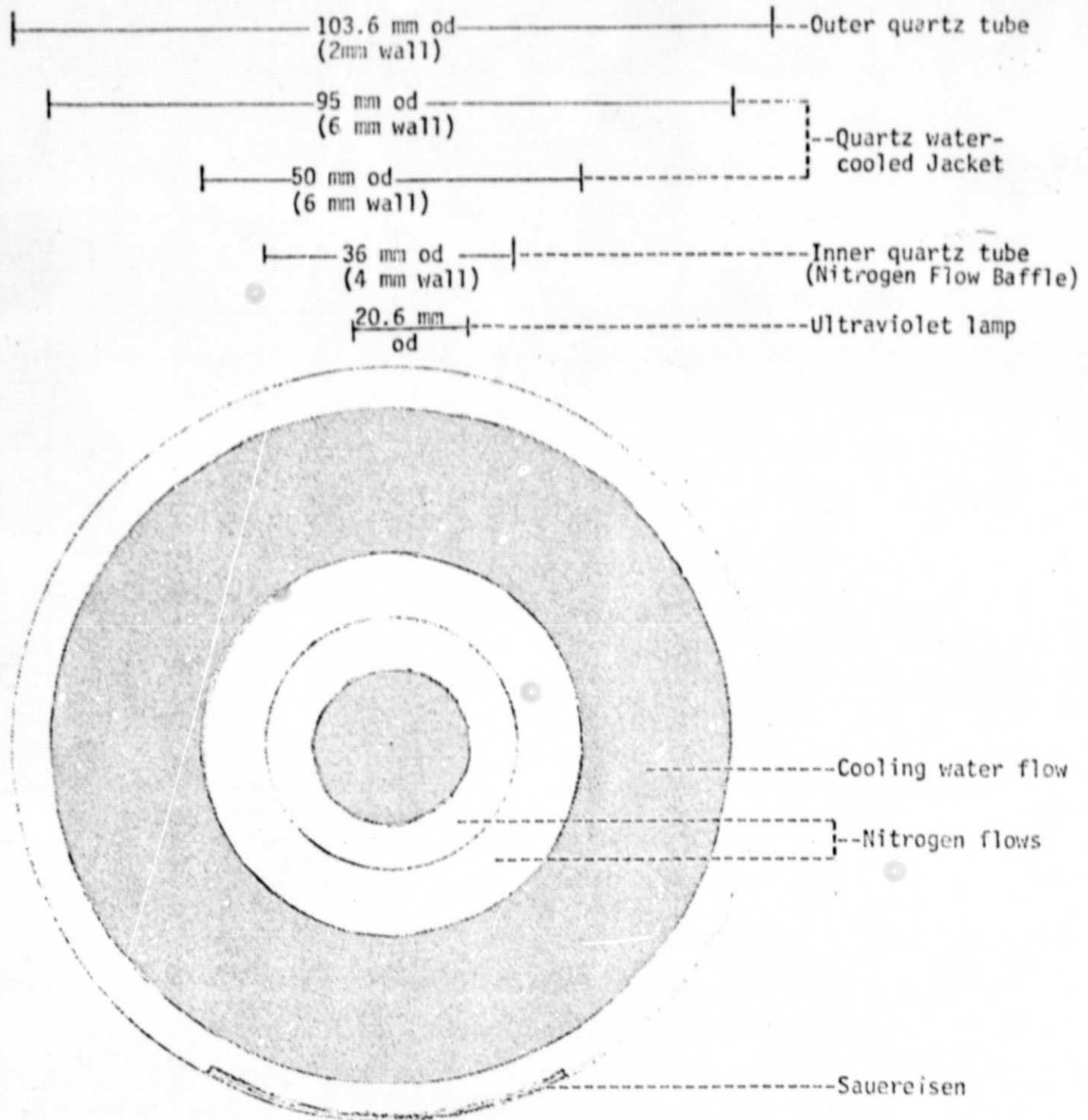


Figure 3 Cross Section of Ultraviolet Source Portion of The Processor

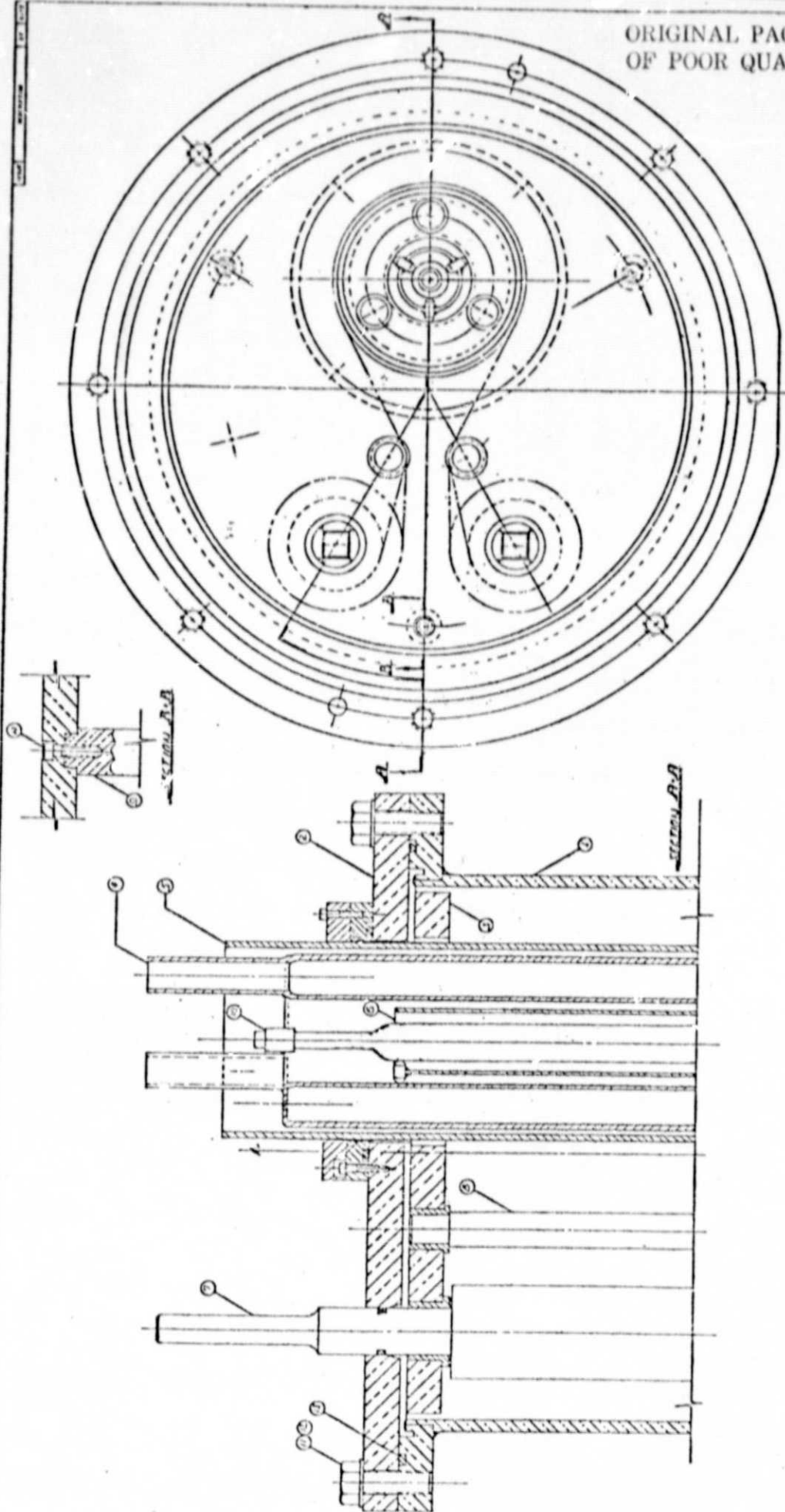
Figure 4 shows the engineering drawings of the two views of the processor. Figure 5 shows the actual processor. The aluminum vessel chamber, spool, roller and support rod were salvaged from the previous processor, while the end covers, their bushing carriers and the other parts are new.

Figure 6 shows the schematic diagram of the cooling system. In order to increase the cooling capacity of the circulating water, which passed through the quartz jacket around the ultraviolet lamp, aqueous solutions of iodine, copper sulfate, nickel sulfate, acetic acid, cobalt sulfate and some combinations thereof were screened at concentrations between 2.5 g to 40 g in 50 gallons of water in the filter tank (Figure 6). Although the cooling capacity had increased in maintaining the desirable temperature range about 150 to 200°C for a few hours, the efficiency of the process was decreased due to the ultraviolet absorption property of the aqueous solutions.

We found that Freon TF (i.e., Freon 113 or trichlorotrifluoroethane) functioned as a better coolant than water and the aqueous solutions. Freon TF is commonly used as an industrial cleaning solvent, it is nonflammable, nonexplosive, exceptionally pure (i.e., 99.8% trichlorotrifluoroethane with not more than 0.2% of other stable chlorofluorocarbons), low in toxicity and commercially available in huge (ton) quantities. Its property of being transparent in the ultraviolet region and absorbing in the infrared serve the purpose of lowering the outer quartz tube temperature without decreasing the efficiency of the process.

By converting the current water-cooling system to Freon TF, we made some modifications to the present cooling system such as replacing all rubber and Tygon tubings, cleaning the copper cooling coil and changing the circulating pump to a magnetic drive pump. These changes reduced the buildup contaminants, which are due to the unique cleaning property of Freon TF solvent, to cause deposits in the quartz cooling jacket allowing

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END VIEW - COVER PLATE REMOVED

Figure 4 The Two Views of The Processor

- 1 Vessel chamber
- 2 Side end cover
- 3 Side end bushing carrier
- 4 Quartz cooling jacket
- 5 Main quartz vacuum seal tube
- 6 Lamp support tube
- 7 Spool
- 8 Roller
- 9 Support rod
- 10 Hg lamp
- 11 Hexagonal head bolt
- 12 Plain washer
- 13 O-ring
- 14 Cap screw.

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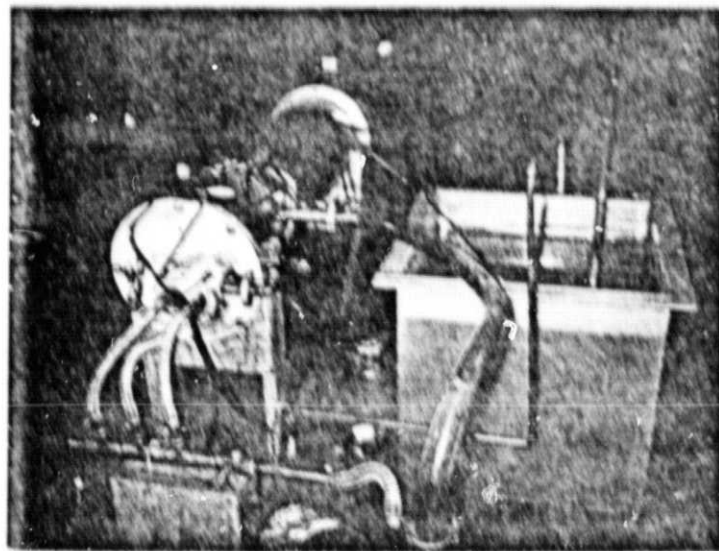
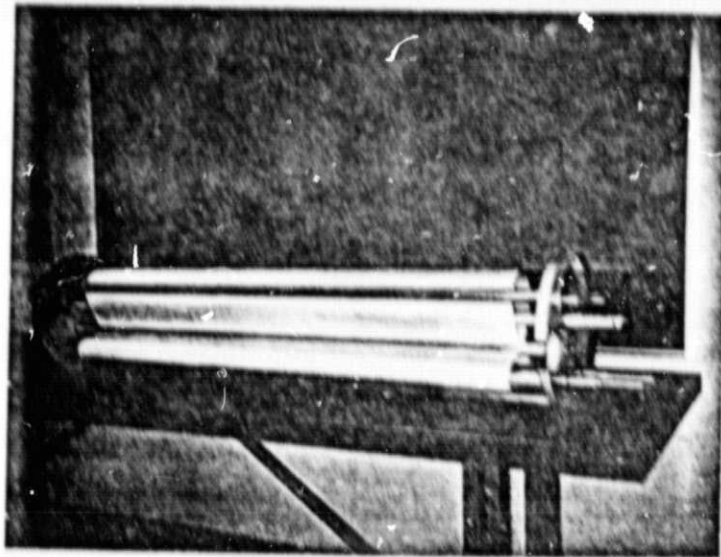


Figure 5. The Processor

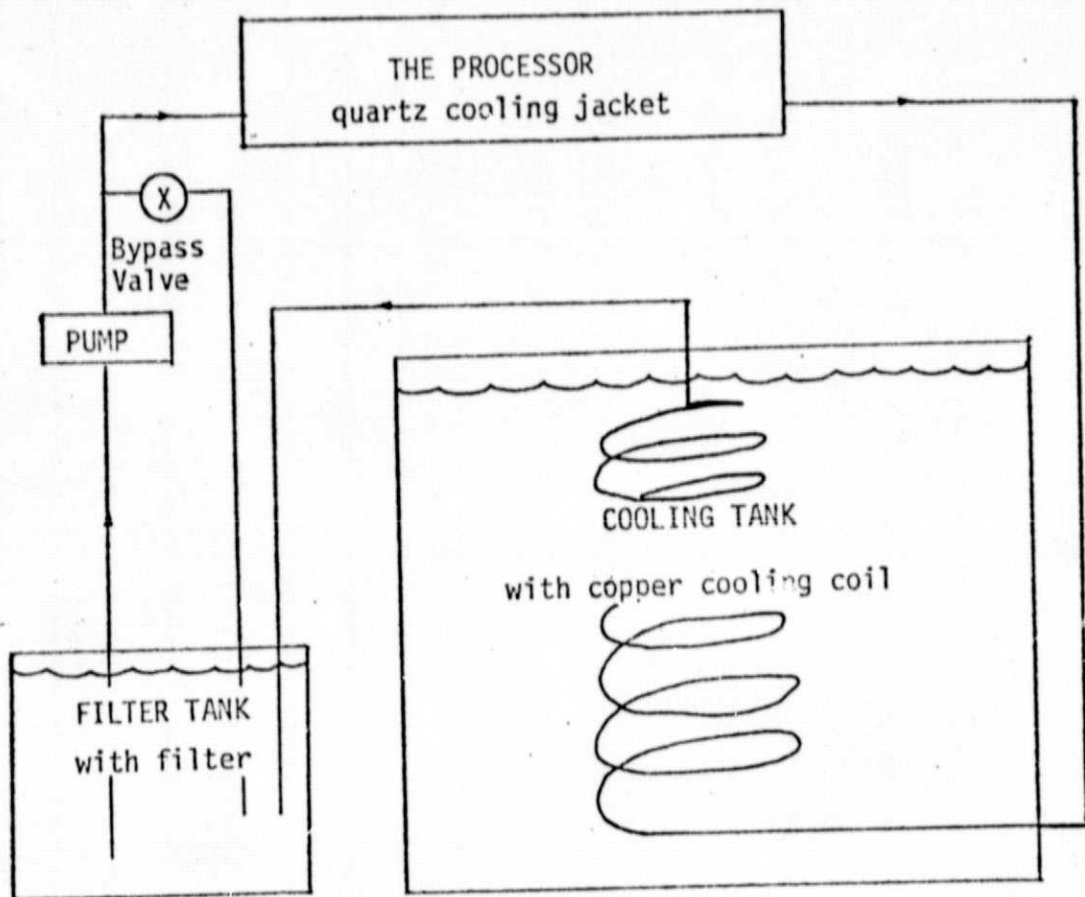


Figure 6 Schematic Diagram of the Cooling System.

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40% ultraviolet transmission. Even with this poor transmission level, the treated Nomex fabric has achieved self-extinguishing properties in a higher oxygen level atmosphere (i.e., 31/69 O₂/N₂ at 10 psia)⁸ except with slight coloration. Freon TF is a better coolant than water.

A new cooling system composed of Teflon FEP tubings and flex tubings is recommended for replacing the present copper cooling coil. The optimization of the Freon TF cooling process is warranted, since it is an important step for significant technology advancement. It will not only further improve the self-extinguishing property of treated Nomex to withstand higher oxygen level atmospheres causing almost no coloration of the treated Nomex, but also adapt the processor to surface treat commercial low cost fabrics.

2.2 Fluorocarbon-grafting Processes

Several batch-continuous processes have been developed to impart fluorocarbon grafts for commercial aromatic polyamide. The natural color woven fabric (HT-10-41) was purchased from Stern and Stern Textiles (Hornell, NY). This Nomex fibrous structure is self-extinguishing in air, but not in an oxygen-enriched environment (e.g. 27/73 O₂/N₂ at 10 psia).

The primary technology consists of a one-step photografting process by exposing the textile surface to a gaseous mixture of fluoroolefins in a nitrogen atmosphere. The fluoroolefin mixtures ranged from neat bromotrifluoroethylene to equal ratio of bromotrifluoroethylene to tetrafluoroethylene in the presence of 90 to 95% nitrogen had achieved the flame-proofing goal by the vertical flame test in an oxygen-enriched environment (i.e. 31/69 O₂/N₂ at 10 psia).

The drawbacks of using neat bromotrifluoroethylene with nitrogen is the coloration of the treated fabric and the interaction with the stainless steel parts. The addition of a few percentage of tetrafluoroethylene in the gaseous mixture decreased the treated fabric coloration to almost nil and stopped any visible interaction with the stainless steel parts inside the processor.

2.3 Production Item

Although Freon TF is a better coolant than water, the replacement of a new cooling system, which totally eliminates deposits inside the quartz cooling jacket, is beyond our means under the current program effort. For this program we used water coolant to treat the ten yards of commercial width Nomex fabric.

The selected photografting process constituted a gaseous mixture of the following composition:

- 1% tetrafluoroethylene
- 4% bromotrifluoroethylene
- 95% nitrogen

An exposure time of almost 3 to 4 hours was used for treating the 10 yards of commercial width (41 inches) Nomex fabric (Sample SAI 546-60), which was delivered to NASA-JSC-EC as partial fulfillment of the work under Contract NAS9-14827. The treated Nomex fabric did not burn in an oxygen-enriched atmosphere (27.1/72.9 O₂/N₂ at 10 psia), while the untreated Nomex (HT-10-41) burned.

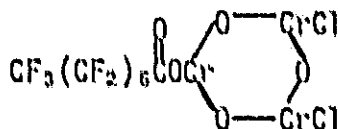
2.4 Technology Transfer to Low Cost Commercial Fabrics

The objective of this phase is to apply the present flame resistant treatment of Nomex fabric to other types of low cost commercial fabrics. The ease of fluorocarbon grafting to other fabrics (e.g., polyester and polyimide) screened by this method suggests that the process has broad applications. It is a feasible universal treatment process for possibly almost all textiles at varied treatment exposure times and temperatures.

2.4.1 Background

Fluorocarbon textile finishes had been reported in the literature by several ways.^{9,10} One common approach is to use a fluorocarbon

compound with a functional group that will be either adsorbed strongly to the surface or undergo a chemical reaction with the fiber surfaces. One example of this type of bonding is the chromium complex of various acids containing long chain fluorocarbon groups.



If this reaction occurs on the surface of a fiber such as nylon, the chromium will complex with amino groups, thus anchoring the fluorocarbon tail to the fiber surface. Unfortunately such "complex" linkages will not withstand normal laundering or dry cleaning processes.^{11, 12}

Laboratory treatments of cotton fabric with perfluoroheptene-1 or perfluorobutadiene in aqueous KOH and NaOH were claimed to form fluorocarbon grafts to cellulose.¹³ Application of fluorocarbon finishes to wool by plasma polymerization were also reported.^{14, 15}

2.4.2 Polyester Fabric

The textile industry has tried many finishes to improve the surface property of polyester, but its smooth and chemically passive nature makes it extremely difficult to retain any finish on the surface. Some soil-release scheme has been developed for polyester/cotton blends by an electric discharge method,¹⁴ but a noticeable stiffening of the "hand" of the material was noted.

When this new surface treatment process developed for aromatic polyamide (Appendix A) was applied to polyester and polyimide fabrics, the ease of fluorocarbon grafting was noted.

Commercial width polyester fabric was photografted in the presence of a gaseous mixture of 1% tetrafluoroethylene, 4% bromotrifluoroethylene and 95% nitrogen with two different exposure times at 200 and 500 seconds. The treated polyester fabrics became irrevrsibly modified with fluorocarbon grafts and were nonwetable with water droplets. Fabric coloration was observed for 500 sec exposure time, but was almost nil for 200 sec. These samples (nos. 546-61A and 546-61B respectively) were mailed to NASA-JSC-EC.

3.0

REFERENCES

- (1) M.S. Toy, "Development of Flame Resistant Treatment for Nomex Fibrous Structures," SAI Tech. Report under Contract NAS9-14827, March, 1977.
- (2) M.S. Toy and R.S. Stringham, "Process for Producing Flame Resistant Polyamides and Products Produced Thereby," NASA Case No. MSC-16074, 1976.
- (3) J.H. Ross and R.M. Stanton, "High Temperature and Flame-Resistant Fibers" ed. by J. Preston and J. Economy, John Wiley, New York, NY, 1973, pp 109-119.
- (4) C.E. Hathaway and G.L. Early, "High Temperature and Flame-Resistant Fibers," ed. by J. Preston and J. Economy, John Wiley, New York, NY, 1973, pp 101-108.
- (5) S.S. Hirsch (to Monsanto Company), U.S. Patent 3,549,307 (December, 27, 1970) and 3,607,798 (September 21, 1971).
- (6) M.S. Toy, R.S. Stringham and F.S. Dawn, J. Appl. Polymer Sci., 21, 2583 (1977).
- (7) Tested for potential irritancy and allergenicity conducted by the Department of Dermatology, Baylor College of Medicine.
- (8) 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 Aeronautics and Space Administration, Washington, D.C. (Feb., 1974).
- (9) H.G. Bryce, "Fluorine Chemistry," Vol. 5, ed. by J.H. Simons, Academic Press, New York, 1964, pp 397-401.

- (10) A.G. Pittman, "Fluoropolymers", ed. by L.A. Wall, New York, Wiley, 1972, pp 419-449.
- (11) F.J. Phillips, L. Segal, and L. Loeb, Textile Res. J., 27, 369 (1967).
- (12) L. Segal, F.J. Phillips, L. Loeb and R.L. Clayton, Textile Res. J., 28, 233 (1958).
- (13) R.D. Englert, R. Swidler, L.P. Berriman and R.H. Wade, U.S. Patents 3,489,504 (Jan. 13, 1970) and 3,353,904 (Nov. 21, 1967).
- (14) M.M. Millard, K.S. Lee and A.E. Pavlath, Textile Res. J., 42, 307 (1972).
- (15) M.M. Millard and A.E. Pavlath, J. Macromole. Sci.-Chem., A10 (3), 579 (1976).
- (16) F.D. Fales, A. Bradley and R.E. Rowe, Research and Development, 27 (3), 53 (1976).

APPENDIX A

J. Appl. Polymer Sci., 21, 2583 (1977)

Photoaddition of Fluoroolefins on Aromatic Polyamide

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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 photodiffusion reaction of haloolefins has been shown to irreversibly modify the fabrics, which were analyzed by water wettability, scanning electron microscopy, x-ray analysis, and ^{19}F 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 O_2/N_2 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 were obtained from Matheson Gas. The fabric and reagents were used as received. The vapors of fluoroolefins were checked by infrared analysis.

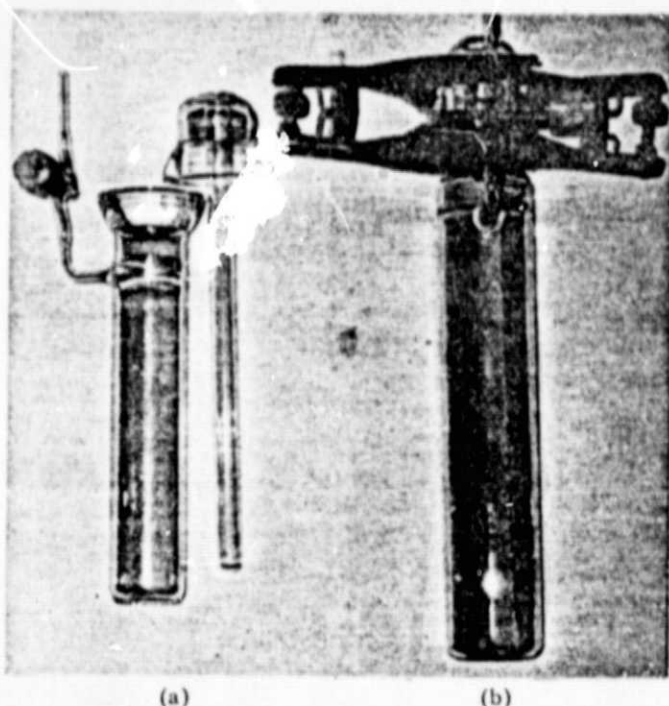


Fig. 1. Reaction vessel: (a) an opened cylindrical Pyrex reactor with side arm and valve for attachment to the manifold (to the left) and quartz sleeve (to the right); (b) a closed reaction vessel with the fabric mounted around the centered quartz tube.

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 (Fig. 1). The cylindrical Pyrex reaction vessel consists of a centered quartz sleeve for receiving a 11-in. Pen Ray mercury-arc lamp (Ultraviolet Products). Pressures were measured with a 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 a coiled Nichrome ignition wire (1 ohm/in.). The sample (2.5 × 5 in.) was mounted vertically between the stainless steel sample holders, leaving 2 × 5 in. 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 × 20 × 2 mm). Both IR transmission and ATR spectra were recorded on a Perkin-Elmer Model 467 spectrometer.

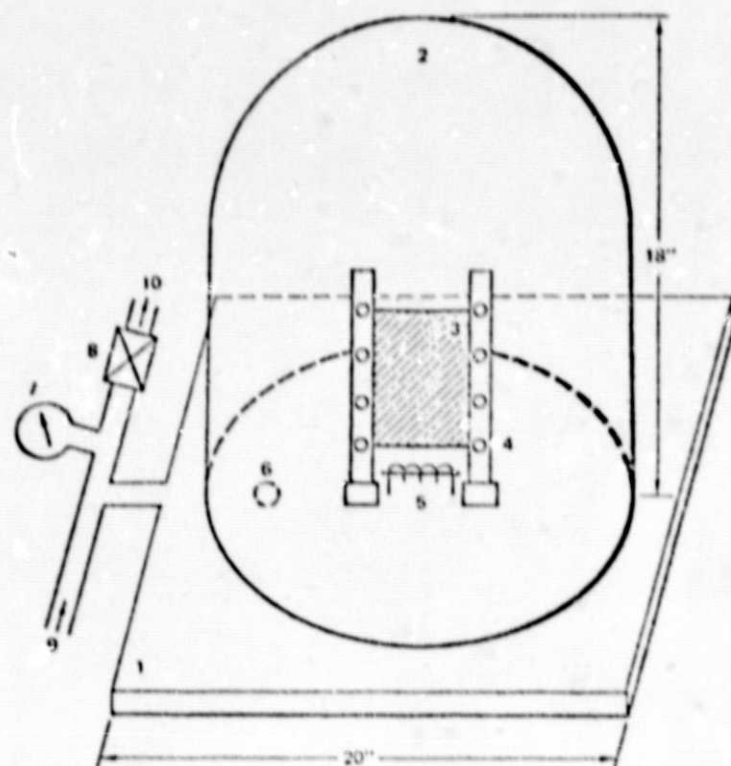


Fig. 2. Flammability test apparatus: (1) metal base plate; (2) bell jar (2 cu ft); (3) sample; (4) sample holders; (5) ignition wire and ignitor; (6) vacuum and gas inlet; (7) vacuum gauge; (8) valve to vacuum; (9) gas inlet; (10) to vacuum pump.

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 ^{19}F NMR spectrum was measured by a Varian XL-100 spectrometer operating at 94.1 MHz. A piece of 4×9 in. (3.6 g) treated Nomex fabric was shredded into individual fibers and dissolved in 4 ml concentrated sulfuric acid with added deuterated water for the internal lock. The viscous solution was poured into a 12 mm 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 1 cm from the surface) in the photografting reaction vessel [Fig. 1(b)]. The side arm was attached to the copper manifold and evacuated. A measured amount of

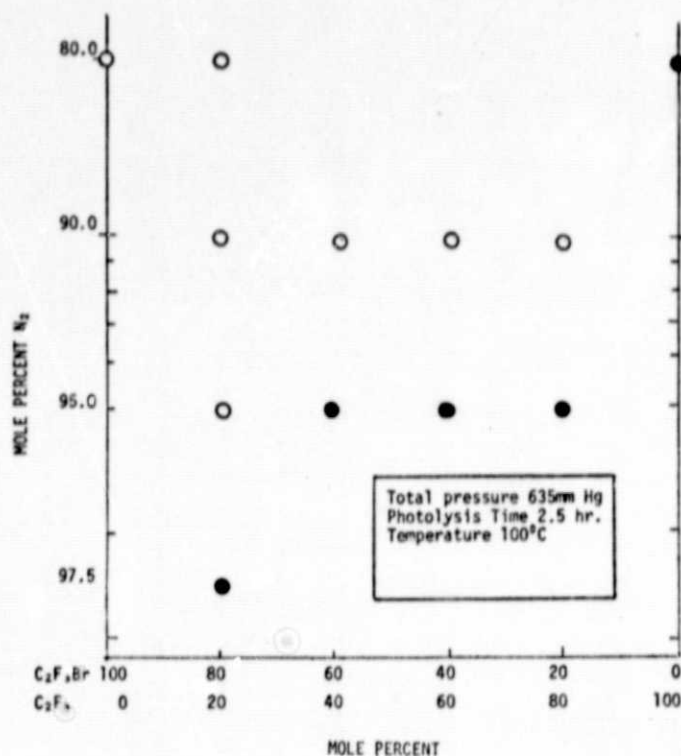


Fig. 3. Effect of fluoroolefin composition on flammability characteristics of photografted Nomex fabrics: (○) self-extinguishing; (●) burned.

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. The amounts 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 (Fig. 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 fabrics which were treated by varied fluoroolefin compositions in the presence of nitrogen. Figure 3 summarizes the results using one exposure to a medium-pressure mercury 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.



(a)



(b)

Fig. 4. Edge views (cut in liquid nitrogen) of treated Nomex fibers: (a) 12,000 \times , angle 75 $^\circ$, 20 kV; (b) after soaking in 70% H₂SO₄ for 80 sec, 11,000 \times , angle 30 $^\circ$, 20 kV.

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 monomolecular-like character of the modified surface.

Figure 4 shows the edge views of treated Nomex fiber before (a) and after (b)

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soaking in 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 ratios of C₂F₃Br to C₂F₄ in the premixed vapor composition show a corresponding higher bromine content on the treated sample.

The ¹⁹FNMR spectrum shows the two major narrow absorptions, $\delta = 144$ and 170 ppm, from CFCI₃ at the relative intensities of 2:1. 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 the National Aeronautics and Space Administration under Contract NAS9-14827. The authors are indebted to Mr. B. Lan for preliminary exploration, Mr. L. Cary for ¹⁹FNMR, 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*, J. Preston and J. Economy, Eds., 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. Pats. 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. Polym. Sci.*, **13**, 1523 (1969).
6. O. Johari and A. V. Samudra, in *Characterization of Solid Surface*, P. F. Kane and G. B. Larabee, Eds., Plenum Press, New York, 1974, p. 118.
7. C. W. Wilson, *J. Polym. Sci.*, **56**, 163 (1962).

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APPENDIX B

Paper and/or Oral Presentation

"A Photoprocess for Fluorocarbon Finishes of Textile Materials"

A PHOTOPROCESS FOR FLUOROCARBON FINISHES OF TEXTILE MATERIALS

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

INTRODUCTION

Textile finishes based on fluorocarbons have been developed and introduced commercially.^{1,2} Most of these fluorocarbon type finishes are applied from aqueous or organic solvent systems, although impregnation or presoaking of textiles in the liquid fluoromonomer or its solution for radiation or glow discharge grafting have also been reported.^{3,4}

This work describes a one step photochemical process to impart fluorocarbon finishes to fibrous structures in which the fibrous substrate is in contact with a gaseous mixture of fluoroolefins in an inert diluent gas.

RESULTS AND DISCUSSION

The ease of imparting fluorocarbon grafts to aromatic polyamide under photolysis was previously reported to upgrade nonflammability properties in an oxygen-enriched environment (e.g., 31/69 O₂/N₂ at 10 psia) and acid resistance.⁴ This work has scaled up the photoprocess with capacity to treat ten yards of commercial width aromatic polyamide (Nomex HT-10-41, woven fabric, natural color) without the apparent change of coloration or physical properties.

We found that gaseous media comprising neat bromotrifluoroethylene to equal mole ratio of mixed tetrafluoroethylene and bromotrifluoroethylene in 95% nitrogen provided fluorocarbon grafts to impart self-extinguishing properties by vertical flammability test⁶ in an oxygen-enriched environment; while the untreated Nomex fabric burned under the same environment. The treated Nomex fabric also became water-nonwetable, soft and silky with improved acid resistance without the apparent change of coloration and the desirable physical properties. The treated Nomex fabric was tested by skin patch test and found to be nonirritant and nonallergenic.⁷

Applications of this photochemical technique of imparting fluorocarbon finishes to other types of textile materials are in progress. Generally, the reaction temperature is between ambient to 250°C depending on the low to high temperature properties of the fibrous products and their exposure times.

EXPERIMENTAL

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 mixtures (e.g., 31/69 and 27/73 O₂/N₂) and fluorotrichloromethane from Matheson Gas. The fabric and reagents were used as received. The vapors of fluoroolefins were checked by infrared analysis.

Figure 1 shows the two views of the photoprocessor. It comprises a cylindrical vacuum-assisted aluminum vessel chamber (28.5 cm id and 122 cm length) containing a quartz sleeve, where the ultraviolet lamp is shielded by a quartz cooling jacket. The ultraviolet source has an output of about 200 watts per inch. The photoprocessor has the capacity of treating ten yards commercial width fabric by a continuous batch process.

REFERENCES

1. H.G. Bryce, "Fluorine Chemistry, "Vol. V, ed. by J.H. Simmons, Academic Press, New York, 1964, pp 399-417.
2. A.G. Pittman, "Fluoropolymers," ed. by L.A. Wall, John Wiley, New York, 1972, pp 419-449.
3. E.E. Magat and D. Tanner, U.S. Patent 3,412,175 (Nov., 1968)
4. M.M. Millard, K.S. Lee and A.E. Pavlath, Textile Res. J., 42 (5), 307 (1972).
5. M.S. Toy, R.S. Stringham and F.S. Dawn, J. Appl. Polymer Sci., 21, 2583 (1977).
6. 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., Feb., 1974.
7. Performed at Department of Dermatology, Baylor College of Medicine.

ACKNOWLEDGEMENT

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END VIEW - COVER PLATE REMOVED

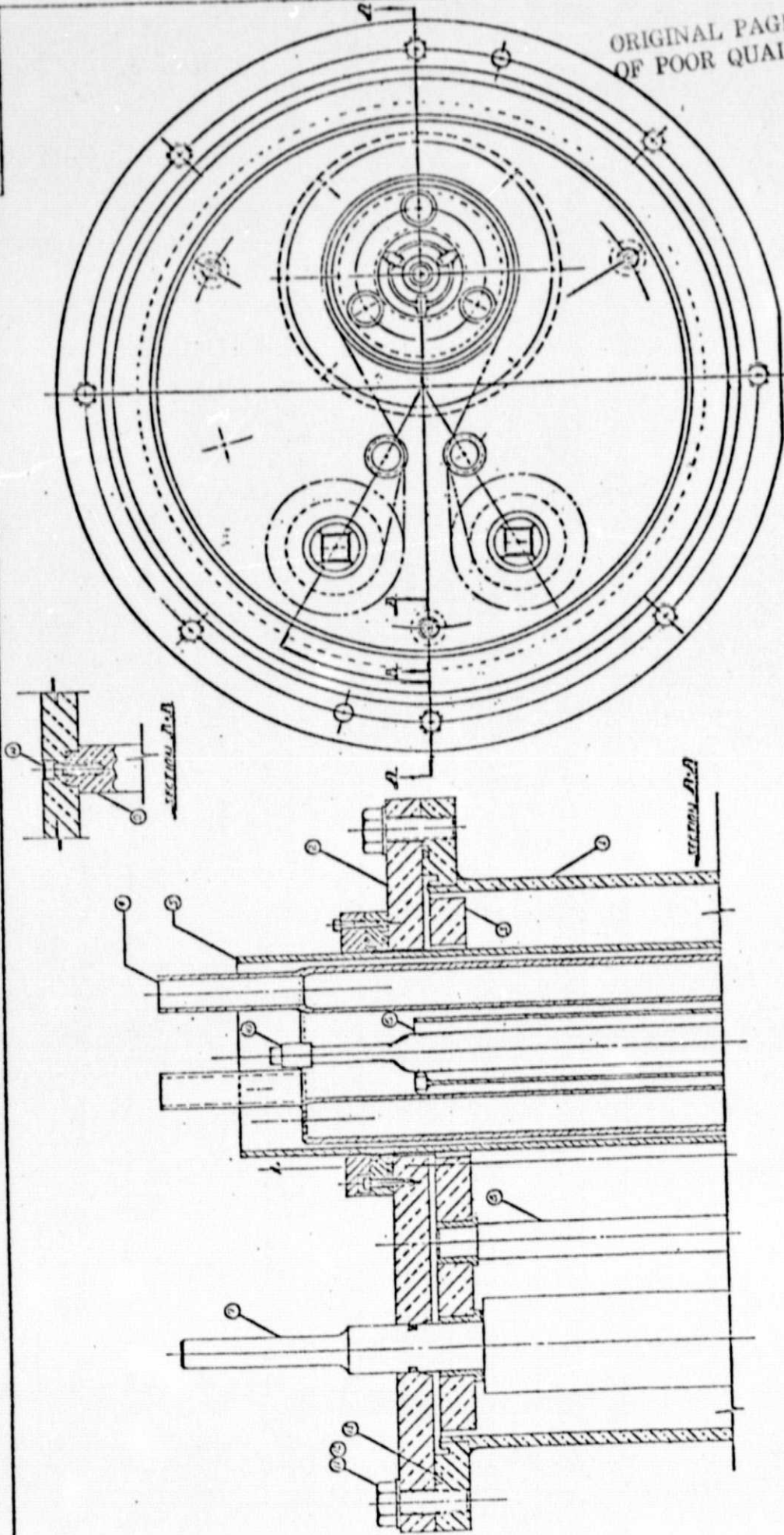


Figure 1 The Two Views of The Processor

- 1 Vessel chamber
- 2 Side end cover
- 3 Side end bushing carrier
- 4 Quartz cooling jacket
- 5 Main quartz vacuum seal tube
- 6 Lamp support tube
- 7 Spool
- 8 Roller
- 9 Support rod
- 10 Hg lamp
- 11 Hexagonal head bolt
- 12 Plain washer
- 13 O-ring
- 14 Cap screw.

APPENDIX C

PROPOSED PATENT DISCLOSURE

(Contract NAS9-14827)

"Process and Processor for Producing
Fluorocarbon Finishes to Fibrous Structures"

PATENT DISCLOSURE

Title: Process and Processor for Producing Fluorocarbon Finishes to Fibrous Structures.

Inventors: Madeline S. Toy, Roger S. Stringham and Lawrence C. Fogg
Science Applications, Incorporated
1257 Tasman Drive
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Abstract of Disclosure

A process and a processor for producing fluorocarbon finishes to fibrous structures in which a fibrous substrate is in contact with a gaseous medium comprising a minor amount of fluoroolefin or fluoroolefin mixtures in an inert diluent in the presence of ultraviolet light.

The invention described herein was made in the performance of work under NASA Contract NAS9-14827 at Science Applications, Inc., 1257 Tasman Drive, Sunnyvale, CA 94086.

This invention relates to a photochemical process and processor providing fluorocarbon grafts to fibrous substrates. More particularly, the invention relates to a new type of photografting process of textile materials to impart chemically bonded fluorocarbon finishes and the method and the processor for producing the same.

Prior to herein invention, textile finishes based on fluorocarbons have been developed and introduced commercially, but these fluorocarbon type finishes are usually applied from aqueous or organic solvent systems.

The objective of this invention is to produce fluorocarbon finishes to fibrous structures in one-step under dry conditions without the need of drying or curing the treated products and which have no chemical by-products to be washed out of the finished products.

Another object of this invention is to impart fluorocarbon finishes to commercial woven fabrics to improve nonflammability and chemical resistance without the changing of physical properties or causing skin irritancy and allergenicity.

Still another object of this invention is to upgrade water repellency, soiling, staining and abrasive resistances to fibrous products without altering appearance or stiffening of the treated products.

The above and other objects of this invention are accomplished by a one-step fluorocarbon-grafting process of the fibrous products in the presence of fluoroolefins, a diluent inert gas and ultraviolet light. The photografting processor comprises a cylindrical vacuum-assisted aluminum vessel chamber containing a quartz sleeve, where the ultraviolet lamp surrounded with a quartz cooling jacket is centered. The ultraviolet source has an output of about 9000 to 10,000 watts at 200 watts per inch.

The fluorocarbon-grafting process irreversibly modifies the fibrous product surface and upgrades its nonflammability, water repellency, chemical inertness, soiling, staining and abrasive resistances properties. In addition, the fabric becomes soft and silky. Generally the reaction temperature is between ambient to 250°C depending on the low to high temperature properties of the fibrous products and their exposure times.

One example of the gaseous media for photografting fluorocarbon finishes to fibrous substrates such as polyesters, polyamides, polyimides, cottons, wools, polyester-cotton blends and polyester-wool blends consist of 1% tetrafluoroethylene and 4% bromotrifluoroethylene in the presence of 95% of nitrogen.

Claims:

1. A method and processor for producing fluorocarbon finishes to fibrous structures in which a fibrous substrate is in contact with a gaseous medium containing fluoroolefins and an inert diluent under photolysis.
2. The method of Claim 1 wherein said fibrous structure comprising textiles and textile fibers.
3. The method of Claim 1 wherein said fibrous structure comprising natural and synthetic organic fibers and mixed blends such as cottons, polyesters, polyamides, polyimides, cotton-polyester blends, wool-polyester blends and etc.
4. The method of Claim 1 wherein the processor consists of a quartz sleeve, which forms the inner wall of a cylindrical vacuum assisted aluminum reactor chamber.
5. The method of Claim 1 wherein the processor uses ultraviolet lamp surrounded with a quartz cooling jacket, which are placed inside the quartz sleeve of Claim 4.